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LONG-RANGE INTERATOMIC INTERACTIONS:
OSCILLATORY TAILS AND HYPERFINE PERTURBATIONS

by

CHANDRA MANI ADHIKARI

A DISSERTATION

Presented to the Faculty of the Graduate School of the
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

in Partial Fulfillment of the Requirements for the Degree of

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in

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Approved by

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ABSTRACT

We study the long-range interaction between two hydrogen atoms, in both the van der Waals and Casimir-Polder regimes. The retardation regime is reached when the finiteness of the speed of light becomes relevant. Provided that both atoms are in the ground states, the retardation regime is achieved when the interatomic distance, R , is larger than $137 a_0$, where a_0 is the Bohr radius.

To study the interaction between two hydrogen atoms in $1S$ and $2S$ states, we differentiate three different ranges for the interatomic distance: van der Waals range ($a_0 \ll R \ll a_0/\alpha$, where α is the fine structure constant), the intermediate or Casimir-Polder range ($a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$, where \mathcal{L} is the Lamb shift energy), and the very long or Lamb shift range ($R \gg \hbar c/\mathcal{L}$). We also study the Dirac- δ perturbation potential acting on the metastable excited states in the context of hyperfine splitting.

The $|2P_{1/2}\rangle$ levels, which are displaced from the reference $2S$ -levels just by the Lamb shift, make the study of hyperfine resolved $2S$ - $2S$ system very interesting. Each S and P state have a hyperfine singlet and a triplet. Thus, there are 8-hyperfine states per hydrogen atom and $8 \times 8 = 64$ states in the two atom system. The Hamiltonian matrix of the quasi-degenerate $2S$ - $2S$ system is thus a (64×64) -matrix. Our treatment, which profits from adjacency graphs, allows us to do the hyperfine-resolved calculation. We examine the evolution of the energy levels in the hyperfine subspaces. We notice that there is a possibility of level crossings in higher dimensional quantum mechanical systems, which is a breakdown of the non-crossing theorem.

For higher excited reference states, we match the scattering amplitude and effective Hamiltonian of the system. In the Lamb-shift range, we find an oscillatory term whose magnitude falls off as R^{-2} and dominates the Wick-rotated term, which otherwise has a retarded Casimir-Polder type of interaction.

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1. INTRODUCTION

1.1. BACKGROUND

The motion of electrons in their orbitals around the atomic nucleus makes an atom polarized to some extent. If two atoms or molecules are brought near each other, then quantum fluctuations mutually induce dipole moments. The weak interaction which links the dipoles is the so-called van der Waals (vdW) interaction. Study of the vdW interaction is now popular not only among the physicists but also among the vast majority of researchers from biochemistry, the pharmaceutical industry, nanotechnology, chemistry, biology, etc. For a biochemist, it is the vdW force which determines the interaction of enzymes with biomolecules [10]. For a pharmacist, the binding nature of a drug molecule to the target molecule is determined by the vdW force [11]. In nanoscience, by virtue of origin, the interaction between polarizable nano structures which have wavelike charge density fluctuation is the vdW interaction [12]. The vdW interaction between two atomic states is proportional to R^{-6} , where R is the interatomic separation. The vdW interaction is a weak interaction, however, if two interacting objects have a significant number of such interactions, the net vdW interaction of the system can be significantly strong [13].

In 1948, the Dutch physicist H. Casimir found that two perfectly conducting parallel plates placed in a vacuum attract each other [14]. This force of attraction is related to the vdW interaction in the retardation regime [15]. In the same year, Casimir and Polder showed that if the distance between the atoms is much larger than the distance related to the retardation time, the interaction potential will be proportional to R^{-1} times the potential in the non-retardation regime. Thus in the dispersive retardation regime, the van der Waals interaction changes the power law

from R^{-6} to R^{-7} . This power law modification has been verified experimentally by D. Tabor and R. H. S. Winterton in 1968 [16]. The Russian physicist E. M. Lifshitz developed a more general theory of vdW interactions about ten years after Casimir and Polder proposed Casimir–Polder (CP) forces [17]. In 1997, S. K. Lamoreaux of Los Alamos National Laboratory measured the Casimir force between a plate and a spherical lens with good accuracy [18]. The Casimir effect received, even more, attention of the scientific world when U. Mohideen and A. Roy of the University of California measured the Casimir force between a plate and a sphere even more accurately in 1998 [19]. Recent experimental work includes measurement of the Casimir force between parallel metallic surfaces of silicon cantilever coated with chromium in the 500 –3000 nm range [20], measurement of the Casimir force between dissimilar metals [21], and the Casimir force measurements in a sphere-plate configuration [22].

1.2. ORGANIZATION OF THE DISSERTATION

This dissertation provides a detailed analysis of the long-range interaction between two electrically neutral hydrogen atoms. Based on the interatomic distances and nature of the state of the atoms of the system, we apply three different approaches to study the long-range interaction. Every approach has its pros and cons. The first approach is to make a Taylor series expansion of the electrostatic interaction. This approach is valid in a short range regime. However, it does not talk anything about the retardation effect. The other approach is a calculation based on a fourth-order time-ordered perturbation theory. This approach is valid for a wide range of interatomic distances ranging from a_0 to ∞ , but it suffers from a limitation that both the interacting atoms must be in the ground state. If an atom interacting with the ground state atom is in the excited reference states we match the effective perturbative Hamiltonian with the scattering matrix amplitude.

This dissertation is organized as follows. In Section 2, we discuss the basic mathematical formulation. We present derivations based on the expansion of electrostatic interaction and time-ordered perturbation theory. We will realize that the interatomic distance has to be distinguished into three regimes. The last subsection of Section 2 focuses on the long-range tails to the vdW interaction. This subsection shows how an oscillatory dependence of the interaction energy naturally arises due to the presence of quasi-degenerate states. In Section 3, we introduce the Sturmian decomposition of the Green function and determine direct and mixing matrix elements for the first few nS -states of hydrogen. Section 4 highlights what is a Dirac- δ perturbation of the vdW energy, why we care it, and how we determine it.

Section 5 is devoted only to the $1S$ - $1S$ system. We calculate the vdW coefficient for the $1S$ - $1S$ system. We also evaluate the δ -modification to the vdW interaction energy for the $1S$ - $1S$ system. In Section 6, we extend our study to the $2S$ - $1S$ system. In the $2S$ - $1S$ system, an atom in the ground state now interacts with the other atom in the $n = 2$ excited states. This causes many complications. We will see how important a role the quasi-degenerate levels play in the interaction energy. We also study the modification of the interaction energy due to the δ -type potential. We make use of our model parameters to verify that our expressions of the interaction energy in the three different regimes are optimal.

Section 7 is all about the hyperfine-resolved $2S$ - $2S$ system. We make use of an applied graph theory to solve the Hamiltonian matrix of the $2S$ - $2S$ system. We extend our analysis to the vdW energy to the nS - $1S$ system, for $3 \leq n \leq 5$, in Section 8. Conclusions are drawn in Section 9. Appendix A is about discrete part of ground state static polarizability. We show that the contribution of continuum wave functions to the ground state static polarizability can not be neglected. Appendix B contains an analysis of the magic wavelengths to the nS - $1S$ systems for $2 \leq n \leq 6$.

2. DERIVATION OF LONG-RANGE INTERACTIONS

2.1. ORIENTATION

Whenever I look into the internet for some quotes, my eyes pause for a moment on the following quote of a famous physicist Galileo Galilei, “The laws of nature are written by the hand of God in the language of mathematics”. This quote speaks the importance of mathematical formulation in any scientific work very loud and clear. We devote this Section to develop some mathematical formulations which we later use to calculate many quantities in this project.

2.2. DERIVATION OF THE vdW AND CP ENERGIES

In what follows, we present a detailed derivation of the vdW and the CP interaction energies. We here discuss two approaches to deduce interaction energies, namely, derivation based on an expansion of electrostatic interaction and derivation based on a non-relativistic quantum electrodynamics using time-ordered perturbation theory.

2.2.1. Derivation Based on Expansion of Electrostatic Interaction.

Let us consider two neutral hydrogen atoms A and B . Let \vec{R}_A and $\vec{\rho}_a$ are the position vectors of the nucleus and the electron of the atom A . Similarly, \vec{R}_B and $\vec{\rho}_b$ are the position vectors of the nucleus and the electron of the atom B as shown in Figure 2.1. The Hamiltonian of the system can be written as

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{AB}, \quad (2.1)$$

where \hat{H}_A and \hat{H}_B are Hamiltonians of the atoms A and B respectively, which read

$$\hat{H}_A = \frac{\vec{p}_a^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_a - \vec{R}_A|} \quad \text{and} \quad \hat{H}_B = \frac{\vec{p}_b^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_b - \vec{R}_B|}, \quad (2.2)$$

where \vec{p}_a and \vec{p}_b are momenta of the atoms A and B respectively. The \hat{H}_{AB} represents the perturbation Hamiltonian of the system. Let us first consider the electrostatic interaction between the atoms A and B .

$$V_{\text{elec}} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_a - \vec{R}_A|} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_b - \vec{R}_B|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{R}_A - \vec{R}_B|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_a - \vec{\rho}_b|} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_a - \vec{R}_B|} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{\rho}_b - \vec{R}_A|}. \quad (2.3)$$

The first and the second terms on the right-hand side of Eq. (2.3) are the electrostatic potentials of atoms A and B respectively. Thus, the remaining terms can be treated as the perturbation on the electrostatic interaction. With this, the perturbation Hamiltonian \hat{H}_{AB} can be written as:

$$\hat{H}_{AB} = -\frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{|\vec{R}_A - \vec{R}_B|} - \frac{1}{|\vec{\rho}_a - \vec{R}_A - \vec{\rho}_b + \vec{R}_B + \vec{R}_A - \vec{R}_B|} + \frac{1}{|\vec{\rho}_a - \vec{R}_A + \vec{R}_A - \vec{R}_B|} + \frac{1}{|\vec{\rho}_b - \vec{R}_B + \vec{R}_B - \vec{R}_A|} \right\}. \quad (2.4)$$

For the sake of simplicity, let us denote $\vec{R}_A - \vec{R}_B = \vec{R}$, $\vec{\rho}_a - \vec{R}_A = \vec{r}^{(A)}$, and $\vec{\rho}_b - \vec{R}_B = \vec{r}^{(B)}$. We have,

$$\hat{H}_{AB} = -\frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{|\vec{R}|} - \frac{1}{|\vec{r}^{(A)} - \vec{r}^{(B)} + \vec{R}|} + \frac{1}{|\vec{r}^{(A)} + \vec{R}|} + \frac{1}{|\vec{r}^{(B)} - \vec{R}|} \right\}. \quad (2.5)$$

The distance between the proton of an atom and its electron is much smaller than the distance between two protons i.e. $|\vec{r}^{(A)}| \ll |\vec{R}|$ and $|\vec{r}^{(B)}| \ll |\vec{R}|$. This allows us to expand Eq. (2.5) into a series. The Taylor series expansion of Eq. (2.5) about $\vec{r}^{(A)}$

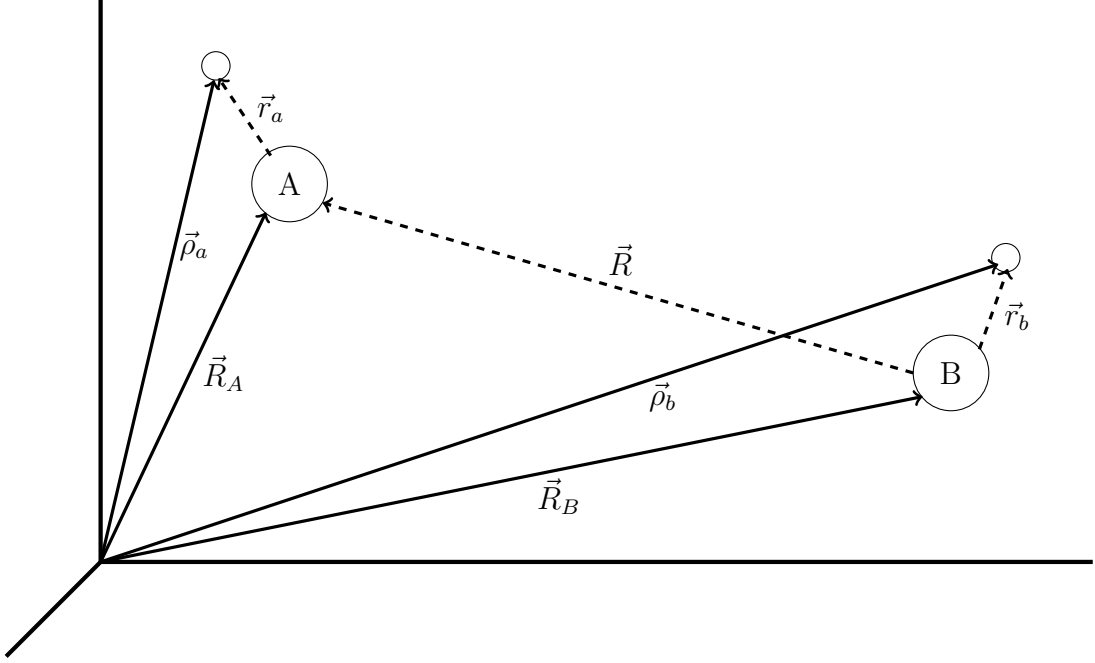


Figure 2.1: The vdW interaction of two neutral hydrogen atoms A and B .

and/or $\vec{r}^{(B)}$, to second order, is given by

$$\begin{aligned}
 \hat{H}_{AB} \approx & -\frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{1}{|\vec{R}|} - \frac{1}{|\vec{R}|} + \sum_i (r^{(A)} - r^{(B)})_i \nu_i(\vec{R}) - \frac{1}{2} \sum_{ij} (r^{(A)} - r^{(B)})_i \right. \\
 & \times (r^{(A)} - r^{(B)})_j \nu_{ij}(\vec{R}) + \frac{1}{|\vec{R}|} - \sum_i r_i^{(A)} \nu_i(\vec{R}) + \frac{1}{2} \sum_{ij} r_i^{(A)} r_j^{(A)} \nu_{ij}(\vec{R}) \\
 & \left. + \frac{1}{|\vec{R}|} + \sum_i r_i^{(B)} \nu_i(\vec{R}) + \frac{1}{2} \sum_{ij} r_i^{(B)} r_j^{(B)} \nu_{ij}(\vec{R}) \right\}, \quad (2.6)
 \end{aligned}$$

where

$$\nu_i(\vec{R}) = -\frac{R_i}{R^3} \quad \text{and} \quad \nu_{ij}(\vec{R}) = \frac{3R_i R_j - \delta_{ij} R^2}{R^5} \quad (2.7)$$

correspond to the dipole and the quadrupole contributions of the interaction potential. We can rewrite $\nu_{ij}(\vec{R})$ as

$$\nu_{ij}(\vec{R}) = -\frac{\beta_{ij}}{R^3} \quad \text{such that} \quad \beta_{ij} = \delta_{ij} - \frac{3R_i R_j}{R^2}. \quad (2.8)$$

After some algebra, Eq. (2.6) leads to

$$\hat{H}_{AB} \approx \frac{e^2}{4\pi\epsilon_0} \sum_{ij} \beta_{ij} \frac{r_i^{(A)} r_j^{(B)}}{R^3}. \quad (2.9)$$

The first order energy shift for a pair of hydrogen atoms in their ground state is given by

$$\Delta E^{(1)} = \langle \psi_{100}^{(a)} \psi_{100}^{(b)} | \hat{H}_{AB} | \psi_{100}^{(a)} \psi_{100}^{(b)} \rangle. \quad (2.10)$$

Due to the configurational symmetry of the ground state of hydrogen atoms, we have,

$$\langle \vec{r}_a - \vec{R}_A \rangle = \langle \vec{r}_b - \vec{R}_B \rangle = 0. \quad (2.11)$$

Consequently, the first order energy shift is zero, i.e., $\Delta E^{(1)} = 0$.

The first non-vanishing energy shift comes from the second order correction.

To second order in perturbation, the energy shift is

$$\begin{aligned} \Delta E^{(2)} &= \sum_{n \neq 1} \frac{\langle \psi_{100}^{(A)} \psi_{100}^{(B)} | \hat{H}_{AB} | \psi_{n\ell m}^{(A)} \psi_{n\ell m}^{(B)} \rangle \langle \psi_{n\ell m}^{(A)} \psi_{n\ell m}^{(B)} | \hat{H}_{AB} | \psi_{100}^{(A)} \psi_{100}^{(B)} \rangle}{E_0^A - E_n^A + E_0^B - E_n^B} \\ &= -\frac{e^4}{(4\pi\epsilon_0)^2} \frac{2}{|\vec{R}_A - \vec{R}_B|^6} \\ &\quad \times \sum_{n \neq 1} \sum_{i,j} \frac{\langle \psi_{100}^{(A)} | x^i | \psi_{n\ell m}^{(A)} \rangle \langle \psi_{n\ell m}^{(B)} | x^j | \psi_{100}^{(B)} \rangle \langle \psi_{100}^{(A)} | x^i | \psi_{n\ell m}^{(A)} \rangle \langle \psi_{n\ell m}^{(B)} | x^j | \psi_{100}^{(B)} \rangle}{E_0^A - E_n^A + E_0^B - E_n^B}. \quad (2.12) \end{aligned}$$

This is in the form

$$\Delta E^{(2)} = -\frac{C}{|\vec{R}_A - \vec{R}_B|^6}, \quad (2.13)$$

where C is the vdW coefficient and given by

$$C = \frac{2e^4}{(4\pi\epsilon_0)^2} \sum_{n \neq 1} \sum_{i,j} \frac{\langle \psi_{100}^{(A)} | x^i | \psi_{nlm}^{(A)} \rangle \langle \psi_{nlm}^{(B)} | x^j | \psi_{100}^{(B)} \rangle \langle \psi_{100}^{(A)} | x^i | \psi_{nlm}^{(A)} \rangle \langle \psi_{nlm}^{(B)} | x^j | \psi_{100}^{(B)} \rangle}{E_0^A - E_n^A + E_0^B - E_n^B}. \quad (2.14)$$

Making use of the identity

$$\sum_{i,j} \langle \psi_{100} | x^i | \psi_{nlm} \rangle \langle \psi_{nlm} | x^j | \psi_{100} \rangle = \frac{\delta^{ij}}{3} \sum_s \langle \psi_{100} | x^s | \psi_{nlm} \rangle \langle \psi_{nlm} | x^s | \psi_{100} \rangle, \quad (2.15)$$

which is valid for any S state, the vdW coefficient given in Eq. (2.14) yields

$$\begin{aligned} C &= \frac{2e^4}{(4\pi\epsilon_0)^2} \sum_{n \neq 1} \sum_s \sum_k \frac{\delta^{ij}}{3} \frac{\delta^{ij}}{3} \\ &\times \frac{\langle \psi_{100}^{(A)} | x^s | \psi_{nlm}^{(A)} \rangle \langle \psi_{nlm}^{(A)} | x^s | \psi_{100}^{(A)} \rangle \langle \psi_{100}^{(B)} | x^k | \psi_{nlm}^{(B)} \rangle \langle \psi_{nlm}^{(B)} | x^k | \psi_{100}^{(B)} \rangle}{E_0^A - E_n^A + E_0^B - E_n^B} \\ &= \frac{2e^4}{(4\pi\epsilon_0)^2} \sum_{n \neq 1} \sum_{s,k} \frac{\delta^{ii}}{9} \frac{\langle \psi_{100}^{(A)} | x^s | \psi_{nlm}^{(A)} \rangle \langle \psi_{nlm}^{(A)} | x^s | \psi_{100}^{(A)} \rangle \langle \psi_{100}^{(B)} | x^k | \psi_{nlm}^{(B)} \rangle \langle \psi_{nlm}^{(B)} | x^k | \psi_{100}^{(B)} \rangle}{E_0^A - E_n^A + E_0^B - E_n^B} \\ &= \frac{2e^4}{3(4\pi\epsilon_0)^2} \sum_{n \neq 1} \sum_s \sum_k \frac{|\langle \psi_{100}^{(A)} | x^s | \psi_{nlm}^{(A)} \rangle|^2 |\langle \psi_{100}^{(B)} | x^k | \psi_{nlm}^{(B)} \rangle|^2}{E_0^A - E_n^A + E_0^B - E_n^B}. \end{aligned} \quad (2.16)$$

With the following integral identity

$$\begin{aligned} \frac{2ab}{\pi} \int_0^\infty \frac{dx}{(a^2 + x^2)(b^2 + x^2)} &= \frac{ab}{\pi} \int_{-\infty}^\infty \frac{dx}{(i|a| + x)(-i|a| + x)(i|b| + x)(-i|b| + x)} \\ &= \frac{ab}{\pi} 2\pi i \left[\frac{1}{2|a|i} \frac{1}{|b|^2 - |a|^2} + \frac{1}{2|b|i} \frac{1}{|a|^2 - |b|^2} \right] \\ &= \text{sgn}(a)\text{sgn}(b) \left[\frac{|a|}{|a|^2 - |b|^2} - \frac{|b|}{|a|^2 - |b|^2} \right] \end{aligned}$$

$$= \frac{\text{sgn}(a)\text{sgn}(b)}{|a| + |b|}, \quad (2.17)$$

where $\text{sgn}(a)$ and $\text{sgn}(b)$ are sign functions, Eq. (2.16) can be written as

$$C = \frac{4e^4\hbar}{3\pi(4\pi\epsilon_0)^2} \sum_{n \neq 1} \sum_{j,k} \int_0^\infty d\omega (E_0^A - E_n^A)(E_0^B - E_n^B) \\ \times \frac{|\langle \psi_{100} | x^j | \psi_{n\ell m} \rangle|^2 |\langle \psi_{n\ell m} | x^k | \psi_{100} \rangle|^2}{\left((E_0^A - E_n^A)^2 + (\hbar\omega)^2 \right) \left((E_0^B - E_n^B)^2 + (\hbar\omega)^2 \right)}. \quad (2.18)$$

The sign function $\text{sgn}(a)$ of the real number a is $+1$ if $a > 0$ and -1 if $a < 0$ and similarly for $\text{sgn}(b)$. The quantity

$$\frac{2e^2}{3} \sum_j (E_0^A - E_n^A) \frac{|\langle \psi_{100} | x^j | \psi_{n\ell m} \rangle|^2}{\left((E_0^A - E_n^A)^2 + (\hbar\omega)^2 \right)} = \alpha_{1S}(i\omega, A), \quad (2.19)$$

is the dipole polarizability of the hydrogen atom A in its ground state. We have a similar expression for the atom B . The polarizability of an atom measures the distortion of the charge distribution of the atom in the presence of the electric field. An atom having high polarizability has large fluctuations in local charge distribution [23]. Thus, from Eq. (2.18), the vdW coefficient can be expressed as

$$C = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega, A) \alpha_{1S}(i\omega, B). \quad (2.20)$$

The important feature of expression (2.20) is the dependence of vdW coefficient on the polarizabilities of the atoms.

2.2.2. Derivation Using Time-Ordered Perturbation Theory. The unperturbed Hamiltonian for a system of two neutral hydrogen atoms A and B is

$$\hat{H}_0 = \frac{\vec{p}_a^2}{2m_a} + V(\vec{r}_a) + \frac{\vec{p}_b^2}{2m_b} + V(\vec{r}_b) + \hat{H}_F, \quad (2.21)$$

where (m_a, m_b) , (\vec{r}_a, \vec{r}_b) , and (\vec{p}_a, \vec{p}_b) are masses, coordinates and momenta of electrons in atoms A and B . And

$$\hat{H}_F = \sum_{\lambda=1}^2 \int d^3k k a_{\lambda}^{\dagger}(\vec{k}) a_{\lambda}(\vec{k}) \quad (2.22)$$

is the electromagnetic field Hamiltonian where a_{λ}^{\dagger} and a_{λ} are the usual creation and annihilation operators. If the two atoms are far enough such that $|\vec{r}_a - \vec{R}_A| \ll |\vec{r}_a - \vec{R}_B|$ and $|\vec{r}_b - \vec{R}_B| \ll |\vec{r}_b - \vec{R}_A|$, where \vec{R}_A and \vec{R}_B are the coordinates of the nuclei, the potential $V(\vec{r}_a)$ and $V(\vec{r}_b)$ can be approximated as

$$V(\vec{r}_a) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_a - \vec{R}_A|}, \quad \text{and} \quad V(\vec{r}_b) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_b - \vec{R}_B|}. \quad (2.23)$$

Substituting $V(\vec{r}_a)$ and $V(\vec{r}_b)$ in Eq. (2.21), the unperturbed Hamiltonian of the system yields

$$\hat{H}_0 = \frac{\vec{p}_a^2}{2m_a} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_a - \vec{R}_A|} + \frac{\vec{p}_b^2}{2m_b} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_b - \vec{R}_B|} + \hat{H}_F. \quad (2.24)$$

The first two terms stand for the Schrödinger-Coulomb Hamiltonian \hat{H}_A , the sum of the third and the fourth terms are the Schrödinger-Coulomb Hamiltonian \hat{H}_B , and the \hat{H}_F is the field Hamiltonian. Along with the dipole approximation, the interaction Hamiltonian in the so-called length gauges formulation of quantum electrodynamics (QED) reads

$$\hat{H}_{AB} = -e\vec{r}_a \cdot \vec{E}(\vec{R}_A) - e\vec{r}_b \cdot \vec{E}(\vec{R}_B), \quad (2.25)$$

where $\vec{E}(\vec{R}_A)$ and $\vec{E}(\vec{R}_B)$ are the electric field operators given as

$$\vec{E}(\vec{R}_A) = \sqrt{\frac{\hbar c}{\epsilon_0}} \sum_{\lambda=1}^2 \int \frac{d^3k}{(2\pi)^{3/2}} \sqrt{\frac{k}{2}} \hat{\epsilon}_{\lambda}(\vec{k}) \left[i a_{\lambda}(\vec{k}) e^{i\vec{k} \cdot \vec{R}_A} - i a_{\lambda}^{\dagger}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_A} \right], \quad (2.26)$$

and

$$\vec{E}(\vec{R}_B) = \sqrt{\frac{\hbar c}{\epsilon_0}} \sum_{\lambda=1}^2 \int \frac{d^3 k}{(2\pi)^{3/2}} \sqrt{\frac{k}{2}} \hat{\epsilon}_\lambda(\vec{k}) \left[i a_\lambda(\vec{k}) e^{i\vec{k} \cdot \vec{R}_B} - i a_\lambda^\dagger(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_B} \right]. \quad (2.27)$$

In terms of the creation, annihilation operators of the field, the interaction Hamiltonian becomes

$$\begin{aligned} \hat{H}_{AB} = & - \sqrt{\frac{\hbar c}{\epsilon_0}} e \sum_{\lambda=1}^2 \int \frac{d^3 k}{(2\pi)^{3/2}} \sqrt{\frac{k}{2}} \left[\left(i a_\lambda(\vec{k}) \hat{\epsilon}_\lambda(\vec{k}) e^{i\vec{k} \cdot \vec{R}_A} - i a_\lambda^\dagger(\vec{k}) \hat{\epsilon}_\lambda(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_A} \right) \cdot \vec{r}_a \right. \\ & \left. + \left(i a_\lambda(\vec{k}) \hat{\epsilon}_\lambda(\vec{k}) e^{i\vec{k} \cdot \vec{R}_B} - i a_\lambda^\dagger(\vec{k}) \hat{\epsilon}_\lambda(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_B} \right) \cdot \vec{r}_b \right]. \end{aligned} \quad (2.28)$$

We take the state with zero photons $|\phi_0\rangle$ as the reference state and calculate the perturbation effect of the interaction Hamiltonian. The creation operator increases the number of particles in a given state $|n\rangle$ by one and brings the system to the state $|n+1\rangle$ while the annihilation operator decreases the number of particles by one and brings the system into the new state $|n-1\rangle$. In the first order perturbation, the annihilation operator kills the state as our system is already in the ground state and the creation operators bring the system into its first excited state. The orthonormality condition,

$$\langle n|m\rangle = \delta_{nm} = \begin{cases} 1, & \text{if } n = m, \\ 0, & \text{if } n \neq m, \end{cases} \quad (2.29)$$

requires that the first order contribution should vanish. In the similar fashion, no odd order perturbation contributes to the interaction energy. The second order terms are the self-energy terms and do not contribute to the CP interaction. Thus, we look

into the fourth order perturbation which reads

$$\Delta E^{(4)} = \langle \phi_0 | \hat{H}_{AB} \frac{1}{(E_0 - \hat{H}_0)'} \hat{H}_{AB} \frac{1}{(E_0 - \hat{H}_0)'} \hat{H}_{AB} \frac{1}{(E_0 - \hat{H}_0)'} \hat{H}_{AB} | \phi_0 \rangle. \quad (2.30)$$

The prime in the operator $\frac{1}{(E_0 - \hat{H}_0)'}$ indicates that the reference state is excluded from the spectral decomposition of the operator.

Consider a CP interaction between two atoms A and B involving two virtual photons. A time-ordered sequence results four different types of intermediate states [24; 25], namely, (1) Both atoms are in ground states, and two virtual photons are present, (2) Only one atom is in the excited state, and only one virtual photon is exchanged, (3) Both atoms are excited state, but no photon is present, and (4) Both atoms are excited state, and two photons are present. Thus, the electrons and photons can couple in $4 \times 3 \times 2 \times 1 = 12$ distinct ways. Figure 2.2 represents all these 12 possible interactions.

Let us first investigate the first diagram of the Figure (2.2). There are four factors which give contributions to the interaction energy, namely, emission of \vec{k}_2 at R_B , emission of \vec{k}_1 at R_B , absorption of \vec{k}_2 at R_A , and absorption of \vec{k}_1 at R_A . The corresponding fourth order energy shift reads

$$\begin{aligned} \Delta E_1^{(4)} = & \left(\frac{\hbar c}{\epsilon_0} \right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \sum_{\lambda_1, \lambda_2} \sum_{\rho, \sigma} \frac{k_1}{2} \frac{k_2}{2} \langle \phi_0 | \left[\left(-i a_{\lambda_1}(\vec{k}_1) e^{-i\vec{k}_1 \cdot \vec{R}_A} + \right. \right. \\ & \left. \left. i a_{\lambda_1}^\dagger(\vec{k}_1) e^{i\vec{k}_1 \cdot \vec{R}_A} \right) \hat{\epsilon}_{\lambda_1}(\vec{k}_1) \cdot \vec{r}_a | \rho \rangle \langle \rho | + \left(i a_{\lambda_1}(\vec{k}_1) e^{i\vec{k}_1 \cdot \vec{R}_B} - i a_{\lambda_1}^\dagger(\vec{k}_1) e^{-i\vec{k}_1 \cdot \vec{R}_B} \right) \right. \\ & \left. \times \hat{\epsilon}_{\lambda_1}(\vec{k}_1) \cdot \vec{r}_b | \sigma \rangle \langle \sigma | \right] \left[\left(-i a_{\lambda_2}(\vec{k}_2) e^{-i\vec{k}_2 \cdot \vec{R}_A} + i a_{\lambda_2}^\dagger(\vec{k}_2) e^{i\vec{k}_2 \cdot \vec{R}_A} \right) \hat{\epsilon}_{\lambda_2}(\vec{k}_2) \cdot \vec{r}_a \right. \\ & \left. + \left(i a_{\lambda_2}(\vec{k}_2) e^{i\vec{k}_2 \cdot \vec{R}_B} - i a_{\lambda_2}^\dagger(\vec{k}_2) e^{-i\vec{k}_2 \cdot \vec{R}_B} \right) \hat{\epsilon}_{\lambda_2}(\vec{k}_2) \cdot \vec{r}_b \right] | \phi_0 \rangle \\ & \frac{1}{E_{1S,a} - E_\rho - \hbar c k_1} \frac{1}{-\hbar c k_1 - \hbar c k_2} \frac{1}{E_{1S,b} - E_\sigma - \hbar c k_2}. \end{aligned} \quad (2.31)$$

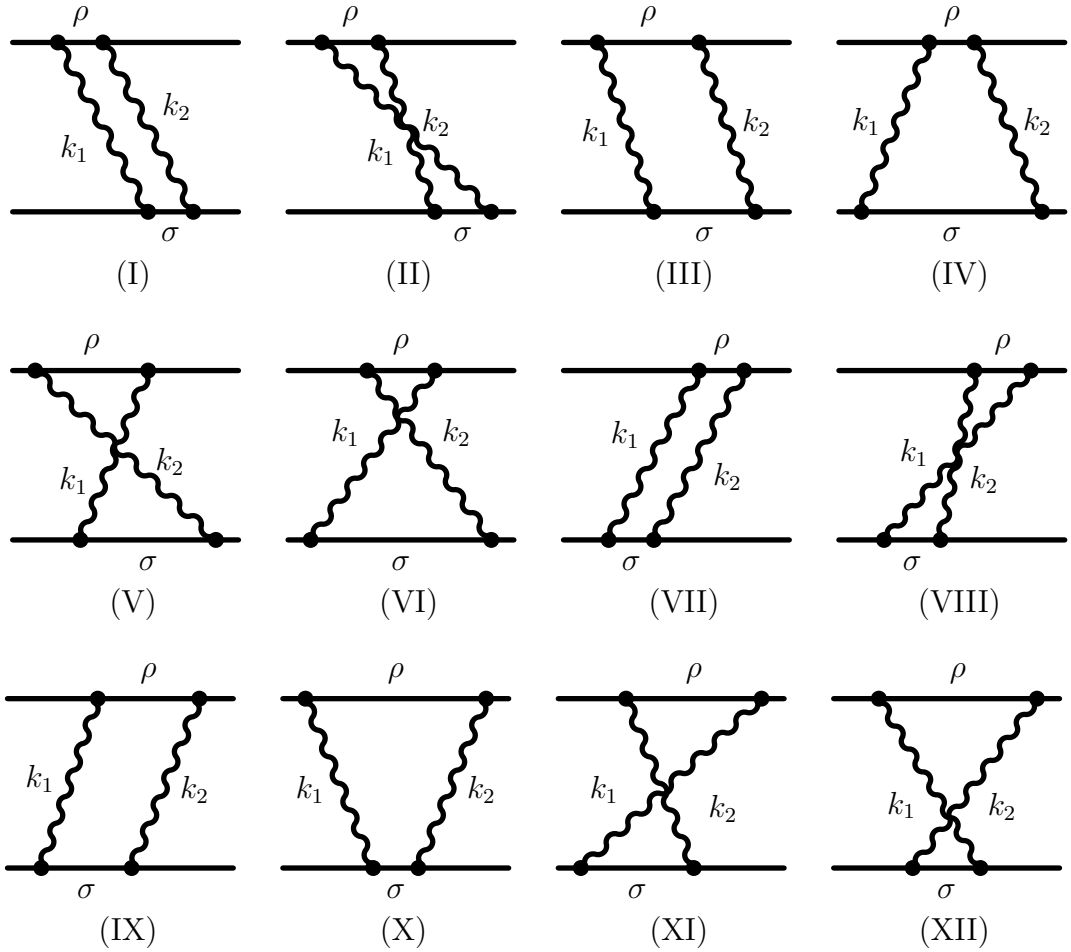


Figure 2.2: Diagram showing the CP interaction between two atoms A and B . The ρ and σ lines are the virtual states associated with the atom A and the atom B . The k_1 is the magnitude of the momentum of the photon to the left, and the k_2 is the magnitude of the momentum of the photon to the right of the line.

The annihilation operator kills the ground state however the creation operator can raise a particular state to the corresponding excited state. Thus, Eq. (2.31) yields

$$\begin{aligned}
\Delta E_1^{(4)} &= \left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \sum_{\lambda_1, \lambda_2} \sum_{\rho, \sigma} \frac{k_1 k_2}{4} (i) \langle \phi_{1S,a} | \hat{\epsilon}_{\lambda_1}(\vec{k}_1) \cdot \vec{r}_a | \rho \rangle e^{i\vec{k}_1 \cdot \vec{R}_A} (-i) \\
&\times \langle \phi_{1S,b} | \hat{\epsilon}_{\lambda_1}(\vec{k}_1) \cdot \vec{r}_b | \sigma \rangle e^{-i\vec{k}_1 \cdot \vec{R}_B} (i) \langle \rho | \hat{\epsilon}_{\lambda_2}(\vec{k}_2) \cdot \vec{r}_a | \phi_{1S,a} \rangle e^{i\vec{k}_2 \cdot \vec{R}_A} (-i) \langle \sigma | \hat{\epsilon}_{\lambda_2}(\vec{k}_2) \cdot \vec{r}_b | \phi_{1S,b} \rangle \\
&\times e^{-i\vec{k}_2 \cdot \vec{R}_B} \frac{1}{E_{1S,a} - E_\rho - \hbar c k_1} \frac{1}{-\hbar c k_1 - \hbar c k_2} \frac{1}{E_{1S,b} - E_\sigma - \hbar c k_2}. \tag{2.32}
\end{aligned}$$

The polarization vectors $\hat{\epsilon}_{\lambda_i}(\vec{k}_i)$, $i = 1, 2$ satisfy

$$\hat{\epsilon}_{\lambda_i}(\vec{k}) \cdot \hat{\epsilon}_{\lambda_j}(\vec{k}) = \delta_{\lambda_i \lambda_j}, \quad (2.33)$$

$$\vec{k} \cdot \hat{\epsilon}_{\lambda_i}(\vec{k}) = 0, \quad (2.34)$$

$$\sum_{\lambda_i=1}^2 \hat{\epsilon}_{\lambda_i}^p(\vec{k}_r) \hat{\epsilon}_{\lambda_i}^q(\vec{k}_r) = \delta^{pq} - \frac{k_r^p k_r^q}{k_r^2}. \quad (2.35)$$

Thus, the contribution to the interaction energy from the first diagram reads

$$\begin{aligned} \Delta E_1^{(4)} &= \left(\frac{\hbar c}{\epsilon_0} \right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \\ &\quad \times \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \\ &\quad \times \sum_{\rho, \sigma} \frac{\langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle}{(E_{1S,a} - E_\rho - \hbar c k_1)(-\hbar c k_1 - \hbar c k_2)(E_{1S,b} - E_\sigma - \hbar c k_2)}. \end{aligned} \quad (2.36)$$

In the diagram (II), the four factors which contribute to the interaction energy are emission of \vec{k}_2 at R_B , emission of \vec{k}_2 at R_A , absorption of \vec{k}_1 at R_B , and absorption of \vec{k}_1 at R_A . This leads to the following contributions to the interaction energy

$$\begin{aligned} \Delta E_2^{(4)} &= \left(\frac{\hbar c}{\epsilon_0} \right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \\ &\quad \times \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \\ &\quad \times \sum_{\rho, \sigma} \frac{\langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle}{(E_{1S,a} - E_\rho - \hbar c k_2)(-\hbar c k_1 - \hbar c k_2)(E_{1S,b} - E_\sigma - \hbar c k_2)}. \end{aligned} \quad (2.37)$$

If we denote a propagator denominator by \mathcal{D} , then for diagrams (I) and (II), we have,

$$\mathcal{D}_I = (E_{1S,a} - E_\rho - \hbar c k_1)(-\hbar c k_1 - \hbar c k_2)(E_{1S,b} - E_\sigma - \hbar c k_2), \quad (2.38)$$

$$\mathcal{D}_{II} = (E_{1S,a} - E_\rho - \hbar c k_2)(-\hbar c k_1 - \hbar c k_2)(E_{1S,b} - E_\sigma - \hbar c k_2). \quad (2.39)$$

The diagram (III) in Figure (2.2) involves the emission of \vec{k}_2 at R_B , the emission of \vec{k}_1 at R_A and the excitation of both atoms. Thus the propagator denominator (\mathcal{D}_{III}) corresponding to the diagram (III) reads

$$\mathcal{D}_{III} = (E_{1S,a} - E_\rho - \hbar ck_1)(E_{1S,a} - E_\sigma + E_{1S,b} - E_\rho)(E_{1S,b} - E_\sigma - \hbar ck_2). \quad (2.40)$$

The corresponding energy shift is

$$\begin{aligned} \Delta E_3^{(4)} &= \left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \\ &\times \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \\ &\times \sum_{\rho, \sigma} \frac{\langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle}{(E_{1S,a} - E_\rho - \hbar ck_1)(E_{1S,a} - E_\sigma + E_{1S,b} - E_\rho)(E_{1S,b} - E_\sigma - \hbar ck_2)}. \end{aligned} \quad (2.41)$$

Let us investigate diagram (IV) in Figure (2.2). The contribution to the interaction energy from the diagram (IV) reads

$$\begin{aligned} \Delta E_4^{(4)} &= \left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \\ &\times \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) e^{i(-\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \\ &\times \sum_{\rho, \sigma} \frac{\langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle}{(E_{1S,b} - E_\sigma - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma)(E_{1S,b} - E_\sigma - \hbar ck_2)}. \end{aligned} \quad (2.42)$$

We change the sign of k_1 under the integral sign to get the same exponential for all diagrams in Figure (2.2). Diagrams (V) and (VI) involve the emission of photon, excitation of both atoms and the absorption of photons. The propagator denominators for the diagrams (V) and (VI) are

$$\begin{aligned} \mathcal{D}_V &= (E_{1S,a} - E_\rho - \hbar ck_2)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma - \hbar ck_1 - \hbar ck_2) \\ &\times (E_{1S,b} - E_\sigma - \hbar ck_2), \end{aligned} \quad (2.43)$$

$$\begin{aligned} \mathcal{D}_{VI} &= (E_{1S,b} - E_\sigma - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma - \hbar ck_1 - \hbar ck_2) \\ &\quad \times (E_{1S,b} - E_\sigma - \hbar ck_2). \end{aligned} \quad (2.44)$$

Under the exchange of the ρ line and the σ line, the six diagrams (I) to (VI) correspond to the other six diagrams (VII) to (XII). The corresponding propagator denominators for the diagrams (VII) to (XII) are

$$\mathcal{D}_{VII} = (E_{1S,b} - E_\sigma - \hbar ck_1)(-\hbar ck_1 - \hbar ck_2)(E_{1S,a} - E_\rho - \hbar ck_2), \quad (2.45)$$

$$\mathcal{D}_{VIII} = (E_{1S,b} - E_\sigma - \hbar ck_2)(-\hbar ck_1 - \hbar ck_2)(E_{1S,a} - E_\rho - \hbar ck_2), \quad (2.46)$$

$$\mathcal{D}_{IX} = (E_{1S,b} - E_\sigma - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma)(E_{1S,a} - E_\rho - \hbar ck_2), \quad (2.47)$$

$$\mathcal{D}_X = (E_{1S,a} - E_\rho - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma)(E_{1S,a} - E_\rho - \hbar ck_2), \quad (2.48)$$

$$\begin{aligned} \mathcal{D}_{XI} &= (E_{1S,b} - E_\sigma - \hbar ck_2)(E_{1S,a} - E_\sigma + E_{1S,b} - E_\rho - \hbar ck_1 - \hbar ck_2) \\ &\quad \times (E_{1S,a} - E_\rho - \hbar ck_2), \end{aligned} \quad (2.49)$$

$$\begin{aligned} \mathcal{D}_{XII} &= (E_{1S,a} - E_\rho - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma - \hbar ck_1 - \hbar ck_2) \\ &\quad \times (E_{1S,a} - E_\rho - \hbar ck_2). \end{aligned} \quad (2.50)$$

The net fourth order energy shift is the sum of the contributions of all the 12 diagrams. Explicitly,

$$\begin{aligned} \Delta E^{(4)} &= \left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2}\right) \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2}\right) e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \\ &\quad \times \sum_{\rho, \sigma} \langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle \sum_{j=I}^{XII} \mathcal{D}_j^{-1}. \end{aligned} \quad (2.51)$$

The propagator denominators corresponding to the diagrams (I), (II) and (IV) are the denominators of the summands of Eqs. (2.36), (2.37) and (2.42). Namely,

$$\mathcal{D}_I = (E_{1S,a} - E_\rho - \hbar ck_1)(-\hbar ck_1 - \hbar ck_2)(E_{1S,b} - E_\sigma - \hbar ck_2), \quad (2.52)$$

$$\mathcal{D}_{II} = (E_{1S,a} - E_\rho - \hbar ck_2)(-\hbar ck_1 - \hbar ck_2)(E_{1S,b} - E_\sigma - \hbar ck_2), \quad (2.53)$$

$$\mathcal{D}_{IV} = (E_{1S,b} - E_\sigma - \hbar ck_1)(E_{1S,a} - E_\rho + E_{1S,b} - E_\sigma)(E_{1S,b} - E_\sigma - \hbar ck_2). \quad (2.54)$$

while remaining \mathcal{D} 's are given by Eq. (2.40) and Eqs. (2.43) to (2.50). We first compute the sum of \mathcal{D} 's. For simplicity, let us denote $E_{1S,a} - E_\rho = E_{a\rho}$ and $E_{1S,b} - E_\sigma = E_{b\sigma}$. Let us now group, simplify, and then assemble all the terms as below.

$$\begin{aligned} \mathcal{D}_I^{-1} + \mathcal{D}_{III}^{-1} &= \frac{-(E_{a\rho} - \hbar ck_1) - (E_{b\sigma} - \hbar ck_2)}{(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_1)(E_{b\sigma} - \hbar ck_2)(\hbar ck_1 + \hbar ck_2)} \\ &= \frac{-1}{(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_2)(\hbar ck_1 + \hbar ck_2)} + \\ &\quad \frac{-1}{(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_1)(\hbar ck_1 + \hbar ck_2)}, \end{aligned} \quad (2.55a)$$

$$\begin{aligned} \mathcal{D}_{IV}^{-1} &= \frac{1}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_2)} \\ &= \frac{1}{(E_{a\rho} + E_{b\sigma})} \left(\frac{1}{(E_{b\sigma} - \hbar ck_1)} - \frac{1}{(E_{b\sigma} - \hbar ck_2)} \right) \frac{1}{(\hbar ck_1 - \hbar ck_2)}, \end{aligned} \quad (2.55b)$$

$$\begin{aligned} \mathcal{D}_{VII}^{-1} + \mathcal{D}_{IX}^{-1} &= \frac{1}{(E_{b\sigma} - \hbar ck_2)(-\hbar ck_1 - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} + \\ &\quad \frac{1}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_2)} \\ &= \frac{-(E_{a\rho} - \hbar ck_2) - (E_{b\sigma} - \hbar ck_1)}{(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_2)(E_{b\sigma} - \hbar ck_1)(\hbar ck_1 + \hbar ck_2)} \\ &= \frac{-1}{(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_1)(\hbar ck_1 + \hbar ck_2)} + \\ &\quad \frac{-1}{(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_2)(\hbar ck_1 + \hbar ck_2)}, \end{aligned} \quad (2.55c)$$

$$\begin{aligned} \mathcal{D}_X^{-1} &= \frac{1}{(E_{a\rho} - \hbar ck_1)(E_{a\rho} + E_{b\sigma})(E_{a\rho} - \hbar ck_2)} \\ &= \frac{1}{(E_{a\rho} + E_{b\sigma})} \left(\frac{1}{(E_{a\rho} - \hbar ck_1)} - \frac{1}{(E_{a\rho} - \hbar ck_2)} \right) \frac{1}{(\hbar ck_1 - \hbar ck_2)}, \end{aligned} \quad (2.55d)$$

$$\begin{aligned} \mathcal{D}_V^{-1} + \mathcal{D}_{VI}^{-1} &= \frac{1}{(E_{a\rho} - \hbar ck_2)(E_{a\rho} + E_{b\sigma} - \hbar ck_1 - \hbar ck_2)(E_{b\sigma} - \hbar ck_2)} \\ &\quad + \frac{1}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} + E_{b\sigma} - \hbar ck_1 - \hbar ck_2)(E_{b\sigma} - \hbar ck_2)} \\ &= \frac{1}{(E_{b\sigma} - \hbar ck_1)(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)}, \end{aligned} \quad (2.55e)$$

$$\begin{aligned}
\mathcal{D}_{xI}^{-1} + \mathcal{D}_{xII}^{-1} &= \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{b\sigma} + E_{a\rho} - \hbar ck_1 - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \\
&\quad + \frac{1}{(E_{a\rho} - \hbar ck_1)(E_{a\rho} + E_{b\sigma} - \hbar ck_1 - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \\
&= \frac{1}{(E_{a\rho} - \hbar ck_1)(E_{a\rho} - \hbar ck_2)(E_{b\sigma} - \hbar ck_2)}. \tag{2.55f}
\end{aligned}$$

The six propagator denominators \mathcal{D}_I^{-1} , \mathcal{D}_{III}^{-1} , \mathcal{D}_{IV}^{-1} , \mathcal{D}_{VII}^{-1} , \mathcal{D}_{IX}^{-1} , and \mathcal{D}_X^{-1} can be grouped as

$$\begin{aligned}
\mathcal{D}_I^{-1} + \mathcal{D}_{III}^{-1} + \mathcal{D}_{IV}^{-1} + \mathcal{D}_{VII}^{-1} + \mathcal{D}_{IX}^{-1} + \mathcal{D}_X^{-1} &= \frac{1}{(E_{a\rho} + E_{b\sigma})} \left[-\frac{1}{(E_{a\rho} - \hbar ck_1)} \right. \\
&\quad \times \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} - \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) - \frac{1}{(E_{b\sigma} - \hbar ck_1)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} \right. \\
&\quad \left. \left. - \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) \right] + \frac{1}{(E_{a\rho} + E_{b\sigma})} \left[-\frac{1}{(E_{a\rho} - \hbar ck_2)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \right. \right. \\
&\quad \left. \left. \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) - \frac{1}{(E_{b\sigma} - \hbar ck_2)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) \right] \\
&= -\frac{1}{(E_{a\rho} + E_{b\sigma})} \left(\frac{1}{E_{a\rho} - \hbar ck_1} + \frac{1}{E_{b\sigma} - \hbar ck_1} \right) \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \frac{1}{\hbar ck_1 - \hbar ck_2} \right) \\
&\quad - \frac{1}{(E_{a\rho} + E_{b\sigma})} \left(\frac{1}{E_{a\rho} - \hbar ck_2} + \frac{1}{E_{b\sigma} - \hbar ck_2} \right) \left(\frac{1}{\hbar ck_1 + \hbar ck_2} + \frac{1}{\hbar ck_1 - \hbar ck_2} \right). \tag{2.56}
\end{aligned}$$

Interchanging k_1 and k_2 in the second term of Eq. (2.56) we get

$$\begin{aligned}
\mathcal{D}_I^{-1} + \mathcal{D}_{III}^{-1} + \mathcal{D}_{IV}^{-1} + \mathcal{D}_{VII}^{-1} + \mathcal{D}_{IX}^{-1} + \mathcal{D}_X^{-1} &= -\frac{2}{(E_{a\rho} + E_{b\sigma})} \\
&\quad \times \left(\frac{1}{(E_{a\rho} - \hbar ck_1)} + \frac{1}{(E_{b\sigma} - \hbar ck_1)} \right) \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} - \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right). \tag{2.57}
\end{aligned}$$

Let us group the three \mathcal{D} 's \mathcal{D}_{II}^{-1} , \mathcal{D}_V^{-1} and \mathcal{D}_{VI}^{-1} .

$$\begin{aligned}
\mathcal{D}_{II}^{-1} + \mathcal{D}_V^{-1} + \mathcal{D}_{VI}^{-1} &= \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(-\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(E_{b\sigma} - \hbar ck_1)} \right) \\
&= \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(-\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(E_{b\sigma} - \hbar ck_1)} - \right. \\
&\quad \left. \frac{1}{(\hbar ck_1 - \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right)
\end{aligned}$$

$$= -\frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) + \frac{1}{(E_{a\rho} - \hbar ck_2)(E_{b\sigma} - \hbar ck_1)(\hbar ck_1 - \hbar ck_2)}. \quad (2.58)$$

The three \mathcal{D} 's, namely \mathcal{D}_{VIII}^{-1} , \mathcal{D}_{XI}^{-1} and \mathcal{D}_{XII}^{-1} can be grouped as

$$\begin{aligned} \mathcal{D}_{VIII}^{-1} + \mathcal{D}_{XI}^{-1} + \mathcal{D}_{XII}^{-1} &= \frac{-1}{(E_{b\sigma} - \hbar ck_2)(\hbar ck_1 + \hbar ck_2)(E_{a\rho} - \hbar ck_2)} + \frac{1}{(E_{a\rho} - \hbar ck_1)(E_{a\rho} - \hbar ck_2)(E_{b\sigma} - \hbar ck_2)} \\ &= \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(-\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(E_{a\rho} - \hbar ck_1)} \right) \\ &= \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(\frac{-1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} - \frac{1}{(\hbar ck_1 - \hbar ck_2)} + \frac{1}{(E_{a\rho} - \hbar ck_1)} \right) \\ &= -\frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) + \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_1)(\hbar ck_1 - \hbar ck_2)}. \end{aligned} \quad (2.59)$$

Adding Eqs. (2.58) and (2.59) we get

$$\begin{aligned} \mathcal{D}_{II}^{-1} + \mathcal{D}_V^{-1} + \mathcal{D}_{VI}^{-1} + \mathcal{D}_{VIII}^{-1} + \mathcal{D}_{XI}^{-1} + \mathcal{D}_{XII}^{-1} &= \frac{-2}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \\ &\times \left(\frac{1}{\hbar ck_1 + \hbar ck_2} + \frac{1}{\hbar ck_1 - \hbar ck_2} \right) + \frac{1}{(E_{a\rho} - \hbar ck_2)(E_{b\sigma} - \hbar ck_1)(\hbar ck_1 - \hbar ck_2)} \\ &+ \frac{1}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_1)(\hbar ck_1 - \hbar ck_2)}. \end{aligned} \quad (2.60)$$

Under the interchange of k_1 and k_2 , the second term in the right hand side of the Eq. (2.60) is equal in magnitude but opposite in sign with the third term. Thus,

$$\begin{aligned} \mathcal{D}_{II}^{-1} + \mathcal{D}_V^{-1} + \mathcal{D}_{VI}^{-1} + \mathcal{D}_{VIII}^{-1} + \mathcal{D}_{XI}^{-1} + \mathcal{D}_{XII}^{-1} \\ = -\frac{2}{(E_{b\sigma} - \hbar ck_2)(E_{a\rho} - \hbar ck_2)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} + \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right). \end{aligned} \quad (2.61)$$

Interchanging k_1 and k_2 in Eq. (2.61) and adding the result to Eq. (2.57), the sum of the reciprocal of all the twelve propagator denominators evaluates to

$$\begin{aligned} \sum_{j=I}^{XII} \mathcal{D}_j^{-1} &= -\frac{2}{(E_{a\rho} + E_{b\sigma})} \left(\frac{1}{E_{a\rho} - \hbar ck_1} + \frac{1}{E_{b\sigma} - \hbar ck_1} \right) \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \right. \\ &\quad \left. \frac{1}{\hbar ck_1 - \hbar ck_2} \right) - \frac{2}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \frac{1}{\hbar ck_1 - \hbar ck_2} \right) \\ &= \frac{-4(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \frac{1}{\hbar ck_1 - \hbar ck_2} \right). \end{aligned} \quad (2.62)$$

The fourth order energy shift is now simplified to

$$\begin{aligned} \Delta E^{(4)} &= -\left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) \\ &\quad \times e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \sum_{\rho, \sigma} \langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle \sum_{j=I}^{XII} \mathcal{D}_j^{-1} \\ &= -\left(\frac{\hbar c}{\epsilon_0}\right)^2 e^4 \int \frac{d^3 k_1}{(2\pi)^3} \int \frac{d^3 k_2}{(2\pi)^3} \frac{k_1 k_2}{4} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) \\ &\quad \times e^{i(\vec{k}_1 + \vec{k}_2) \cdot (\vec{R}_A - \vec{R}_B)} \sum_{\rho, \sigma} \langle \phi_{1S,a} | x^m | \rho \rangle \langle \rho | x^n | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^r | \sigma \rangle \langle \sigma | x^s | \phi_{1S,b} \rangle \\ &\quad \times \frac{4(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \frac{1}{\hbar ck_1 - \hbar ck_2} \right). \end{aligned} \quad (2.63)$$

Let us use the identity (2.15) in Eq. (2.63). We get,

$$\begin{aligned} \Delta E^{(4)} &= -\left(\frac{\hbar c}{\epsilon_0}\right)^2 \frac{e^4}{576\pi^6} \int d^3 k_1 \int d^3 k_2 k_1 k_2 \delta^{mn} \delta^{rs} \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) \left(\delta^{ns} - \frac{k_2^n k_2^s}{k_2^2} \right) \\ &\quad \times e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{R}} \sum_{\rho, \sigma} \sum_j \sum_\ell \langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle \\ &\quad \times \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{a\rho} + E_{b\sigma})(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left(\frac{1}{\hbar ck_1 + \hbar ck_2} - \frac{1}{\hbar ck_1 - \hbar ck_2} \right), \end{aligned} \quad (2.64)$$

where, $\vec{R}_A - \vec{R}_B = \vec{R}$. Now substitute $\int d^3k = \int_0^\infty k^2 dk \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$ in Eq. (2.64)

and carry out the integration of the angular part first. Note that

$$\begin{aligned}
\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) e^{i\vec{k}_1 \cdot \vec{R}} &= 2\pi \int_0^\pi \sin\theta d\theta \left(\delta^{mr} - \frac{k_1^m k_1^r}{k_1^2} \right) e^{ik_1 R \cos\theta} \\
&= 2\pi \left(\delta^{mr} + \frac{1}{k_1^2} \frac{\partial}{\partial R^m} \frac{\partial}{\partial R^r} \right) \int_{-1}^1 du e^{ik_1 Ru} \\
&= 2\pi \left(\delta^{mr} + \frac{1}{k_1^2} \frac{\partial}{\partial R^m} \frac{\partial}{\partial R^r} \right) \frac{2 \sin k_1 R}{k_1 R} \\
&= 4\pi \left[\left(\delta^{mr} - \frac{R^m R^r}{R^2} \right) \frac{\sin k_1 R}{k_1 R} + \left(\delta^{mr} - 3 \frac{R^m R^r}{R^2} \right) \frac{\cos k_1 R}{(k_1 R)^2} \right. \\
&\quad \left. - \left(\delta^{mr} - 3 \frac{R^m R^r}{R^2} \right) \frac{\sin k_1 R}{(k_1 R)^3} \right]. \tag{2.65}
\end{aligned}$$

With the help of Eq. (2.65), Eq. (2.64) can be re-expressed as

$$\begin{aligned}
\Delta E^{(4)} &= - \left(\frac{\hbar c}{\epsilon_0} \right)^2 \frac{e^4}{36\pi^4} \sum_{\rho, \sigma} \sum_{j, \ell} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \int_0^\infty dk_1 \\
&\times \int_0^\infty dk_2 k_1^3 k_2^3 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left(\frac{1}{(\hbar ck_1 + \hbar ck_2)} - \frac{1}{(\hbar ck_1 - \hbar ck_2)} \right) \delta^{mn} \delta^{rs} \\
&\left[\left(\delta^{mr} - \frac{R^m R^r}{R^2} \right) \frac{\sin k_1 R}{k_1 R} + \left(\delta^{mr} - 3 \frac{R^m R^r}{R^2} \right) \frac{\cos k_1 R}{(k_1 R)^2} - \left(\delta^{mr} - 3 \frac{R^m R^r}{R^2} \right) \frac{\sin k_1 R}{(k_1 R)^3} \right] \\
&\left[\left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \frac{\sin k_2 R}{k_2 R} + \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \frac{\cos k_2 R}{(k_2 R)^2} - \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \frac{\sin k_2 R}{(k_2 R)^3} \right] \\
&= - \frac{\hbar c e^4}{36\pi^4 \epsilon_0^2} \sum_{\rho, \sigma} \sum_{j, \ell} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \\
&\times \int_0^\infty dk_1 k_1^3 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} A^{mr}(k_1 R) \delta^{mn} \delta^{rs} \\
&\times \left(\int_0^\infty dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)} - \int_0^\infty dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 - k_2)} \right), \tag{2.66}
\end{aligned}$$

where

$$A^{ns}(x) = \left[\left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \frac{\sin x}{x} + \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \frac{\cos x}{x^2} - \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \frac{\sin x}{x^3} \right]. \tag{2.67}$$

The $A^{ns}(x)$ is an even function of x . Thus Eq. (2.66) can be equivalently written as below extending the integration limit from $-\infty$ to $+\infty$:

$$\begin{aligned} \Delta E^{(4)} = & -\frac{\hbar c e^4}{36\pi^4 \epsilon_0^2} \sum_{\rho, \sigma} \sum_{j, \ell} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \int_0^\infty dk_1 k_1^3 \\ & \times \frac{(E_{a\rho} + E_{b\sigma} - \hbar c k_1)}{(E_{b\sigma} - \hbar c k_1)(E_{a\rho} - \hbar c k_1)} A^{mr}(k_1 R) \delta^{mn} \delta^{rs} \int_{-\infty}^\infty dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)}. \end{aligned} \quad (2.68)$$

Let us evaluate the k_2 -integral first. The k_2 -integral has a pole of order one at $k_2 = -k_1$. Let $k_2 R = x$ and $k_1 R = x_1$. Then the k_2 -integral can be written as

$$\begin{aligned} \int_{-\infty}^\infty dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)} &= \frac{1}{R^3} \int_{-\infty}^\infty dx x^3 \frac{A^{ns}(x)}{(x_1 + x)} \\ &= \frac{1}{R^3} \left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \left\{ \int_{-\infty}^\infty dx \frac{x^2}{x + x_1} \frac{e^{ix}}{2i} - \int_{-\infty}^\infty dx \frac{x^2}{x + x_1} \frac{e^{-ix}}{2i} \right\} \\ &+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left\{ \int_{-\infty}^\infty dx \frac{x}{x + x_1} \frac{e^{ix}}{2} + \int_{-\infty}^\infty dx \frac{x}{x + x_1} \frac{e^{-ix}}{2} \right\} \\ &+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left\{ \int_{-\infty}^\infty dx \frac{1}{x + x_1} \frac{e^{ix}}{2i} - \int_{-\infty}^\infty dx \frac{1}{x + x_1} \frac{e^{-ix}}{2i} \right\}. \end{aligned} \quad (2.69)$$

All the first integrals under curly brackets in Eq. (2.69) diverge as $x \rightarrow \infty$ while all the second integrals in the same equation diverge as $x \rightarrow -\infty$. Let us introduce a convergence factor $e^{-\eta|x|}$ to make our integrands divergence-free. We have,

$$\begin{aligned} \int_{-\infty}^\infty dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)} &= \frac{1}{R^3} \left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \lim_{\eta \rightarrow 0} \left\{ \int_{-\infty}^\infty dx \frac{x^2}{x + x_1} \frac{e^{ix - \eta|x|}}{2i} - \int_{-\infty}^\infty dx \frac{x^2}{x + x_1} \frac{e^{-ix - \eta|x|}}{2i} \right\} \\ &+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \lim_{\eta \rightarrow 0} \left\{ \int_{-\infty}^\infty dx \frac{x}{x + x_1} \frac{e^{ix - \eta|x|}}{2} + \int_{-\infty}^\infty dx \frac{x}{x + x_1} \frac{e^{-ix - \eta|x|}}{2} \right\} \\ &+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \lim_{\eta \rightarrow 0} \left\{ \int_{-\infty}^\infty dx \frac{1}{x + x_1} \frac{e^{ix - \eta|x|}}{2i} - \int_{-\infty}^\infty dx \frac{1}{x + x_1} \frac{e^{-ix - \eta|x|}}{2i} \right\}. \end{aligned} \quad (2.70)$$

We evaluate integrals in Eq. (2.70) with the help of contours as shown in Figure 2.3 and perform the integration. We finally take the limit $\eta \rightarrow 0$ which yields

$$\begin{aligned}
\int_{-\infty}^{\infty} dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)} &= \frac{1}{R^3} \left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \left\{ \frac{1}{2} (2\pi i) x_1^2 \frac{e^{-ix_1}}{2i} - \frac{1}{2} (-2\pi i) x_1^2 \frac{e^{ix_1}}{2i} \right\} \\
&+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left\{ \frac{1}{2} (2\pi i) (-x_1) \frac{e^{-ix_1}}{2} + \frac{1}{2} (-2\pi i) (-x_1) \frac{e^{ix_1}}{2} \right\} \\
&+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left\{ \frac{1}{2} (2\pi i) \frac{e^{-ix_1}}{2i} - \frac{1}{2} (-2\pi i) \frac{e^{ix_1}}{2i} \right\} \\
&= \frac{1}{R^3} \left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \pi x_1^2 \cos x_1 - \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \pi x_1 \sin x_1 \\
&+ \frac{1}{R^3} \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \pi \cos x_1. \tag{2.71}
\end{aligned}$$

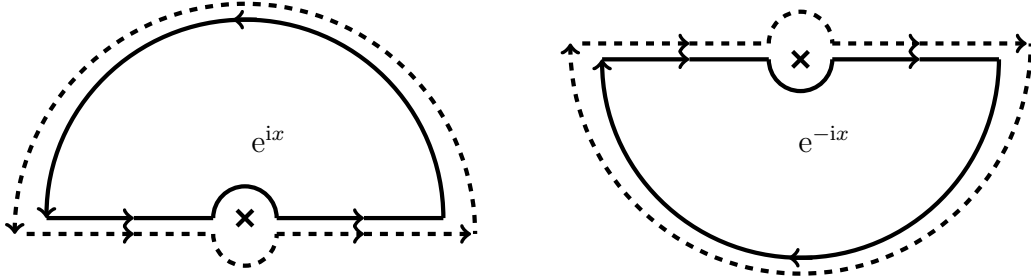


Figure 2.3: The contours to compute integrals in Eq. (2.70). We close the contour in the upper half plane to evaluate the integral containing the exponential factor e^{ix} . As the pole $x = -x_1$ align along the real axis, the integral has a value $\frac{1}{2}(2\pi i)$ times the residue at the pole. The contour is closed in the lower half plane to calculate the integral containing e^{-ix} . In such a case, the integral has a value $\frac{1}{2}(-2\pi i)$ times the residue at the pole enclosed by the contour. The negative sign is because the contour is negatively oriented.

Here we have used the following well known Euler's formula,

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta, \tag{2.72}$$

to express complex exponential functions into trigonometric functions. Rearranging Eq. (2.71), we have

$$\int_{-\infty}^{\infty} dk_2 k_2^3 \frac{A^{ns}(k_2 R)}{(k_1 + k_2)} = \frac{\pi x_1^3}{R^3} \left\{ \left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \frac{\cos x_1}{x_1} - \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left[\frac{\sin x_1}{x_1^2} + \frac{\cos x_1}{x_1^3} \right] \right\}. \quad (2.73)$$

Replacing the assumed variable x_1 by its value $x_1 = k_1 R$, we get

$$\int_{-\infty}^{\infty} dk_2 k_2^3 \frac{A(k_2 R)}{(k_1 + k_2)} = \pi k_1^3 \left[\left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \frac{\cos k_1 R}{k_1 R} - \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left(\frac{\sin k_1 R}{(k_1 R)^2} + \frac{\cos k_1 R}{(k_1 R)^3} \right) \right]. \quad (2.74)$$

Substituting the value of the integral (2.74) in Eq. (2.68), we have

$$\begin{aligned} \Delta E^{(4)} &= -\frac{\hbar c e^4}{36\pi^4 \epsilon_0^2} \sum_{\rho, \sigma} \sum_j \sum_{\ell} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^{\ell} | \sigma \rangle \langle \sigma | x^{\ell} | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \\ &\times \int_0^{\infty} dk_1 \pi k_1^6 \frac{(E_{a\rho} + E_{b\sigma} - \hbar c k_1)}{(E_{b\sigma} - \hbar c k_1)(E_{a\rho} - \hbar c k_1)} \delta^{mn} \delta^{rs} \\ &\times \left[\left(\delta^{mr} - \frac{R^m R^r}{R^2} \right) \frac{\sin k_1 R}{k_1 R} + \left(\delta^{mr} - 3 \frac{R^m R^r}{R^2} \right) \left(\frac{\cos k_1 R}{(k_1 R)^2} - \frac{\sin k_1 R}{(k_1 R)^3} \right) \right] \\ &\times \left[\left(\delta^{ns} - \frac{R^n R^s}{R^2} \right) \frac{\cos k_1 R}{k_1 R} + \left(\delta^{ns} - 3 \frac{R^n R^s}{R^2} \right) \left(\frac{\sin k_1 R}{(k_1 R)^2} + \frac{\cos k_1 R}{(k_1 R)^3} \right) \right]. \quad (2.75) \end{aligned}$$

The Kronecker delta satisfies the following relations:

$$\delta^{ij} \delta^{jk} = \delta^{ik}, \quad \delta^{ii} = 3, \quad (2.76)$$

as a result, Eq. (2.75) gets simplified to

$$\Delta E^{(4)} = -\frac{\hbar c e^4}{36\pi^4 \epsilon_0^2} \sum_{\rho, \sigma} \sum_j \sum_{\ell} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^{\ell} | \sigma \rangle \langle \sigma | x^{\ell} | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})}$$

$$\begin{aligned}
& \times \int_0^\infty dk_1 \pi k_1^6 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left[\frac{\sin 2k_1 R}{(k_1 R)^2} - 2 \frac{\sin^2 k_1 R}{(k_1 R)^3} - \frac{\sin 2k_1 R}{(k_1 R)^4} + \right. \\
& \quad \left. 2 \frac{\cos^2 k_1 R}{(k_1 R)^3} - \frac{\sin 2k_1 R}{(k_1 R)^4} - 3 \frac{\sin 2k_1 R}{(k_1 R)^4} + 3 \frac{\sin 2k_1 R}{(k_1 R)^6} - 6 \frac{\cos^2 k_1 R}{(k_1 R)^5} + 6 \frac{\sin^2 k_1 R}{(k_1 R)^5} \right] \\
& = - \frac{\hbar c e^4}{36\pi^4 \epsilon_0^2} \sum_{\rho, \sigma} \sum_j \sum_\ell \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \\
& \quad \times \int_0^\infty dk_1 \pi k_1^6 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1)}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \left[\frac{\sin 2k_1 R}{(k_1 R)^2} - 2 \frac{\sin^2 k_1 R}{(k_1 R)^3} + 2 \frac{\cos^2 k_1 R}{(k_1 R)^3} \right. \\
& \quad \left. - 5 \frac{\sin 2k_1 R}{(k_1 R)^4} - 6 \frac{\cos^2 k_1 R}{(k_1 R)^5} + 6 \frac{\sin^2 k_1 R}{(k_1 R)^5} + 3 \frac{\sin 2k_1 R}{(k_1 R)^6} \right]. \tag{2.77}
\end{aligned}$$

We make use of the following identities

$$\cos kR = \frac{e^{ikR} + e^{-ikR}}{2} \quad \text{and} \quad \sin kR = \frac{e^{ikR} - e^{-ikR}}{2i}, \tag{2.78}$$

such that the Eq. (2.77) can be expressed in the following form

$$\begin{aligned}
\Delta E^{(4)} & = - \frac{\hbar c e^4}{36\pi^3 \epsilon_0^2} \sum_{\rho, \sigma} \sum_j \sum_\ell \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle \langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{a\rho} + E_{b\sigma})} \\
& \quad \times \left[\frac{1}{2i} \int_0^\infty dk_1 k_1^6 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1) e^{2ik_1 R}}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \right. \\
& \quad \times \left\{ \frac{1}{(k_1 R)^2} + \frac{2i}{(k_1 R)^3} - \frac{5}{(k_1 R)^4} - \frac{6i}{(k_1 R)^5} + \frac{3}{(k_1 R)^6} \right\} \\
& \quad - \frac{1}{2i} \int_0^\infty dk_1 k_1^6 \frac{(E_{a\rho} + E_{b\sigma} - \hbar ck_1) e^{-2ik_1 R}}{(E_{b\sigma} - \hbar ck_1)(E_{a\rho} - \hbar ck_1)} \\
& \quad \times \left. \left\{ \frac{1}{(k_1 R)^2} - \frac{2i}{(k_1 R)^3} - \frac{5}{(k_1 R)^4} + \frac{6i}{(k_1 R)^5} + \frac{3}{(k_1 R)^6} \right\} \right]. \tag{2.79}
\end{aligned}$$

Now, let us introduce a new variable u which has values $u = i k_1 c$ in the first k_1 -integral and $u = -i k_1 c$ in the second k_1 -integral inside the square bracket $\left[\right]$ in Eq. (2.79). Consequently, We get

$$\Delta E^{(4)} = - \frac{\hbar c e^4}{c^5 36\pi^3 R^2 \epsilon_0^2} \sum_{\rho, \sigma} \sum_j \sum_\ell \int_0^\infty du u^4 E_{a\rho} \frac{\langle \phi_{1S,a} | x^j | \rho \rangle \langle \rho | x^j | \phi_{1S,a} \rangle}{(E_{a\rho}^2 + \hbar^2 u^2)} E_{b\sigma}$$

$$\begin{aligned}
& \times \frac{\langle \phi_{1S,b} | x^\ell | \sigma \rangle \langle \sigma | x^\ell | \phi_{1S,b} \rangle}{(E_{b\sigma}^2 + \hbar^2 u^2)} e^{-2uR/c} \left[1 + \frac{2c}{uR} + \frac{5c^2}{(uR)^2} + \frac{6c^3}{(uR)^3} + \frac{3c^4}{(uR)^4} \right] \\
& = - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty du \alpha(a, iu) \alpha(b, iu) \frac{u^4 e^{-2uR/c}}{R^2} \\
& \quad \left[1 + \frac{2c}{uR} + \frac{5c^2}{(uR)^2} + \frac{6c^2}{(uR)^3} + \frac{3c^4}{(uR)^4} \right] \tag{2.80}
\end{aligned}$$

$$\begin{aligned}
& = - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha(a, i\omega) \alpha(b, i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \quad \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \tag{2.81}
\end{aligned}$$

where the quantities $\alpha(a, iu)$ and $\alpha(b, iu)$ are the dynamic polarizabilities of atoms A and B respectively and given by

$$\begin{aligned}
\alpha(a, iu) &= \frac{2e^2}{3} \sum_\rho \sum_j E_{a\rho} \langle \phi_{1S,a} | x^j \frac{|\rho\rangle \langle \rho|}{(E_{a\rho}^2 + \hbar^2 u^2)} x^j | \phi_{1S,a} \rangle \\
&= \frac{2e^2}{3} \sum_j \langle \phi_{1S,a} | x^j \frac{E_{a\rho}}{(E_{a\rho}^2 + \hbar^2 u^2)} x^j | \phi_{1S,a} \rangle, \tag{2.82}
\end{aligned}$$

$$\begin{aligned}
\alpha(b, iu) &= \frac{2e^2}{3} \sum_\sigma \sum_\ell E_{b\sigma} \langle \phi_{1S,b} | x^\ell \frac{|\sigma\rangle \langle \sigma|}{(E_{b\sigma}^2 + \hbar^2 u^2)} x^\ell | \phi_{1S,b} \rangle \\
&= \frac{2e^2}{3} \sum_\sigma \sum_\ell \langle \phi_{1S,b} | x^\ell \frac{E_{b\sigma}}{(E_{b\sigma}^2 + \hbar^2 u^2)} x^\ell | \phi_{1S,b} \rangle. \tag{2.83}
\end{aligned}$$

Making use of $u = \pm ik_1 c = \pm \omega$, the dynamic polarizabilities can be rewritten as

$$\begin{aligned}
\alpha(a, i\omega) &= \frac{2e^2}{3} \sum_j \langle \phi_{1S,a} | x^j \frac{H - E_{1S,a}}{(H - E_{1S,a})^2 + \hbar^2 \omega^2} x^j | \phi_{1S,a} \rangle \\
&= \frac{e^2}{3} \sum_\pm \sum_j \langle \phi_{1S,a} | x^j \frac{1}{(H - E_{1S,a}) \pm i\hbar\omega} x^j | \phi_{1S,a} \rangle, \tag{2.84}
\end{aligned}$$

$$\alpha(b, i\omega) = \frac{e^2}{3} \sum_\pm \sum_\ell \langle \phi_{1S,b} | x^\ell \frac{1}{(H - E_{1S,b}) \pm i\hbar\omega} x^\ell | \phi_{1S,b} \rangle. \tag{2.85}$$

It is obvious to state from Eqs. (2.84) and (2.85) that the dynamic polarizability of an atom is the sum of two matrix elements of the Schödinger-Coulomb propagator.

$$\alpha(a, \omega) = P(a, \omega) + P(a, -\omega) \quad (2.86)$$

where,

$$P(a, \pm\omega) = \frac{e^2}{3} \sum_{j=1}^3 \langle n_a | x^j \frac{1}{E_n - E_a \pm \hbar\omega - i\epsilon} x^j | n_a \rangle. \quad (2.87)$$

For large ω , the polarizability shows ω^{-2} behavior. The expression for the CP interaction between any two atoms A and B given by the Eq. (2.81) is valid for any interatomic separation R provided their wave functions do not overlap.

2.3. CHIBISOV'S APPROACH

Let us consider two neutral hydrogen atoms in which one atom is in the ground state $1S$ and the other in the excited nS state. Consider the case in which the wave function of the system is in the state of quantum entanglement. The wave function of the system can be expressed as

$$\Psi = K_{1n} |1S\rangle_A |nS\rangle_B + K_{n1} |nS\rangle_A |1S\rangle_B. \quad (2.88)$$

Total Hamiltonian of the system \hat{H} is

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{AB} = \hat{H}_S + \hat{H}_{AB}, \quad (2.89)$$

where \hat{H}_S stands for the Schrödinger Hamiltonian. \hat{H}_A and \hat{H}_B are Hamiltonians of the atom A and the atom B which are respectively

$$\hat{H}_A = \frac{\vec{p}_a^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_a - \vec{R}_A|} \quad \text{and} \quad \hat{H}_B = \frac{\vec{p}_b^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_b - \vec{R}_B|}. \quad (2.90)$$

As derived in section 2.2, the interaction Hamiltonian \hat{H}_{AB} is given by

$$\hat{H}_{AB} \approx \frac{e^2}{4\pi\epsilon_0} \sum_{ij} \beta_{ij} \frac{r_i^{(A)} r_j^{(B)}}{R^3}. \quad (2.91)$$

Taking the entangled state $|\Psi\rangle$ given by Eq. (2.88) as the eigenstate, the eigenvalue equation of the system with the Hamiltonian \hat{H} is

$$\hat{H}|\Psi\rangle = \left(\hat{H}_A + \hat{H}_B + \hat{H}_{AB}\right)|\Psi\rangle = E|\Psi\rangle. \quad (2.92)$$

The total wave function of the system can be expressed as sum of all possible products

$$|\Psi\rangle = \sum_{pq} K_{pq} |pS\rangle_A |qS\rangle_B, \quad (2.93)$$

where K_{pq} is the expansion coefficient. In the first order perturbation approximation, the expansion coefficients K_{pq} are approximated as

$$K_{pq} = K_{pq}^{(0)} + K_{pq}^{(1)}, \quad (2.94)$$

where $K_{pq}^{(0)}$ are the unperturbed coefficients of expansion and the $K_{pq}^{(1)}$ are the first order corrections to the expansion coefficients. The first order correction $K_{pq}^{(1)}$ is given as

$$K_{pq}^{(1)} = K_{1n}^{(0)} \frac{\langle 1SnS | \hat{H}_{AB} | pq \rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} + K_{n1}^{(0)} \frac{\langle nS1S | \hat{H}_{AB} | pq \rangle}{E_{n1}^{(0)} - E_{pq}^{(0)}}. \quad (2.95)$$

In the eigen basis of the sum of the Hamiltonian $\hat{H}_A + \hat{H}_B + \hat{H}_{AB}$, the eigenvalue Eq. (2.92) can be expressed as

$$\begin{aligned} & \left(\hat{H}_A + \hat{H}_B + \hat{H}_{AB} \right) \sum_{pq} K_{pq} |pq\rangle = E \sum_{pq} K_{pq} |pq\rangle, \\ \text{Or, } & \sum_{pq} K_{pq} \sum_{rs} |rs\rangle \langle rs| \hat{H}_{AB} |pq\rangle = \sum_{pq} K_{pq} (E - E_{pq}^{(0)}) |pq\rangle. \end{aligned} \quad (2.96)$$

Here we have used the completeness relation

$$\sum_{rs} |rs\rangle \langle rs| = 1. \quad (2.97)$$

Eq. (2.96) can be re-expressed as

$$\sum_{pq} \left\{ K_{pq} (E - E_{pq}^{(0)}) - \sum_{rs} K_{rs} \langle rs| \hat{H}_{AB} |pq\rangle \right\} |pq\rangle = 0, \quad (2.98)$$

which implies

$$K_{pq} (E_{pq}^{(0)} - E) + \sum_{rs} K_{rs} \langle rs| \hat{H}_{AB} |pq\rangle = 0. \quad (2.99)$$

Using Eq. (2.95) in Eq. (2.99), the two equations with the expansion coefficients $K_{1n}^{(0)}$ and $K_{n1}^{(0)}$ are

$$\begin{aligned} & K_{1n}^{(0)} \left(E_{1n}^{(0)} - E + \langle 1SnS | \hat{H}_{AB} | 1SnS \rangle + \sum_{pq \neq 1n} \frac{\langle 1SnS | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | 1SnS \rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right) \\ & + K_{n1}^{(0)} \left(\langle nS1S | \hat{H}_{AB} | 1SnS \rangle + \sum_{pq \neq 1n} \frac{\langle nS1S | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | 1SnS \rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right) = 0, \end{aligned} \quad (2.100)$$

and

$$\begin{aligned}
& K_{n1}^{(0)} \left(E_{n1}^{(0)} - E + \langle nS1S | \hat{H}_{AB} | nS1S \rangle + \sum_{pq \neq n1} \frac{\langle nS1S | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | nS1S \rangle}{E_{n1}^{(0)} - E_{pq}^{(0)}} \right) \\
& + K_{1n}^{(0)} \left(\langle 1SnS | \hat{H}_{AB} | nS1S \rangle + \sum_{pq \neq n1} \frac{\langle 1SnS | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | nS1S \rangle}{E_{n1}^{(0)} - E_{pq}^{(0)}} \right) = 0.
\end{aligned} \tag{2.101}$$

The homogeneous linear Eqs. (2.100) and (2.101) can also be written as the homogeneous matrix equation

$$\begin{pmatrix} W & X \\ Y & Z \end{pmatrix} \begin{pmatrix} K_{1n}^{(0)} \\ K_{n1}^{(0)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{2.102}$$

where

$$W = E_{1n}^{(0)} - E + \langle 1SnS | \hat{H}_{AB} | 1SnS \rangle + \sum_{pq \neq 1n} \frac{|\langle 1SnS | \hat{H}_{AB} | pq \rangle|^2}{E_{1n}^{(0)} - E_{pq}^{(0)}}, \tag{2.103a}$$

$$X = \langle nS1S | \hat{H}_{AB} | 1SnS \rangle + \sum_{pq \neq 1n} \frac{\langle nS1S | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | 1SnS \rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}}, \tag{2.103b}$$

$$Y = \langle 1SnS | \hat{H}_{AB} | nS1S \rangle + \sum_{pq \neq n1} \frac{\langle 1SnS | \hat{H}_{AB} | pq \rangle \langle pq | \hat{H}_{AB} | nS1S \rangle}{E_{n1}^{(0)} - E_{pq}^{(0)}}, \tag{2.103c}$$

$$Z = E_{n1}^{(0)} - E + \langle nS1S | \hat{H}_{AB} | nS1S \rangle + \sum_{pq \neq n1} \frac{|\langle nS1S | \hat{H}_{AB} | pq \rangle|^2}{E_{n1}^{(0)} - E_{pq}^{(0)}}. \tag{2.103d}$$

The interaction Hamiltonian \hat{H}_{AB} is symmetric with respect to the order of the selection of $1S$ and nS in the eigenstates $|1SnS\rangle$ and $|nS1S\rangle$. Namely,

$$\langle 1SnS | \hat{H}_{AB} | 1SnS \rangle = \langle nS1S | \hat{H}_{AB} | nS1S \rangle. \tag{2.104}$$

Indeed, $\langle 1SnS|\hat{H}_{AB}|1SnS\rangle = \langle nS1S|\hat{H}_{AB}|nS1S\rangle = 0$ as the interaction Hamiltonian, as required by the selection rule, does not couple S states. In addition to this, with the interchange of 1 and n , the following two quantities are equal.

$$\sum_{pq \neq 1n} \frac{|\langle 1SnS|\hat{H}_{AB}|pq\rangle|^2}{E_{1n}^{(0)} - E_{pq}^{(0)}} = \sum_{pq \neq n1} \frac{|\langle nS1S|\hat{H}_{AB}|pq\rangle|^2}{E_{n1}^{(0)} - E_{pq}^{(0)}}. \quad (2.105)$$

As a result, the diagonal elements of the 2×2 matrix in (2.102) are equal. And for the same reasons the off-diagonal elements in (2.102) are also equal. Thus, the matrix in (2.102) is a 2×2 symmetric Toeplitz matrix [26]. To have non-trivial solutions, we require the determinant of the matrix to be zero which implies $K_{1n}^{(0)} = \pm K_{n1}^{(0)}$. Provided the determinant of the matrix vanishes, the 2×2 matrix in Eq. (2.102) gives

$$\begin{aligned} & \left(E_{1n}^{(0)} - E + \sum_{pq \neq 1n} \frac{|\langle 1SnS|\hat{H}_{AB}|pq\rangle|^2}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right)^2 \\ &= \left(\sum_{pq \neq 1n} \frac{\langle nS1S|\hat{H}_{AB}|pq\rangle \langle pq|\hat{H}_{AB}|1SnS\rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right)^2. \end{aligned} \quad (2.106)$$

Solving energy E from Eq. (2.106), we get

$$\begin{aligned} E &= E_{1n}^{(0)} - \sum_{pq \neq 1n} \frac{|\langle 1SnS|\hat{H}_{AB}|pq\rangle|^2}{E_{1n}^{(0)} - E_{pq}^{(0)}} \pm \sum_{pq \neq 1n} \frac{\langle nS1S|\hat{H}_{AB}|pq\rangle \langle pq|\hat{H}_{AB}|1SnS\rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} \\ &= E_{1n}^{(0)} - \frac{2e^4}{3(4\pi\epsilon_0)^2 |\vec{R}_A - \vec{R}_B|^6} \sum_{pq \neq 1n} \left(\sum_{ij} \frac{|\langle 1S|x^i|p\rangle \langle nS|x^j|q\rangle|^2}{E_{1n}^{(0)} - E_{pq}^{(0)}} \pm \right. \\ & \quad \left. \sum_{ij} \frac{(\langle nS|x^i|p\rangle \langle 1S|x^j|q\rangle)^* (\langle 1S|x^i|p\rangle \langle nS|x^j|q\rangle)}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right) \end{aligned} \quad (2.107)$$

$$\begin{aligned} &= E_{1n}^{(0)} - \frac{2e^4}{3(4\pi\epsilon_0)^2 |\vec{R}_A - \vec{R}_B|^6} \sum_{pq \neq 1n} \left(\sum_{rs} \frac{\langle 1S|x^r|p\rangle \langle p|x^r|1S\rangle \langle nS|x^s|q\rangle \langle q|x^s|nS\rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right. \\ & \quad \left. \pm \sum_{rs} \frac{(\langle 1S|x^r|p\rangle \langle p|x^r|nS\rangle) (\langle nS|x^s|q\rangle \langle q|x^s|1S\rangle)}{E_{1n}^{(0)} - E_{pq}^{(0)}} \right). \end{aligned} \quad (2.108)$$

In the second line of equation (2.107) we have used the following identities

$$\sum_{i,j} \langle \psi_{100} | x^i | \psi_{n\ell m} \rangle \langle \psi_{n\ell m} | x^j | \psi_{100} \rangle = \frac{\delta^{ij}}{3} \sum_s \langle \psi_{100} | x^s | \psi_{n\ell m} \rangle \langle \psi_{n\ell m} | x^s | \psi_{100} \rangle \quad (2.109)$$

and

$$\delta^{ij} \delta^{ij} = \delta^{ii} = 3. \quad (2.110)$$

Let us define

$$D_6(nS; 1S) = \frac{2e^4}{3(4\pi\epsilon_0)^2} \sum_{pq \neq 1n} \sum_{rs} \frac{\langle 1S | x^r | p \rangle \langle p | x^r | 1S \rangle \langle nS | x^s | q \rangle \langle q | x^s | nS \rangle}{E_{1n}^{(0)} - E_{pq}^{(0)}}, \quad (2.111)$$

and

$$M_6(nS; 1S) = \frac{2e^4}{3(4\pi\epsilon_0)^2} \sum_{pq \neq 1n} \sum_{rs} \frac{(\langle 1S | x^r | p \rangle \langle p | x^r | nS \rangle) (\langle nS | x^s | q \rangle \langle q | x^s | 1S \rangle)}{E_{1n}^{(0)} - E_{pq}^{(0)}}, \quad (2.112)$$

such that

$$E = E_{1n}^{(0)} - \frac{D_6(nS; 1S) \pm M_6(nS; 1S)}{|\vec{R}_A - \vec{R}_B|^6}. \quad (2.113)$$

By the notations $D_6(nS; 1S)$ and $M_6(nS; 1S)$, we are referring to the direct and the mixing term contributions to the vdW $C_6(nS; 1S)$ coefficient such that

$$C_6(nS; 1S) = D_6(nS; 1S) \pm M_6(nS; 1S). \quad (2.114)$$

The \pm sign depends on the symmetry of the wave function of the two-atom state. Making use of the standard integral identity (2.17), we can express Eqs. (2.111) and

(2.112) in terms of integrals over ω as

$$D_6(nS; 1S) = \frac{4e^4}{3(4\pi\epsilon_0)^2} \sum_{pq \neq 1n} \left(E_1^{(0)} - E_p^{(0)} \right) \left(E_n^{(0)} - E_q^{(0)} \right) \int_0^\infty d\omega \sum_{rs} \frac{\langle 1S|x^r|p \rangle \langle p|x^r|1S \rangle \langle nS|x^s|q \rangle \langle q|x^s|nS \rangle}{\left((E_1^{(0)} - E_p^{(0)})^2 + \hbar^2\omega^2 \right) \left((E_n^{(0)} - E_q^{(0)})^2 + \hbar^2\omega^2 \right)}, \quad (2.115)$$

and

$$M_6(nS; 1S) = \frac{4e^4}{3(4\pi\epsilon_0)^2} \sum_{pq \neq 1n} \left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_p^{(0)} \right) \left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_q^{(0)} \right) \int_0^\infty d\omega \times \sum_{rs} \frac{(\langle 1S|x^r|p \rangle \langle p|x^r|nS \rangle) (\langle nS|x^s|q \rangle \langle q|x^s|1S \rangle)}{\left(\left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_p^{(0)} \right)^2 + \hbar^2\omega^2 \right) \left(\left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_q^{(0)} \right)^2 + \hbar^2\omega^2 \right)}. \quad (2.116)$$

Identifying

$$\frac{2}{3}e^2 \sum_{pq \neq 1n} \sum_s \left(E_n^{(0)} - E_q^{(0)} \right) \frac{\langle nS|x^s|q \rangle \langle q|x^s|nS \rangle}{\left((E_n^{(0)} - E_q^{(0)})^2 + \hbar^2\omega^2 \right)} = \alpha_{nS}(i\omega), \quad (2.117)$$

and

$$\frac{2}{3}e^2 \sum_{pq \neq 1n} \sum_s \left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_q^{(0)} \right) \frac{\langle nS|x^s|q \rangle \langle q|x^s|1S \rangle}{\left(\left(\frac{1}{2}(E_1^{(0)} + E_n^{(0)}) - E_q^{(0)} \right)^2 + \hbar^2\omega^2 \right)} = \alpha_{nS1S}(i\omega), \quad (2.118)$$

the direct and the mixing vdW coefficients can be rewritten as

$$D_6(nS; 1S) = \frac{4e^4}{3(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{nS}(i\omega) \alpha_{1S}(i\omega), \quad (2.119)$$

$$M_6(nS; 1S) = \frac{4e^4}{3(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1SnS}(i\omega) \alpha_{nS1S}(i\omega). \quad (2.120)$$

There are some advantages of using the average energy corresponding to the states of interest as the reference energy. First, there is no state which is degenerate with the reference state. Next, the issue of the contributions arising from the intermediate P -states is resolved. However, it requires calculating the quantum number associated with the reference state. Taking $1S$ state as one state of interest and nS as another, the energy associated with the reference state is

$$E_{\text{ref}} = \frac{E_1 + E_n}{2} = -\frac{\alpha^2 mc^2}{2n_{\text{ref}}^2}. \quad (2.121)$$

Solving for n_{ref} , Eq. (2.121) yields

$$\frac{1}{n_{\text{ref}}^2} = \frac{1}{2} + \frac{1}{2n^2}. \quad (2.122)$$

It is obvious to note that $n_{\text{ref}} = 1$ when $n = 1$ and $n_{\text{ref}} = \sqrt{2}$ when $n = \infty$. Thus the quantum number corresponding to the reference state always lies in the range $1 \leq n_{\text{ref}} < \sqrt{2}$. A downside of this approach is that this is valid only in the short range. Here, by the short range of the interatomic distance, we mean that the interatomic distance must be less than the wavelength corresponding to a typical atomic transition. To put it another way, R must satisfy

$$a_0 \ll R \ll a_0/\alpha, \quad (2.123)$$

where a_0 is the Bohr radius and $\alpha = 1/137.035\,999\,139$, is the fine-structure constant. This is so-called vdW range.

2.4. ASYMPTOTIC REGIMES

To study the interaction between two atoms in S -states, we differentiate three different ranges for the interatomic distance: van der Waals range ($a_0 \ll R \ll a_0/\alpha$),

CP range ($a_0/\alpha \ll R \ll 1/\mathcal{L}$, where \mathcal{L} is lamb shift energy [27]), and Lamb shift range ($R \gg 1/\mathcal{L}$). Equivalently, we will call them the short range, the intermediate range, and the long range of the interatomic distances.

In this work, we consider the interaction between two atoms in which one atom sits in the ground state while the other one can be either in the ground state or one of the excited nS -states. The ground state is nondegenerate. However, the excited state has quasi-degenerate neighbors. If an atom is in an excited state, the polarizability of the atom $\alpha_{nS}(\omega)$ is the sum

$$\alpha_{nS}(\omega) = \tilde{\alpha}_{nS}(\omega) + \bar{\alpha}_{nS}(\omega), \quad (2.124)$$

where $\tilde{\alpha}_{nS}(\omega)$ is the nondegenerate contribution to the nS polarizability while $\bar{\alpha}_{nS}(\omega)$ represents the contribution of the quasi-degenerate nP levels. The dipole polarizability $\alpha_{nS}(\omega)$ is computed by a sum over all states. The degenerate polarizability $\bar{\alpha}_{nS}(\omega)$ is a sum over quasi-degenerate neighbors. Mathematically,

$$\bar{\alpha}_{nS}(\omega) = \frac{e^2}{3} \sum_{\pm} \sum_j \sum_{\mu=-1}^1 \sum_{nP_j=\frac{1}{2}, \frac{3}{2}} \frac{|\langle nS|x^j|nP(m=\mu)\rangle|^2}{E_{nP_j} - E_{nS} \pm \hbar\omega - i\epsilon}. \quad (2.125)$$

The symbol nP_j indicates the total angular quantum number j of the quasi-degenerate P -states which are resonant. The total orbital angular quantum number l has the value 1 for P -state. Thus, the total angular quantum number j , and hence nP_j , can have values $\frac{1}{2}$ and $\frac{3}{2}$. The energy difference between the quasi-degenerate levels with the principal quantum number n , $(E_{nP_{1/2}} - E_{nS})$ and $(E_{nP_{3/2}} - E_{nS})$ are respectively the Lamb shift \mathcal{L}_n and the fine structure splitting \mathcal{F}_n . Mathematically,

$$E_{nP_{1/2}} - E_{nS_{1/2}} \equiv \mathcal{L}_n, \quad (2.126a)$$

$$E_{nS_{1/2}} - E_{nP_{3/2}} \equiv \mathcal{F}_n. \quad (2.126b)$$

The nondegenerate polarizability $\tilde{\alpha}_{nS}(\omega)$ is the sum over all states excluding degenerate levels. It is the measurement of the polarizability due to states having the different principal quantum number. More explicitly,

$$\tilde{\alpha}_{nS}(\omega) = \frac{e^2}{3} \sum_{\pm} \sum_j \sum_{\mu=-1}^1 \sum_{k>n} \frac{|\langle nS|x^j|nP(m=\mu)\rangle|^2}{E_k - E_{nS} \pm \hbar\omega - i\epsilon}. \quad (2.127)$$

The sum over k in the non degenerate polarizability indicates that we include all the possible states whose principal quantum number is greater than the reference state. The total interaction energy can be written as the sum

$$\Delta E_{nS;1S}^{(4)} = \Delta \tilde{E}_{nS;1S}^{(4)} + \Delta \bar{E}_{nS;1S}^{(4)} + \mathcal{P}_{nS;1S}, \quad (2.128)$$

where $\Delta \tilde{E}_{nS;1S}^{(4)}$ and $\Delta \bar{E}_{nS;1S}^{(4)}$ are the nondegenerate and the degenerate contributions to the interaction energy respectively. The $\mathcal{P}_{nS;1S}$ is the pole term contribution, which arises as the integration contour picks up a number of poles under the Wick-rotation. Detailed discussion of the pole term is presented in Sec.2.5. Being the Wick-rotated contribution, the $\Delta \tilde{E}_{nS;1S}^{(4)}$ and $\Delta \bar{E}_{nS;1S}^{(4)}$ can be renamed as $\tilde{\mathcal{W}}_{nS;1S}$ and $\bar{\mathcal{W}}_{nS;1S}$ respectively, such that the total Wick-rotated contribution reads

$$\mathcal{W}_{nS;1S} = \tilde{\mathcal{W}}_{nS;1S} + \bar{\mathcal{W}}_{nS;1S}, \quad (2.129)$$

which allows us to write

$$\Delta E_{nS;1S}^{(4)} = \tilde{\mathcal{W}}_{nS;1S} + \bar{\mathcal{W}}_{nS;1S} + \mathcal{P}_{nS;1S} = \mathcal{W}_{nS;1S} + \mathcal{P}_{nS;1S}. \quad (2.130)$$

The Wick-rotated nondegenerate $\widetilde{\mathcal{W}}_{nS;1S}$ and the degenerate $\overline{\mathcal{W}}_{nS;1S}$ contributions are given by

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S} &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha(1S, i\omega) \tilde{\alpha}(nS, i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \end{aligned} \quad (2.131a)$$

$$\begin{aligned} \overline{\mathcal{W}}_{nS;1S} &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha(1S, i\omega) \bar{\alpha}(nS, i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (2.131b)$$

For the short range ($a_0 \ll R \ll a_0/\alpha$) of interatomic distances, there is no oscillatory suppression in the interaction energy and the first four terms under the bracket $\left[\right]$ in both Eqs. (2.131a) and (2.131b) are negligible in comparison to the fifth term. Furthermore, the exponential can be approximated to unity. Thus we can approximate the Wick-rotated contributions $\widetilde{\mathcal{W}}_{nS;1S}$ and $\overline{\mathcal{W}}_{nS;1S}$ as

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S} &\approx -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha(1S, i\omega) \tilde{\alpha}(nS, i\omega) \frac{\omega^4}{R^2} \frac{3c^4}{(\omega R)^4} \\ &= -\frac{3\hbar}{\pi (4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha(1S, i\omega) \tilde{\alpha}(nS, i\omega); \quad a_0 \ll R \ll a_0/\alpha, \end{aligned} \quad (2.132a)$$

$$\begin{aligned} \overline{\mathcal{W}}_{nS;1S} &\approx -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha(1S, i\omega) \bar{\alpha}(nS, i\omega) \frac{\omega^4}{R^2} \frac{3c^4}{(\omega R)^4} \\ &= -\frac{3\hbar}{\pi (4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha(1S, i\omega) \bar{\alpha}(nS, i\omega); \quad a_0 \ll R \ll a_0/\alpha. \end{aligned} \quad (2.132b)$$

Both the nondegenerate and the degenerate contributions to the energy follow the R^{-6} power law in the short range.

Let us examine the behavior of the interaction for very large interatomic distances ($R \gg \hbar c/\mathcal{L}$). As the interatomic distance is very large, the exponential term and the negative powers of R vary very fast but not the polarizabilities

[28]. Specifically, we can approximate the dynamic polarizabilities of atoms by their static values. *i.e.* $\alpha(1S, i\omega) = \alpha(1S, \omega = 0)$, $\tilde{\alpha}(nS, i\omega) = \tilde{\alpha}(nS, \omega = 0)$, and $\bar{\alpha}(nS, i\omega) = \bar{\alpha}(nS, \omega = 0)$. Consequently, we have

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S} &\approx -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha(1S, \omega = 0) \tilde{\alpha}(nS, \omega = 0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ &= -\frac{23 \hbar c}{4\pi (4\pi\epsilon_0)^2} \frac{\alpha(1S, \omega = 0) \tilde{\alpha}(nS, \omega = 0)}{R^7}, \quad R \gg \hbar c / \mathcal{L}. \end{aligned} \quad (2.133a)$$

$$\begin{aligned} \overline{\mathcal{W}}_{nS;1S} &\approx -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha(1S, \omega = 0) \bar{\alpha}(nS, \omega = 0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ &= -\frac{23 \hbar c}{4\pi (4\pi\epsilon_0)^2} \frac{\alpha(1S, \omega = 0) \bar{\alpha}(nS, \omega = 0)}{R^7}, \quad R \gg \hbar c / \mathcal{L}. \end{aligned} \quad (2.133b)$$

Hence, in the long range of interatomic distances, both the nondegenerate and the degenerate contributions has R^{-7} dependence. We recovered the famous CP result.

Let us now investigate the interaction energy in the intermediate interatomic distances ($a_0/\alpha \ll R \ll \hbar c/\mathcal{F} < \hbar c/\mathcal{L}$). The transition energies, in the nondegenerate cases, are in the order of the Hartree energy and the polarizabilities due to the nondegenerate states can be approximated by their static values. Thus, we still get a R^{-7} power law dependence of the interaction energy.

To illustrate the analytic considerations of power law behavior of the interaction energy, we consider model integrals. In the nondegenerate case, the model integral can be expressed as

$$\begin{aligned} I(a, b, R) &= \int_0^\infty d\omega \frac{a}{(a - i\epsilon)^2 + \omega^2} \frac{b}{(b - i\epsilon)^2 + \omega^2} \frac{\omega^4 e^{-2\omega R}}{R^2} \\ &\quad \times \left[1 + \frac{2}{\omega R} + \frac{5}{(\omega R)^2} + \frac{6}{(\omega R)^3} + \frac{3}{(\omega R)^4} \right], \end{aligned} \quad (2.134)$$

where a and b are the energy parameters. Let us choose the parameters:

$$a = 1, \quad b = 1/4, \quad \text{and} \quad \epsilon = 10^{-6}. \quad (2.135)$$

For small interatomic distance, the curve for a model integral with no approximation (blue curve), matches with a $1/R^6$ asymptotic (red-dashed) curve while for large interatomic distance, the model curve matches with $1/R^7$ asymptotic (green-dashed) curve (see Figure 2.4). $a_0/\alpha \approx 137.036 a_0$ is the transition from $1/R^6$ to $1/R^7$ asymptotic.

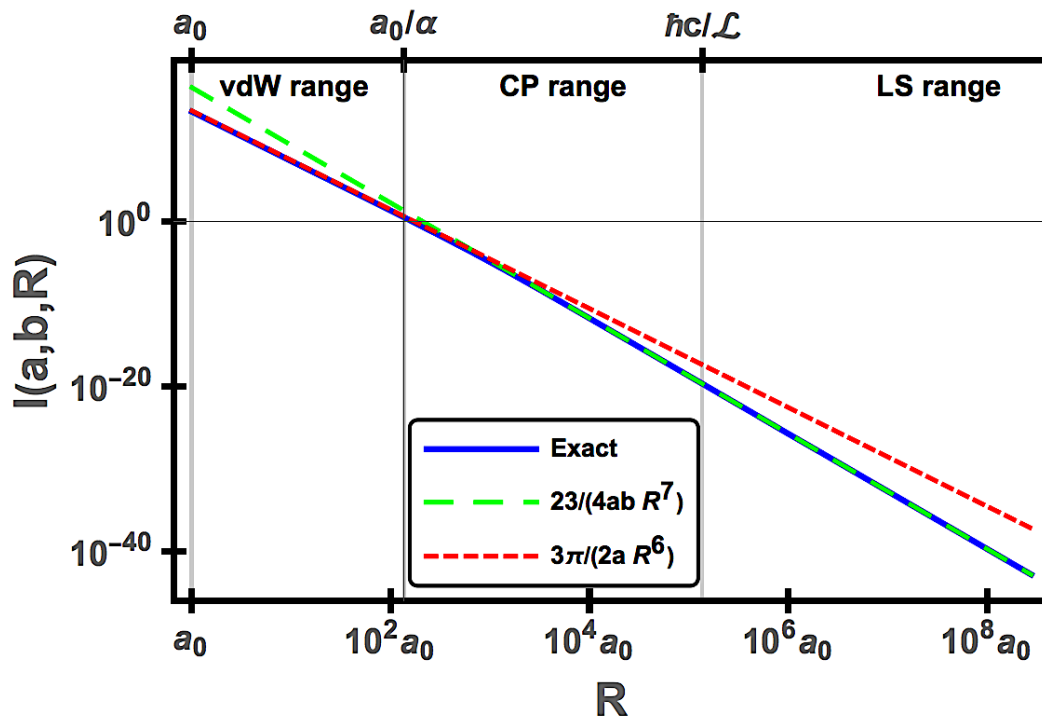


Figure 2.4: Figure showing a numerical model for the interaction energy as a function of interatomic distance in three different range. The interaction energy shows $1/R^7$ asymptotic for $R \gg a_0/\alpha$.

In the presence of the quasi-degenerate states, the model integral can be written as

$$J(a, b, R) = \int_0^{\infty} d\omega \frac{a}{(a - i\epsilon)^2 + \omega^2} \frac{(-\eta)}{(-\eta - i\epsilon)^2 + \omega^2} \frac{\omega^4 e^{-2\omega R}}{R^2} \times \left[1 + \frac{2}{\omega R} + \frac{5}{(\omega R)^2} + \frac{6}{(\omega R)^3} + \frac{3}{(\omega R)^4} \right], \quad (2.136)$$

where η is the energy shift of the degenerate levels which represents the Lamb shift or fine structure. One good choice of the numerical values of the parameters are

$$a = 1, \quad \eta = 10^{-3}, \quad \text{and} \quad \epsilon = 10^{-6}. \quad (2.137)$$

Figure 2.5 shows an exact, and approximate $1/R^6$ and $1/R^7$ asymptotic for interaction energy. For small interatomic distance, the curve for a model integral with no approximation (blue curve), matches with a $1/R^6$ asymptotic (red-dashed) curve while for large interatomic distance, the model curve matches with $1/R^7$ asymptotic (green-dashed) curve. $\hbar c/\mathcal{L}$ is the transition from $1/R^6$ to $1/R^7$ asymptotic.

Now, it is time to clarify why we choose $R \gg \hbar c/\mathcal{L}$. As the long range of the interatomic distances instead of $R \gg \hbar c/\mathcal{F}$. As $\mathcal{F} \approx 10\mathcal{L}$, the interatomic distances $\hbar c/\mathcal{F}$ and $\hbar c/\mathcal{L}$ differ by an order of magnitude. One might argue that there is a window

$$\frac{\hbar c}{\mathcal{F}} < R < \frac{\hbar c}{\mathcal{L}}. \quad (2.138)$$

However, the window is so narrow that it does not give any meaningful sense and the claim $R \gg \hbar c/\mathcal{L}$. As a separation of the intermediate interatomic distance from the long interatomic distance holds well.

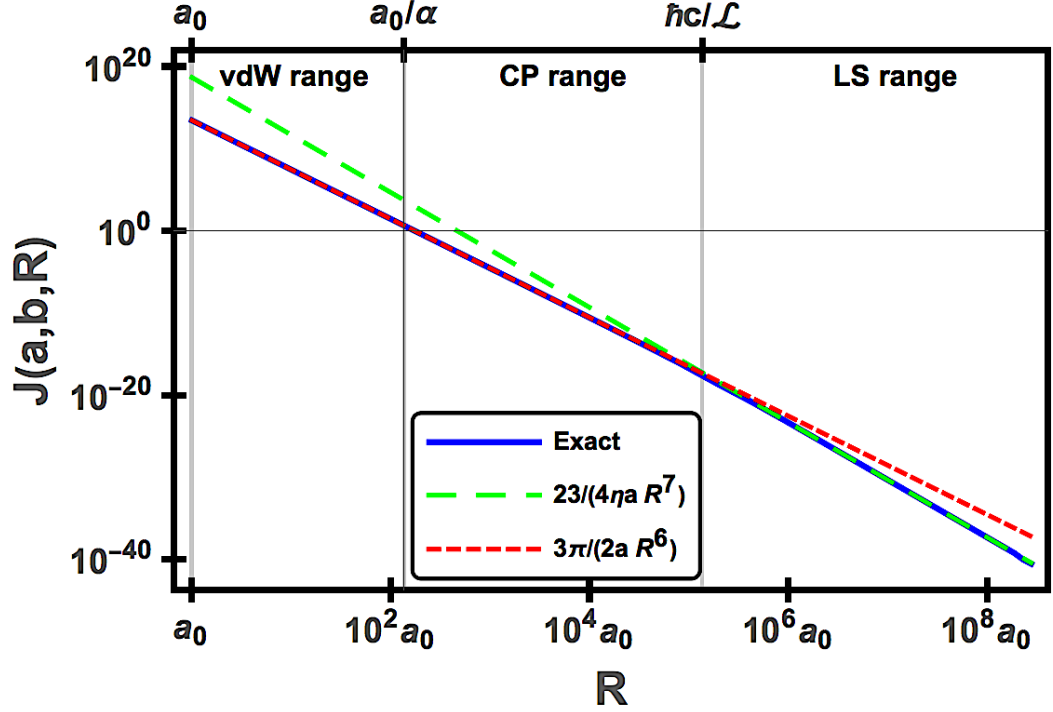


Figure 2.5: Figure showing a numerical model for the interaction energy as a function of interatomic distance in three different range. In the presence of quasi-degenerate states, the $1/R^6$ range extends much farther out up to $\hbar c/\mathcal{L}$.

2.5. LONG-RANGE TAILS IN THE vdW INTERACTION

Study of the vdW interaction in the long-range distance between two electrically neutral hydrogen atoms in their ground state is simpler as it follows the R^{-7} power law as predicted by Casimir and Polder [15], where R is the interatomic distance. Problems arise when one of the atoms is in the excited state. The presence of the quasi-degenerate states available for the transition of virtual photons gives rise the oscillatory dependence of the interaction energy with the amplitude falling off as R^{-2} , when the R is sufficiently large [29; 30; 31; 32]. So far the experimental verification is concerned, an oscillatory distance dependence in the vacuum-induced level

shifts has been observed in a single trapped barium ion in the presence of a single mirror [33; 34].

2.5.1. S-matrix in the Interaction Picture. The interaction picture, in which both the state vectors and the operators evolve in time, is applied to determine the scattering matrix elements. We split the total Hamiltonian of the system, H , as

$$H = H_0 + V(t) \quad (2.139)$$

such that the H_0 is the unperturbed part of the Hamiltonian and $V(t)$ carries all the interactions from the system. The operators in the interaction picture evolve freely, and the dynamics of the state vectors depend on the interaction.

We consider two neutral atoms A and B . Let $\vec{\rho}_A$ and \vec{R}_A be the position vectors of the electron and the nucleus of atom A and $\vec{\rho}_B$ and \vec{R}_B be the position vectors of the electron and the nucleus of atom B . The relative coordinates of the states are $\vec{r}_A = \vec{\rho}_A - \vec{R}_A$ and $\vec{r}_B = \vec{\rho}_B - \vec{R}_B$. Let $\vec{R} = \vec{R}_A - \vec{R}_B$ be the distance between the nuclei. If $|\psi_A(\vec{r}_A), \psi_B(\vec{r}_B)\rangle$ and $|\psi'_A(\vec{r}_A), \psi'_B(\vec{r}_B)\rangle$ be the ket vectors associated to the initial state and the final state respectively and $|\Phi(t)\rangle$ be the ket evolved from the free initial state, the S -matrix element is the projection of the evolved state vector $|\Phi(t)\rangle$ on the final state. Mathematically,

$$S_{A'B'AB} = \langle \psi'_A(\vec{r}_A), \psi'_B(\vec{r}_B) | \Phi(t) \rangle = \langle \psi'_A(\vec{r}_A), \psi'_B(\vec{r}_B) | \hat{S} | \psi_A(\vec{r}_A), \psi_B(\vec{r}_B) \rangle, \quad (2.140)$$

where \hat{S} is the scattering operator [35], which satisfies the unitary condition, $\hat{S}\hat{S}^\dagger = \mathbb{1}$. Using the definition of the time evolution operator, U , in the interaction picture, which reads

$$U(t, t_0) = \hat{T} \exp \left(-i \int_{t_0}^t dt' V(t') \right), \quad (2.141)$$

one can write

$$S_{A'B'AB} = \lim_{t \rightarrow \infty} \lim_{t_0 \rightarrow -\infty} \langle \psi'_A(\vec{r}_A), \psi'_B(\vec{r}_B) | U(t, t_0) | \psi_A(\vec{r}_A), \psi_B(\vec{r}_B) \rangle. \quad (2.142)$$

The n^{th} order term of the Dyson series [29] for the time evolution operator in the interaction picture reads

$$U^{(n)}(t, t_0) = \frac{(-i)^n}{n! \hbar^n} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n V(t_1) V(t_2) \cdots V(t_n). \quad (2.143)$$

As the \hat{S} operator is related to the evolution operator as

$$\hat{S} = U(\infty, -\infty), \quad (2.144)$$

the n^{th} order contribution to \hat{S} is given by

$$\hat{S}^{(n)} = \frac{(-i)^n}{n! \hbar^n} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \cdots \int_{-\infty}^{\infty} dt_n \hat{T}[V(t_1) V(t_2) \cdots V(t_n)]. \quad (2.145)$$

To the 4th order, the contribution to \hat{S} is given by

$$\hat{S}^{(4)} = \frac{1}{24 \hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 \hat{T}[V(t_1) V(t_2) V(t_3) V(t_4)]. \quad (2.146)$$

The four indices can be paired in three different ways, namely: $\{(1,2)\text{and } (3,4)\}$, $\{(1,3)\text{and } (2,4)\}$, $\{(1,4)\text{and } (2,3)\}$, however each pairing yields the same integral value as they differ only on how we call them. Thus,

$$\hat{S}^{(4)} = \frac{1}{8 \hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 \hat{T}[V(t_1) V(t_2)] T[V(t_3) V(t_4)]. \quad (2.147)$$

To the dipole approximation [36], the interaction $V(t)$ can be approximated as

$$V(t) = -\vec{d}_A \cdot \vec{E}(\vec{\rho}_A, t) - \vec{d}_B \cdot \vec{E}(\vec{\rho}_B, t) \approx -\vec{d}_A \cdot \vec{E}(\vec{R}_A, t) - \vec{d}_B \cdot \vec{E}(\vec{R}_B, t), \quad (2.148)$$

where $\vec{d} = e\vec{r}$ is the electric dipole operator of an atom. Assuming that the unperturbed state of the system contains atoms on the state $|\psi\rangle = |\psi_A, \psi_B\rangle$ and the electromagnetic field in the vacuum state $|0\rangle$,

$$\begin{aligned} \langle S^{(4)} \rangle &= \langle \psi | \langle 0 | \hat{S}^{(4)} | 0 \rangle | \psi \rangle = \frac{1}{8\hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 \\ &\times \langle \psi | \langle 0 | \{ \hat{T}[V(t_1)V(t_2)] \} | 0 \rangle \langle 0 | \{ \hat{T}[V(t_3)V(t_4)] \} | 0 \rangle | \psi \rangle. \end{aligned} \quad (2.149)$$

Let us say, \hat{T}_E is the time ordering operator for the electric field operators and \hat{T}_d is the time ordering operator for the dipole moments. Making use of Eq. (2.148) to Eq. (2.149), we have

$$\begin{aligned} \langle S^{(4)} \rangle &\approx \frac{1}{8\hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 \hat{T}_d \langle \psi | \left\{ \left\{ \langle 0 | \hat{T}_E \left[(\vec{d}_A(t_1) \cdot \vec{E}(\vec{R}_A, t_1)) \right. \right. \right. \\ &\quad \left. \left. \left. (\vec{d}_B(t_2) \cdot \vec{E}(\vec{R}_B, t_2)) \right] | 0 \rangle + \langle 0 | \hat{T}_E \left[(\vec{d}_B(t_1) \cdot \vec{E}(\vec{R}_B, t_1)) (\vec{d}_A(t_2) \cdot \vec{E}(\vec{R}_A, t_2)) \right] | 0 \rangle \right\} \right. \\ &\quad \times \left\{ \langle 0 | \hat{T}_E \left[(\vec{d}_A(t_3) \cdot \vec{E}(\vec{R}_A, t_3)) (\vec{d}_B(t_4) \cdot \vec{E}(\vec{R}_B, t_4)) \right] | 0 \rangle \right. \\ &\quad \left. \left. + \langle 0 | \hat{T}_E \left[(\vec{d}_B(t_3) \cdot \vec{E}(\vec{R}_B, t_3)) (\vec{d}_A(t_4) \cdot \vec{E}(\vec{R}_A, t_4)) \right] | 0 \rangle \right\} \right\}. \end{aligned} \quad (2.150)$$

The integrand of Eq. (2.151) is the sum of four terms which have different naming of the indices but the same integral value. Thus one may write

$$\begin{aligned} \langle S^{(4)} \rangle &= \frac{1}{2\hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 \langle 0 | \hat{T}_E \left[E_i(\vec{R}_A, t_1) E_j(\vec{R}_B, t_2) \right] | 0 \rangle \\ &\quad \times \langle 0 | \hat{T}_E \left[E_k(\vec{R}_A, t_3) E_\ell(\vec{R}_B, t_4) \right] | 0 \rangle \langle \psi_A | \hat{T}_d \left[d_{Ai}(t_1) d_{Ak}(t_3) \right] | \psi_A \rangle \\ &\quad \times \langle \psi_B | \hat{T}_d \left[d_{Bj}(t_2) d_{B\ell}(t_4) \right] | \psi_B \rangle. \end{aligned} \quad (2.151)$$

In terms of the scalar and the vector potential the electric field operator can be written as

$$\vec{E} = -\vec{\nabla}\Phi - \frac{\partial\vec{A}}{\partial t}. \quad (2.152)$$

With a proper choice of the gauge in which the scalar potential Φ is zero, the electric field can be written as $\vec{E} = -\frac{\partial\vec{A}}{\partial t}$. This is the so called temporal gauge. In this gauge,

$$\begin{aligned} \langle 0|\hat{T}_E[E_i(\vec{R}_A, t_1) E_j(\vec{R}_B, t_2)]|0\rangle &= \frac{\partial^2}{\partial t_1 \partial t_2} \langle 0|\hat{T}_E[A_i(\vec{R}_A, t_1) A_j(\vec{R}_B, t_2)]|0\rangle \\ &= i \frac{\partial^2}{\partial t_1 \partial t_2} D_{ij}(\vec{R}, t_1 - t_2) = -i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 D_{ij}(\omega, \vec{R}) e^{-i\omega(t_1 - t_2)}, \end{aligned} \quad (2.153)$$

where $\vec{R} = \vec{R}_A - \vec{R}_B$ and

$$D_{ij}(\omega, \vec{R}) = \frac{\hbar e^{i|\omega|R/c}}{4\pi\epsilon_0 c^2} \left[\alpha_{ij} - \beta_{ij} \left[\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right] \right] \quad (2.154)$$

is the photon propagator in the mixed frequency-position representation. The tensor structures α_{ij} and β_{ij} are given by

$$\alpha_{ij} = \delta_{ij} - \frac{R_i R_j}{R^2}, \quad \text{and} \quad \beta_{ij} = \delta_{ij} - 3 \frac{R_i R_j}{R^2}. \quad (2.155)$$

While the time ordering product of the electric dipole moment operators reads

$$\langle \psi_A | \hat{T}_d [d_{Ai}(t_1) d_{Ak}(t_3)] | \psi_A \rangle = -i\hbar \alpha_{A,ik}(t_1 - t_3) = -i\hbar \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t_1 - t_3)} \alpha_{A,ik}(\omega), \quad (2.156)$$

where the polarizability $\alpha_{A,ik}(\omega)$ is given as

$$\alpha_{A,ik}(\omega) = \sum_{\nu_A} \left(\frac{\langle \psi_A | d_{Ai} | \nu_A \rangle \cdot \langle \nu_A | d_{Aj} | \psi_A \rangle}{E_{\nu_A} - \hbar\omega - i\epsilon} + \frac{\langle \psi_A | d_{Ai} | \nu_A \rangle \cdot \langle \nu_A | d_{Aj} | \psi_A \rangle}{E_{\nu_A} + \hbar\omega - i\epsilon} \right). \quad (2.157)$$

With the help of Eqs. (2.153) and (2.156), Eq. (2.151) yields

$$\begin{aligned}
\langle S^{(4)} \rangle &= \frac{1}{2\hbar^4} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_4 (-i) \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \omega_1^2 D_{ij}(\omega_1, \vec{R}) e^{-i\omega_1(t_1-t_2)} \\
&\times (-i) \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \omega_2^2 D_{kl}(\omega_2, \vec{R}) e^{-i\omega_2(t_3-t_4)} \times (-i\hbar) \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi} e^{-i\omega_3(t_1-t_3)} \alpha_{A,ik}(\omega_3) \\
&\times (-i\hbar) \int_{-\infty}^{\infty} \frac{d\omega_4}{2\pi} e^{-i\omega_4(t_2-t_4)} \alpha_{B,j\ell}(\omega_4)
\end{aligned} \tag{2.158}$$

Let us now carry out the t -integral.

$$\begin{aligned}
\langle S^{(4)} \rangle &= \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \omega_1^2 D_{ij}(\omega_1, \vec{R}) \\
&\times e^{-i\omega_1(t_1-t_2)} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \omega_2^2 D_{kl}(\omega_2, \vec{R}) e^{-i\omega_2 t_3} \\
&\times \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi} e^{-i\omega_3(t_1-t_3)} \alpha_{A,ik}(\omega_3) e^{i\omega_2 t_2} \alpha_{B,j\ell}(-\omega_2) \\
&= \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \omega_1^2 D_{ij}(\omega_1, \vec{R}) e^{-i\omega_1(t_1-t_2)} \\
&\times \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \omega_2^2 D_{kl}(\omega_2, \vec{R}) e^{-i\omega_2 t_1} \alpha_{A,ik}(\omega_2) e^{i\omega_2 t_2} \alpha_{B,j\ell}(-\omega_2) \\
&= \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \omega_1^2 D_{ij}(\omega_1, \vec{R}) e^{-i\omega_1 t_1} \\
&\times (-\omega_1)^2 D_{kl}(-\omega_1, \vec{R}) e^{i\omega_1 t_1} \alpha_{A,ik}(-\omega_1) \alpha_{B,j\ell}(\omega_1) \\
&= \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{kl}(\omega, \vec{R}) \alpha_{A,ik}(\omega) \alpha_{B,j\ell}(\omega) \\
&= \frac{T}{2\hbar^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{kl}(\omega, \vec{R}) \alpha_{A,ik}(\omega) \alpha_{B,j\ell}(\omega).
\end{aligned} \tag{2.159}$$

Here $T = \int_{t_i}^{t_f} dt = t_f - t_i$ denotes the total interval of time in which the transition occurs. In the intermediate steps of Eq. (2.159), we have used the following property of the Dirac-delta function

$$\int_{-\infty}^{\infty} dx f(x) \delta(x - x_0) = f(x_0), \tag{2.160}$$

which indicates that the integral takes the value of the function at the Delta-peak.

2.5.2. Interaction Energy for nS - $1S$ Systems. By the definition of the S matrix element

$$\langle S^{(4)} \rangle = -\frac{i}{\hbar} T \langle \psi' | V | \psi \rangle = -\frac{i}{\hbar} T \Delta E^{(\text{direct})}, \quad (2.161)$$

the direct term contribution to the interaction energy can be written from Eq. (2.159) as

$$\Delta E^{(\text{direct})} = \frac{i}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{kl}(\omega, \vec{R}) \alpha_{A,ik}(\omega) \alpha_{B,j\ell}(\omega), \quad (2.162)$$

where, the photon propagator $D_{ij}(\omega, \vec{R})$, and the polarizability $\alpha_{A,ik}(\omega)$ are given by Eqs. (2.154) and (2.157) respectively. Whereas, the mixing term contribution reads

$$\Delta E^{(\text{mixing})} = \frac{i}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{kl}(\omega, \vec{R}) \alpha_{\underline{A}B,ik}(\omega) \alpha_{\underline{A}B,j\ell}^*(\omega), \quad (2.163)$$

where $\alpha_{\underline{A}B,ik}(\omega)$ is the mixed polarizability taking atom A as the reference atom and mathematically it is given by

$$\alpha_{\underline{A}B,ij}(\omega) = \sum_{\nu_A} \left(\frac{\langle \psi_A | d_{Ai} | \nu_A \rangle \cdot \langle \nu_A | d_{Aj} | \psi_B \rangle}{E_{\nu,A} - \hbar\omega - i\epsilon} + \frac{\langle \psi_A | d_{Ai} | \nu_A \rangle \cdot \langle \nu_A | d_{Aj} | \psi_B \rangle}{E_{\nu,A} + \hbar\omega - i\epsilon} \right). \quad (2.164)$$

Similarly, if we take atom B as a reference, the mixed polarizability, is now denoted as $\alpha_{\underline{A}B,j\ell}(\omega)$, which reads

$$\alpha_{\underline{A}B,ij}(\omega) = \sum_{\nu_A} \left(\frac{\langle \psi_A | d_{Bi} | \nu_A \rangle \cdot \langle \nu_A | d_{Bj} | \psi_B \rangle}{E_{\nu,B} - \hbar\omega - i\epsilon} + \frac{\langle \psi_A | d_{Bi} | \nu_A \rangle \cdot \langle \nu_A | d_{Bj} | \psi_B \rangle}{E_{\nu,B} + \hbar\omega - i\epsilon} \right). \quad (2.165)$$

Now the total interaction energy between two identical atoms in their arbitrary states can be written as the sum

$$\Delta E = \Delta E^{(\text{direct})} + \Delta E^{(\text{mixing})}, \quad (2.166)$$

For the sake of simplicity, we consider the atom B in the ground state and the atom A in the excited state through out our derivation. Let $|m_A\rangle$ be a virtual state of atom A . In the Wick-rotated contour, in which the integration contour for $\omega \in (0, \infty)$ is rotated to the imaginary axis, poles terms arises naturally. The poles are present at $\omega = \pm \frac{E_{m,A}}{\hbar} \mp i\epsilon$. The Wick-rotated contour, however, picks up poles at $\omega = -\frac{E_{m,A}}{\hbar} - i\epsilon$ only (see Figure 2.6). Thus each of the direct term and mixing term can be expressed as the sum of the wick-rotated term and the pole term. In this section, we concentrate only on pole terms.

The direct type contribution of the virtually low-lying P -states can be written as the sum

$$\mathcal{Q}^{(\text{direct})}(R) = \mathcal{P}^{(\text{direct})}(R) + \frac{i}{2}\Gamma^{(\text{direct})}(R) \quad (2.167)$$

We now call the real part of $\mathcal{Q}(R)$ as the pole type contribution. In other word, now and onwards, whenever we say pole term we are referring to the real part, $\mathcal{P}(R)$. The imaginary part is half of the width term $\Gamma(R)$. The pole term for the direct-type contribution, $\mathcal{P}^{(\text{direct})}(R)$, is given by

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) &= \text{Re} \frac{i}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{k\ell}(\omega, \vec{R}) \\ &\quad \sum_{\pm} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle}{E_{m,A} \pm \hbar\omega - i\epsilon} \alpha_{B,j\ell}(\omega) \\ &= -\text{Re} \frac{i}{\hbar} (2\pi i) \underset{\omega = -E_{m,A}/\hbar + i\epsilon}{\text{Res}} \frac{1}{\hbar} \frac{\omega^4}{2\pi} D_{ij}(\omega, \vec{R}) D_{k\ell}(\omega, \vec{R}) \end{aligned}$$

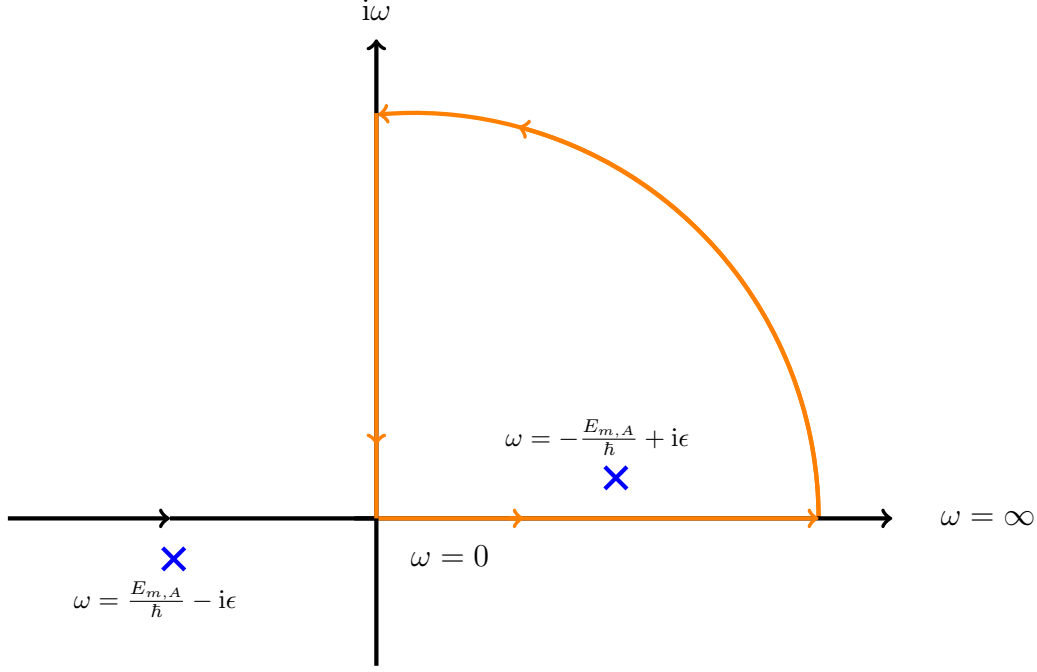


Figure 2.6: The figure shows an integration contour in the complex ω -plane when we carry out the Wick rotation. In the Wick rotation, the $\omega \in (0, \infty)$ axis is rotated by 90° in a counter clockwise direction to an imaginary axis. The counter picks up only the poles at $\omega = -\frac{E_{m,A}}{\hbar} + i\epsilon$. Thus, the contribution of the integration is $2\pi i$ times the sum of residues at the poles enclosed by the contour.

$$\begin{aligned}
& \sum_{\pm} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle}{E_{m,A}/\hbar \pm \omega - i\epsilon} \alpha_{B,j\ell}(\omega) \\
&= \text{Re} \frac{1}{\hbar^2} \sum_{m_A} \langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle \frac{\hbar^2}{(4\pi\epsilon_0 c^2)^2 R^2} \\
& \quad \times \text{Res}_{\omega = -E_{m,A}/\hbar + i\epsilon} \left\{ \sum_{\pm} \frac{\omega^4 e^{2i|\omega|R/c}}{E_{m,A}/\hbar \pm \omega - i\epsilon} \left[\alpha_{ij} + \beta_{ij} \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right) \right] \right. \\
& \quad \left. \times \left[\alpha_{kl} + \beta_{kl} \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right) \right] \alpha_{B,j\ell}(\omega) \right\}. \tag{2.168}
\end{aligned}$$

Let us first expand the following:

$$\omega^4 \left[\alpha_{ij} + \beta_{ij} \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right) \right] \left[\alpha_{kl} + \beta_{kl} \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right) \right]$$

$$\begin{aligned}
&= \omega^4 \left[\alpha_{ij} \alpha_{kl} + (\alpha_{ij} \beta_{kl} + \beta_{ij} \alpha_{kl}) \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right) + \beta_{ij} \beta_{kl} \left(\frac{ic}{|\omega|R} - \frac{c^2}{\omega^2 R^2} \right)^2 \right] \\
&= \alpha_{ij} \alpha_{kl} \omega^4 + (\alpha_{ij} \beta_{kl} + \beta_{ij} \alpha_{kl}) i \frac{|\omega|^3 c}{R} - (\alpha_{ij} \beta_{kl} + \beta_{ij} \alpha_{kl} + \beta_{ij} \beta_{kl}) \frac{\omega^2 c^2}{R^2} \\
&\quad - 2\beta_{ij} \beta_{kl} i \frac{|\omega| c^3}{R^3} + \beta_{ij} \beta_{kl} \frac{c^4}{R^4} \\
&= \frac{c^4}{R^4} \left[\left(\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \frac{\omega^2 R^2}{c^2} + \alpha_{ij} \alpha_{kl} \frac{\omega^4 R^4}{c^4} \right) \right. \\
&\quad \left. - i \left(2\beta_{ij} \beta_{kl} \frac{|\omega|R}{c} - 2\alpha_{ij} \beta_{kl} \frac{|\omega|^3 R^3}{c^3} \right) \right]. \tag{2.169}
\end{aligned}$$

With the help of Eq. (2.169), Eq. (2.168) yields

$$\begin{aligned}
\mathcal{P}^{(\text{direct})}(R) &= \text{Re} \frac{c^4}{(4\pi\epsilon_0 c^2)^2 R^6} \sum_{m_A} \langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle \\
&\quad \times \underset{\omega = -E_{m,A}/\hbar + i\epsilon}{\text{Res}} \left\{ \alpha_{B,j\ell}(\omega) \sum_{\pm} \frac{e^{2i|\omega|R/c}}{E_{m,A}/\hbar \pm \omega - i\epsilon} \right. \\
&\quad \times \left[\left(\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \frac{\omega^2 R^2}{c^2} + \alpha_{ij} \alpha_{kl} \frac{\omega^4 R^4}{c^4} \right) \right. \\
&\quad \left. \left. - i \left(2\beta_{ij} \beta_{kl} \frac{|\omega|R}{c} - 2\alpha_{ij} \beta_{kl} \frac{|\omega|^3 R^3}{c^3} \right) \right] \right\} \\
&= - \text{Re} \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{B,j\ell} \left(\frac{E_{m,A}}{\hbar} \right) e^{-2iE_{m,A}R/(\hbar c)} \\
&\quad \times \left[\left(\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \frac{E_{m,A}^2 R^2}{\hbar^2 c^2} + \alpha_{ij} \alpha_{kl} \frac{E_{m,A}^4 R^4}{\hbar^4 c^4} \right) \right. \\
&\quad \left. + i \left(2\beta_{ij} \beta_{kl} \frac{E_{m,A} R}{\hbar c} - 2\alpha_{ij} \beta_{kl} \frac{E_{m,A}^3 R^3}{\hbar^3 c^3} \right) \right] \\
&= - \text{Re} \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{B,j\ell} \left(\frac{E_{m,A}}{\hbar} \right) \left(\cos \left(\frac{2E_{m,A}R}{\hbar c} \right) \right. \\
&\quad \left. - i \sin \left(\frac{2E_{m,A}R}{\hbar c} \right) \right) \left[\left(\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \frac{E_{m,A}^2 R^2}{\hbar^2 c^2} \right. \right. \\
&\quad \left. \left. + \alpha_{ij} \alpha_{kl} \frac{E_{m,A}^4 R^4}{\hbar^4 c^4} \right) + i \left(2\beta_{ij} \beta_{kl} \frac{E_{m,A} R}{\hbar c} - 2\alpha_{ij} \beta_{kl} \frac{E_{m,A}^3 R^3}{\hbar^3 c^3} \right) \right]. \tag{2.170}
\end{aligned}$$

Thus the direct pole term to the interaction energy reads

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) = & - \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{B,j\ell} \left(\frac{E_{m,A}}{\hbar} \right) \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \right. \\ & \left[\beta_{ij}\beta_{k\ell} - (2\alpha_{ij}\beta_{k\ell} + \beta_{ij}\beta_{k\ell}) \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \alpha_{ij} \alpha_{k\ell} \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] \\ & \left. + 2 \frac{E_{m,A}R}{\hbar c} \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[\beta_{ij}\beta_{k\ell} - \alpha_{ij}\beta_{k\ell} \left(\frac{E_{m,A}R}{\hbar c} \right)^2 \right] \right\}. \quad (2.171) \end{aligned}$$

In the similar way the pole term contribution of the mixing term to the interaction energy reads

$$\begin{aligned} \mathcal{P}^{(\text{mixing})}(R) = & \frac{i}{\hbar} \int_0^\infty \frac{d\omega}{2\pi} \omega^4 D_{ij}(\omega, \vec{R}) D_{k\ell}(\omega, \vec{R}) \\ & \sum_{\pm} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Aj} | \psi_A \rangle}{E_{m,A} \pm \hbar\omega - i\epsilon} \alpha_{A\bar{B},j\ell}(\omega) \\ = & \text{Re} \underset{\omega = -E_{m,A}/\hbar + i\epsilon}{\text{Res}} \frac{1}{\hbar^2} \omega^4 D_{ij}(\omega, \vec{R}) D_{k\ell}(\omega, \vec{R}) \\ & \sum_{\pm} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Aj} | \psi_A \rangle}{E_{m,A}/\hbar \pm \omega - i\epsilon} \alpha_{A\bar{B},j\ell}(\omega). \quad (2.172) \end{aligned}$$

The following replacement in Eqs. (2.171) and (2.172) yields the width term $\Gamma^{(\text{direct})}$ and $\Gamma^{(\text{mixing})}$ respectively:

$$\cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \rightarrow \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right), \quad \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \rightarrow -\cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \quad (2.173)$$

Substituting the value of the photon propagator and evaluating the residue at the pole, in the same way as we did for direct pole term, we get,

$$\begin{aligned} \mathcal{P}^{(\text{mixing})}(R) = & - \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_B \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{A\bar{B},j\ell} \left(\frac{E_{m,A}}{\hbar} \right) \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \right. \\ & \left[\beta_{ij}\beta_{k\ell} - (2\alpha_{ij}\beta_{k\ell} + \beta_{ij}\beta_{k\ell}) \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \alpha_{ij} \alpha_{k\ell} \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] \end{aligned}$$

$$+ \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[2 \beta_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right) - 2 \alpha_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right)^2 \right] \}. \quad (2.174)$$

For S -states, $\alpha_{B,j\ell}(\omega) = \delta_{j\ell} \alpha_B(\omega)$, and $\alpha_{\underline{AB},j\ell}(\omega) = \delta_{j\ell} \alpha_{\underline{AB}}(\omega)$. Thus, for S -states, the pole terms for the direct and mixing type contributions to the interaction energy are

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) &= - \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_B \left(\frac{E_{m,A}}{\hbar} \right) \delta_{j\ell} \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \right. \\ &\quad \left[\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \alpha_{ij} \alpha_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] \\ &\quad \left. + \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[2 \beta_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right) - 2 \alpha_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right) \right] \right\} \\ &= - \sum_{m_A} \frac{2 \langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_A \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_B \left(\frac{E_{m,A}}{\hbar} \right) \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[3 \right. \right. \\ &\quad \left. \left. - 5 \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] + \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[6 \frac{E_{m,A}R}{\hbar c} - 2 \left(\frac{E_{m,A}R}{\hbar c} \right)^2 \right] \right\}. \end{aligned} \quad (2.175)$$

and

$$\begin{aligned} \mathcal{P}^{(\text{mixing})}(R) &= - \sum_{m_A} \frac{\langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_B \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{\underline{AB}} \left(\frac{E_{m,A}}{\hbar} \right) \delta_{j\ell} \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \right. \\ &\quad \left[\beta_{ij} \beta_{kl} - (2\alpha_{ij} \beta_{kl} + \beta_{ij} \beta_{kl}) \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \alpha_{ij} \alpha_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] \\ &\quad \left. + \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[2 \beta_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right) - 2 \alpha_{ij} \beta_{kl} \left(\frac{E_{m,A}R}{\hbar c} \right)^2 \right] \right\} \\ &= - \sum_{m_A} \frac{2 \langle \psi_A | d_{Ai} | m_A \rangle \langle m_A | d_{Ak} | \psi_B \rangle}{(4\pi\epsilon_0)^2 R^6} \alpha_{\underline{AB}} \left(\frac{E_{m,A}}{\hbar} \right) \left\{ \cos \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[3 \right. \right. \\ &\quad \left. \left. - 5 \left(\frac{E_{m,A}R}{\hbar c} \right)^2 + \left(\frac{E_{m,A}R}{\hbar c} \right)^4 \right] + \sin \left(2 \frac{E_{m,A}R}{\hbar c} \right) \left[6 \frac{E_{m,A}R}{\hbar c} - 2 \left(\frac{E_{m,A}R}{\hbar c} \right)^2 \right] \right\}. \end{aligned} \quad (2.176)$$

Thus, in general, the pole type contribution contains terms which follow R^{-2} , R^{-3} , R^{-4} , R^{-5} and R^{-6} . The pole term can also be expressed as the sum of cosine term and a sine term. Let us now analyze Eq. (2.168) in the very short-range regime.

2.5.3. Close-Range Limit, $a_0 \ll R \ll a_0/\alpha$. By the close range limit we are referring to the vdW range of the interaction, although to a cruel approximation we can take $R \rightarrow 0$ in the close range limit. In the close-range limit, Eq. (2.168) can be approximated as

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) &= \text{Re} \frac{1}{\hbar^2} \sum_{m_A} \langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle \frac{\hbar^2}{(4\pi\epsilon_0 c^2)^2 R^2} \\ &\quad \times \underset{\omega = -E_{m,A}/\hbar + i\epsilon}{\text{Res}} \left\{ \sum_{\pm} \frac{1}{E_{m,A}/\hbar \pm \omega - i\epsilon} \beta_{ij} \beta_{kl} \frac{c^4}{R^4} \alpha_{B,j\ell}(\omega) \right\} \\ &= -\frac{\beta_{ij} \beta_{kl}}{(4\pi\epsilon_0)^2 R^6} \sum_{m_A} \langle \psi_A | d_{Ai} | m_A \rangle \cdot \langle m_A | d_{Ak} | \psi_A \rangle \alpha_{B,j\ell} \left(\frac{E_{m,A}}{\hbar} \right). \end{aligned} \quad (2.177)$$

For the hydrogen atom B being at the ground state i.e., $1S$ -state and the atom A being at the excited nS -state, Eq. (2.177) simplifies as

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) &= -\frac{\beta_{ij} \beta_{kl}}{(4\pi\epsilon_0)^2 R^6} \frac{\delta_{ik}}{3} \sum_m \langle nS | e \vec{r} | mP \rangle \cdot \langle mP | e \vec{r} | nS \rangle \delta_{j\ell} \alpha_{1S} \left(\frac{E_{mP} - E_{nS}}{\hbar} \right) \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_m \langle nS | \vec{r} | mP \rangle \cdot \langle mP | \vec{r} | nS \rangle \alpha_{1S} \left(\frac{E_{mP} - E_{nS}}{\hbar} \right). \end{aligned} \quad (2.178)$$

Similarly, the mixing pole term is given as

$$\mathcal{P}^{(\text{mixing})}(R) = -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_m \langle \underline{1S} | \vec{r} | mP \rangle \cdot \langle mP | \vec{r} | nS \rangle \alpha_{\underline{1S}nS} \left(\frac{E_{mP} - E_{nS}}{\hbar} \right), \quad (2.179)$$

where the $1S$ state is underlined in the polarizability, $\alpha_{\underline{1S}nS}$, to indicate that $E = E_{1S}$ is taken as the reference energy. Note that, in the close-range limit, both the direct and mixing pole terms follow the R^6 power law. We do get the same result taking the limit $R \rightarrow 0$ in Eqs. (2.175) and (2.176).

2.5.4. Intermediate Range, $a_0/\alpha \ll R \ll \hbar c/\mathcal{L}$. To determine the direct and the pole term in the intermediate range, we use the most general expressions of them which are given by Eqs. (2.175) and (2.176).

2.5.5. Very Long-Range Limit, $\hbar c/\mathcal{L} \ll R$. If the interatomic distance, R , is sufficiently large, a cruel approximation might be $R \rightarrow \infty$. In this range $\cos\left(2\frac{E_{m,A}R}{\hbar c}\right)\left(\frac{E_{m,A}R}{\hbar c}\right)^4$ is dominant in comparison to the other sine and cosine terms in both Eqs. (2.175) and (2.176). Thus, we have

$$\begin{aligned} \mathcal{P}^{(\text{direct})}(R) &= - \sum_{m_A} \frac{2\langle\psi_A|e\vec{r}|m_A\rangle\langle m_A|e\vec{r}|\psi_A\rangle}{3(4\pi\epsilon_0)^2R^6} \alpha_B \left(\frac{E_{m,A}}{\hbar}\right) \left(\frac{E_{m,A}R}{\hbar c}\right)^4 \cos\left(2\frac{E_{m,A}R}{\hbar c}\right) \\ &= - \frac{2e^2}{3(4\pi\epsilon_0)^2R^2} \sum_{m=2}^n \langle nS|\vec{r}|mP\rangle \cdot \langle mP|\vec{r}|nS\rangle \\ &\quad \times \alpha_{1S} \left(\frac{E_{mP,nS}}{\hbar}\right) \left(\frac{E_{mP,nS}}{\hbar c}\right)^4 \cos\left(2\frac{E_{mP,nS}R}{\hbar c}\right), \end{aligned} \quad (2.180)$$

and

$$\begin{aligned} \mathcal{P}^{(\text{mixing})}(R) &= - \sum_{m_A} \frac{2\langle\psi_A|e\vec{r}|m_A\rangle\langle m_A|e\vec{r}|\psi_B\rangle}{3(4\pi\epsilon_0)^2R^6} \alpha_{AB} \left(\frac{E_{m,A}}{\hbar}\right) \left(\frac{E_{m,A}R}{\hbar c}\right)^4 \cos\left(2\frac{E_{m,A}R}{\hbar c}\right) \\ &= - \frac{2e^2}{3(4\pi\epsilon_0)^2R^2} \sum_{m=2}^n \langle nS|\vec{r}|mP\rangle \cdot \langle mP|\vec{r}|1S\rangle \\ &\quad \times \alpha_{nS1S} \left(\frac{E_{mP,nS}}{\hbar}\right) \left(\frac{E_{mP,nS}}{\hbar c}\right)^4 \cos\left(2\frac{E_{mP,nS}R}{\hbar c}\right). \end{aligned} \quad (2.181)$$

At the very large interatomic separation (R), the pole term contains an oscillatory term whose magnitude depends on R^{-2} .

3. MATRIX ELEMENTS OF THE PROPAGATOR

3.1. STURMIAN DECOMPOSITION OF THE GREEN FUNCTION

For the Schrödinger Hamiltonian of the hydrogen atom

$$H_S = \frac{\vec{P}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}, \quad (3.1)$$

the total Schrödinger-Coulomb Green function $G(\vec{r}_1, \vec{r}_2, z)$ is the solution of the second order differential equation

$$\left(-\frac{\nabla^2}{2m} - z \right) G(\vec{r}_1, \vec{r}_2, z) = \delta^3(\vec{r}_1 - \vec{r}_2). \quad (3.2)$$

The variable z is the complex generalization of the energy. It depends on the energy of level n as follows:

$$z = E_n - \hbar\omega. \quad (3.3)$$

The Green function in the coordinate-space representation is given by

$$G(\vec{r}_1, \vec{r}_2, \nu) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} g_{\ell}(\vec{r}_1, \vec{r}_2, \nu) Y_{\ell m}(\theta_1, \phi_1) Y_{\ell m}^*(\theta_2, \phi_2), \quad (3.4)$$

where ν is an energy parameter associated with the generalization of the complex energy variable z by

$$\nu^2 = n^2 \frac{E_n}{z}. \quad (3.5)$$

It is worth noting that ν depicts the generalization of the principal quantum number n . $Y_{\ell m}(\theta_1, \phi_1)$ and $Y_{\ell m}(\theta_2, \phi_2)$ in Eq. (3.4) are usual spherical harmonics while $g_\ell(\vec{r}_1, \vec{r}_2, \nu)$ is the radial Green function. In this work, we use the so-called Sturmian form of the radial Green function [37; 38; 39]

$$g_\ell(\vec{r}_1, \vec{r}_2, \nu) = \frac{2m}{\hbar^2} \left(\frac{2}{a_0\nu} \right)^{2\ell+1} \exp\left(-\frac{(r_1 + r_2)}{a_0\nu}\right) (r_1 r_2)^\ell \times \sum_{k=0}^{\infty} \frac{k! L_k^{2\ell+1}\left(\frac{2r_1}{a_0\nu}\right) L_k^{2\ell+1}\left(\frac{2r_2}{a_0\nu}\right)}{(k + 2\ell + 1)!(k + \ell + 1 - \nu)}, \quad (3.6)$$

where a_0 is the Bohr's radius given by

$$a_0 = \frac{\hbar}{\alpha m c}. \quad (3.7)$$

$L_k^{2\ell+1}\left(\frac{2r_1}{a_0\nu}\right)$ and $L_k^{2\ell+1}\left(\frac{2r_2}{a_0\nu}\right)$ in Eq. (3.6) are the generalized Laguerre polynomials.

3.2. ENERGY ARGUMENT OF THE GREEN FUNCTION

For principal quantum number n ,

$$E_n = -\frac{\alpha^2 m c^2}{2n^2}. \quad (3.8)$$

The dimensionless energy parameter t can be defined as

$$t \equiv \sqrt{\frac{E_n}{z}} = \sqrt{\frac{E_n}{E_n - \hbar\omega}} = \left(1 - \frac{\hbar\omega}{E_n}\right)^{-1/2}. \quad (3.9)$$

We can re-express the z variable as

$$z \equiv E_n - \hbar\omega = -\frac{\alpha^2 m c^2}{2\nu^2} = -\frac{\alpha^2 m c^2}{2n^2} \frac{n^2}{\nu^2} = E_n \frac{n^2}{\nu^2}, \quad (3.10)$$

where ν is the generalized principal quantum number. Rearranging the left hand side and the right most term of Eq. (3.10), we get

$$\frac{\nu^2}{n^2} = \frac{E_n}{z} = t^2 \quad \implies \nu = n t. \quad (3.11)$$

Substituting the energy eigenvalue in Eq. (3.9) from Eq. (3.8), the parameter t yields

$$t_n = \left(1 + \frac{2n^2\hbar\omega}{\alpha^2 mc^2}\right)^{-1/2} \quad (3.12)$$

or,

$$\frac{1}{t_n^2} = 1 + \frac{2n^2\hbar\omega}{\alpha^2 mc^2}. \quad (3.13)$$

When $\omega = 0$, $t = 1$ and when $\omega = \infty$, $t = 0$. Thus any integral over ω from 0 to ∞ is equivalent to the integral over t than from 1 to 0. In some situation, the integration over t is simpler than the integration over ω .

Indeed, we are going to consider the Wick-rotated form of expressions in our calculations. Thus, in our computations, $i\omega$ will be appeared in place of ω . An ω can have both the positive and the negative value. We, therefore, replace ω by $\pm i\omega$ in Eq. (3.13). Let us denote the t after such replacement as T_n^\pm .

$$\frac{1}{T_n^{\pm 2}} = 1 \pm i \frac{2n^2\hbar\omega}{\alpha^2 mc^2}. \quad (3.14)$$

Rearranging equation (3.14), we get the following expression for ω ,

$$\hbar\omega = \frac{\alpha^2 mc^2}{2n^2} \frac{1 - t^2}{t^2}. \quad (3.15)$$

Substituting Eq. (3.15) in Eq. (3.14) and solving for T_n , it is found that the T_n depends only on t and reads as follows:

$$T_n^\pm = \frac{t}{\sqrt{\pm i + t^2(1 \mp i)}}. \quad (3.16)$$

The T_n for the different values of n are related with each other as

$$T_m^\pm = \frac{n T_n^\pm}{\sqrt{m^2 + (n^2 - m^2) T_n^{\pm 2}}}. \quad (3.17)$$

3.3. ANGULAR ALGEBRA (CLEBSCH-GORDAN COEFFICIENTS)

In this section, we discuss the addition of angular momenta and Clebsch-Gordan coefficients. In general, for every quantum mechanical system, there exists a vector operator $\vec{J} = \vec{L} + \vec{S}$, called the total angular momentum, where \vec{L} and \vec{S} are the orbital and the spin angular momenta. \vec{J} obeys the following commutation relations

$$[J_i, J_j] = i \sum_k \epsilon_{ijk} J_k, \quad [\vec{J}, J^2] = 0, \quad (3.18)$$

where J^2 is the sum

$$J^2 = J_i^2 + J_j^2 + J_k^2, \quad (3.19)$$

and ϵ_{ijk} is the Levi-Civita symbol defined by

$$\epsilon_{ijk} = \begin{cases} +1 & \text{for even permutation of } (i, j, k) \\ -1 & \text{for odd permutation of } (i, j, k) \\ 0 & \text{otherwise.} \end{cases}$$

The commutation relation (3.18) tells that each component of \vec{J} commutes with J^2 . This indicates that any component of \vec{J} and J^2 can have at least one non-zero common eigenstate. For the sake of simplicity, \vec{J} is chosen along the z-axis. We denote the common eigenstate of the J^2 and J_z as $|j, m\rangle$. J^2 and J_z satisfy the following eigenvalue equations.

$$J^2|j, m\rangle = j(j+1)|j, m\rangle, \quad (3.20)$$

$$J_z|j, m\rangle = m|j, m\rangle, \quad (3.21)$$

where $j(j+1)$ and m are the eigenvalues of J^2 and J_z respectively associated with the eigenstate $|j, m\rangle$. Let us consider two quantum mechanical state spaces having basis vectors $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ associated with angular momentum \vec{J}_1 and \vec{J}_2 respectively. The vector sum of the angular momenta associated with the quantum mechanical spaces

$$\vec{J} = \vec{J}_1 + \vec{J}_2, \quad (3.22)$$

is the total angular momentum vector \vec{J} for the combined space. The $J^2 = J_1^2 + J_2^2 + 2\vec{J}_1 \cdot \vec{J}_2$ and $J_z = (\vec{J}_1 + \vec{J}_2) \cdot \hat{z} = J_{1z} + J_{2z}$ of the combined space commute with each other. Thus, there exist nonzero common eigenstates $|j, m\rangle$ such that eigenvalues of J_1^2 , J_2^2 , J^2 , J_{1z} , J_{2z} , and J_z are $j_1(j_1+1)$, $j_2(j_2+1)$, $j(j+1)$, m_1 , m_2 and m respectively. All j 's and m 's are either integers or half integers. j_1 and j_2 fulfil the triangular inequality

$$|j_1 - j_2| \leq J \leq |j_1 + j_2|. \quad (3.23)$$

And m_1 , m_2 and m satisfy the following selection rules:

$$m_1 \in -|j_1|, \dots, |j_1| \quad m_2 \in -|j_2|, \dots, |j_2| \quad m_1 + m_2 = m. \quad (3.24)$$

Making use of commutation relations for angular momenta, one can easily verify that J_1, J_2, J^2, J_z and J_1, J_2, J_{1z}, J_{2z} form two different complete set of commuting observables (CSCO) [40] associated with the orthonormal basis states $|j_1, j_2, j, m\rangle$ (simply denoted as $|j, m\rangle$) and $|j_1, j_2, m_1, m_2\rangle$ respectively. One obvious question which arises is how we can express a given state $|j, m\rangle$ in terms of $|j_1, j_2, m_1, m_2\rangle$. The answer is that we can use the completeness relation of $|j_1, j_2, m_1, m_2\rangle$:

$$\sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2| = 1, \quad (3.25)$$

i.e.

$$\begin{aligned} |j, m\rangle &= \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2|j, m\rangle \\ &= \sum_{m_1, m_2} \langle j_1, j_2, m_1, m_2|j, m\rangle |j_1, j_2, m_1, m_2\rangle \\ &= \sum_{m_1, m_2} C_{j_1 j_2 m_1 m_2}^{jm} |j_1, j_2, m_1, m_2\rangle. \end{aligned} \quad (3.26)$$

where $C_{j_1 j_2 m_1 m_2}^{jm} = \langle j_1, j_2, m_1, m_2|j, m\rangle$ are the so-called Clebsch-Gordan coefficients. They depict coupling between angular momenta of two quantum mechanical systems. The Clebsch-Gordan coefficients can also be expressed in terms of Wigner's $3 - j$ symbol [41] as given below:

$$C_{j_1 j_2 m_1 m_2}^{jm} = \langle j_1, j_2, m_1, m_2|j, m\rangle = (-1)^{j_1 - j_2 + m} \sqrt{2j + 1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}. \quad (3.27)$$

Here is the list of few Clebsch-Gordan coefficients:

$$C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} = 1, \quad C_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{2}}, \quad C_{\frac{1}{2}0-\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}-\frac{1}{2}} = \frac{1}{\sqrt{3}}, \quad C_{\frac{1}{2}\frac{1}{2}1-\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} = \sqrt{\frac{2}{3}}. \quad (3.28)$$

As stated by the Wigner-Eckart theorem, the matrix elements of a tensor operator T_{kq} sandwiched between the basis states $|\tau, j, m\rangle$ is given by

$$\langle \tau j m | T_{kq} | \tau' j' m' \rangle = \frac{C_{j'm'kq}^{jm}}{\sqrt{2j+1}} \langle \tau j | \vec{T}^k | \tau' j' \rangle. \quad (3.29)$$

The index τ is a collection of supplementary quantum numbers associated with observables other than J^2 and J_z which are necessary to form a complete set of commuting observables (CSCO). The quantum number τ satisfies

$$\langle \tau j m | \tau' j' m' \rangle = \delta_{\tau\tau'} \delta_{jj'} \delta_{mm'}. \quad (3.30)$$

The quantity $\langle \tau j | \vec{T}^k | \tau' j' \rangle$ in equation (3.29) is a reduced matrix element which is independent of m and m' . It can be concluded from Eq. (3.29) that the orientational dependence of the matrix element can be determined from its geometrical consideration.

3.4. 1S, 2S, 3S, 4S, AND 5S MATRIX ELEMENTS

The matrix element of the Schrödinger Coulomb propagator [42], if both atoms are in nS states, in the co-ordinate space representation is defined as

$$\begin{aligned} P(\phi_n, \omega) &= \frac{e^2}{3} \langle \phi_n | x^j \frac{1}{H_s - E_n + \hbar\omega} x^j | \phi_n \rangle \\ &= \frac{e^2}{3} \langle nS | x^j G(r_1, r_2, \nu = t) x^j | nS \rangle. \end{aligned} \quad (3.31)$$

The wave function $\langle r, \theta, \phi | nS \rangle = \Psi_{n00}(r, \theta, \phi)$ contains the radial part $R_{n0}(r)$ and the angular part $Y_{00}(\theta, \phi)$ such that

$$\Psi_{n00}(r, \theta, \phi) = R_{n0}(r) Y_{00}(\theta, \phi). \quad (3.32)$$

It is easy to separate the total integration into the radial part and the angular part. The angular integration evaluates to one. Thus, Eq. (3.31) reduces to the following radial integration.

$$P(\phi_n, \omega) = \frac{e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{nS}(r_1) r_1 g_\ell(r_1, r_2, \nu) r_2 R_{nS}(r_2). \quad (3.33)$$

3.4.1. 1S Matrix Element. Let us first consider two hydrogen atoms in their ground states. The radial part of the ground state wave function reads

$$R_{10}(r) = 2 \frac{1}{a_0^{3/2}} e^{-r/a_0}. \quad (3.34)$$

Substituting $R_{10}(r)$ from Eq. (3.34) and the Sturmian form of the radial Green function from Eq. (3.6), the Q -matrix element $P(1S, t)$ can be written as

$$P(1S, t) = \frac{64me^2}{3\hbar^2 a_0^6 t^3} \int_0^\infty r_1^4 dr_1 \int_0^\infty r_2^4 dr_2 \exp\left(-\frac{(r_1 + r_2)}{a_0 t}\right) \exp\left(-\frac{(r_1 + r_2)}{a_0}\right) \sum_{k=0}^\infty \frac{k! L_k^{2l+1}\left(\frac{2r_1}{a_0 t}\right) L_k^{2l+1}\left(\frac{2r_2}{a_0 t}\right)}{(k + 2l + 1)!(k + l + 1 - t)}. \quad (3.35)$$

Let us introduce the dimensionless quantities $\rho_1 = \frac{2r_1}{a_0 t}$ and $\rho_2 = \frac{2r_2}{a_0 t}$. We then have

$$P(1S, t) = \frac{\hbar^2 e^2}{48\alpha^4 m^3 c^4} \sum_{k=0}^\infty \frac{k!}{(k + 3)!} \frac{t^7}{(k + 2 - t)} \int_0^\infty \rho_1^4 d\rho_1 e^{-(\frac{1+t}{2})\rho_1} L_k^3(\rho_1) \int_0^\infty \rho_2^4 d\rho_2 e^{-(\frac{1+t}{2})\rho_2} L_k^3(\rho_2). \quad (3.36)$$

We use the following standard integral identity [43]

$$\int_0^\infty d\rho e^{s\rho} \rho^\gamma L_n^\mu(\rho) = \frac{\Gamma(\gamma+1)\Gamma(n+\mu+1)}{n!\Gamma(\mu+1)} (-s)^{-(\gamma+1)} {}_2F_1\left(-n, \gamma+1; \mu+1; -\frac{1}{s}\right), \quad (3.37)$$

to evaluate the integration in Eq. (3.36), where ${}_2F_1\left(-n, \gamma+1; \mu+1; -\frac{1}{s}\right)$ is a hypergeometric function of the form ${}_2F_1(a, b; c; z)$. The hypergeometric function is defined by the following power series

$${}_2F_1(a, b; c; z) = \sum_{k=0}^{\infty} \frac{(a)_k (b)_k}{(c)_k} \frac{z^k}{k!}, \quad (3.38)$$

where

$$(q)_k = \frac{\Gamma(k+q)}{\Gamma(q)} = q(q+1)(q+2) \dots (q+k-1), \quad (3.39)$$

is a Pochhammer symbol. If c is not a negative integer, the hypergeometric series (3.38) converges for all $|z| < 1$, and converges for $|z| = 1$, if $\Re(c - a - b) > 0$, where \Re stands for the real part. It is worth listing values of the hypergeometric function in the following special cases.

$${}_2F_1(0, b; c; z) = 1, \quad (3.40a)$$

$${}_2F_1(a, b; b; z) = \frac{1}{(1-z)^a}, \quad (3.40b)$$

$${}_2F_1(a, b+1; b; z) = \frac{(a-b)z + b}{b(1-z)^{a+1}}, \quad (3.40c)$$

$${}_2F_1(1, 1; 2; z) = -\frac{\ln(1-z)}{z}. \quad (3.40d)$$

In what follows, the following contiguous relations for hypergeometric functions are also of great use.

$${}_2F_1(a, b; c; z) = \frac{(c-1)}{z(c-a-1)} \left[{}_2F_1(a, b-1; c-1; z) + (z-1) {}_2F_1(a, b; c-1; z) \right]. \quad (3.41a)$$

$${}_2F_1(a, b; c; z) = -\frac{(b-c)}{z(b-a)-2b+c} {}_2F_1(a, b-1; c; z) + \frac{b(z-1)}{z(b-a)-2b+c} {}_2F_1(a, b+1; c; z). \quad (3.41b)$$

With the help of identity (3.37), Eq. (3.36) gives

$$P(1S, t) = \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{2t^2(-3-18t-42t^2-42t^3-t^4+36t^5+38t^6)}{3(-1+t)(1+t)^7} - \frac{256t^{10} {}_2F_1\left(1, 2-t; 3-t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(-2+t)(-1+t)(1+t)^9} \right]. \quad (3.42)$$

The contiguous relation (3.41a) lowers ${}_2F_1\left(1, 2-t; 3-t; \left(\frac{1-t}{1+t}\right)^2\right)$ into ${}_2F_1\left(1, 1-t; 2-t; \left(\frac{1-t}{1+t}\right)^2\right)$ and ${}_2F_1\left(1, 2-t; 2-t; \left(\frac{1-t}{1+t}\right)^2\right)$. The relation (3.40b) implies that

$$\left(\left(\frac{1-t}{1+t} \right)^2 - 1 \right) {}_2F_1\left(1, 2-t; 2-t; \left(\frac{1-t}{1+t} \right)^2\right) = -1. \quad (3.43)$$

We apply the contiguous relation (3.41a) one more time. This lowers ${}_2F_1\left(1, 1-t; 2-t; \left(\frac{1-t}{1+t}\right)^2\right)$ into ${}_2F_1\left(1, -t; 1-t; \left(\frac{1-t}{1+t}\right)^2\right)$ and ${}_2F_1\left(1, 1-t; 1-t; \left(\frac{1-t}{1+t}\right)^2\right)$. After some algebra $P(1S, t)$ works out to the following closed form

$$P(1S, t) = \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{2t^2(-3+3t+12t^2-12t^3-19t^4+19t^5+26t^6+38t^7)}{3(-1+t)^5(1+t)^4} - \frac{256t^9 {}_2F_1\left(1, -t; 1-t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(-1+t)^5(1+t)^5} \right]. \quad (3.44)$$

For $t \rightarrow 1$ i.e. for $\omega \rightarrow 0$ Eq. (3.44) gives the following:

$$P(1S, t) = \frac{9e^2 \hbar^2}{4\alpha^4 m^3 c^4} + O(t - 1)^1. \quad (3.45)$$

For large ω , i.e. when $t \rightarrow 0$, $P(1S, t)$ takes the following form

$$P(1S, \omega) = \frac{3\hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar\omega} - \frac{3\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \quad (3.46)$$

Let us make some analytical comparison. For large ω , $\frac{1}{X+\omega}$ can be expanded as given below.

$$\frac{1}{X + \omega} = \frac{1}{\omega} - \frac{1}{\omega^2} X + \frac{1}{\omega^3} X^2 + \dots \quad (3.47)$$

Thus,

$$\begin{aligned} \langle nS | r^j \frac{1}{H - E_{nS} + \hbar\omega} r^j | n'S \rangle &= \frac{\langle nS | r^2 | n'S \rangle}{\hbar\omega} - \frac{\langle nS | r^j (H - E_{n'S}) r^j | n'S \rangle}{\hbar^2 \omega^2} + O(\omega^{-3}) \\ &= \frac{1}{\hbar\omega} \langle nS | r^2 | n'S \rangle - \frac{1}{2\hbar^2 \omega^2} \langle nS | r^j \left[(H - E_{nS}) + (E_{n'S} - E_{nS}) \right. \\ &\quad \left. + (H - E_{n'S}) \right] r^j | n'S \rangle + O(\omega^{-3}). \end{aligned} \quad (3.48)$$

For the $1S$ - $1S$ system,

$$\begin{aligned} &\langle 1S | r^j \frac{1}{H - E_{1S} + \hbar\omega} r^j | 1S \rangle \\ &= \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle - \frac{1}{\hbar^2 \omega^2} \langle 1S | r^j (H - E_{1S}) r^j | 1S \rangle + O(\omega^{-3}) \\ &= \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle - \frac{1}{2\hbar^2 \omega^2} \langle 1S | r^j \left[(H - E_{1S}) + (E_{1S} - E_{1S}) + \right. \\ &\quad \left. (H - E_{1S}) \right] r^j | 1S \rangle + O(\omega^{-3}) \\ &= \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle - \frac{1}{2\hbar^2 \omega^2} \left(\langle 1S | r^j [(H - E_{1S}), r^j] | 1S \rangle \right) \end{aligned}$$

$$\begin{aligned}
& + \langle 1S | [r^j, (H - E_{1S})] r^j | 1S \rangle \Big) + O(\omega^{-3}) \\
& = \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle - \frac{1}{2\hbar^2\omega^2} \left(\langle 1S | r^j (-i\hbar \frac{p^j}{m}) | 1S \rangle + \langle 1S | (i\hbar \frac{p^j}{m}) r^j | 1S \rangle \right) + O(\omega^{-3}) \\
& = \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle + \frac{i\hbar}{2m\hbar^2\omega^2} \left(\langle 1S | [r^j, p^j] | 1S \rangle \right) + O(\omega^{-3}) \\
& = \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle + (3i\hbar) \frac{i\hbar}{2m\hbar^2\omega^2} \langle 1S | 1S \rangle + O(\omega^{-3}). \tag{3.49}
\end{aligned}$$

We have used $[(H - E_{1S}), \mathcal{O}] | 1S \rangle = (H - E_{1S}) \mathcal{O} | 1S \rangle$ in the second line, $[(H - E_{1S}), r^j] = -i\hbar p^j/m$ in the third line and the commutation relation $[r^j, p^j] = 3i\hbar$ in the fifth line of the above expression. \mathcal{O} refers to an arbitrary operator. Since, $|1S\rangle$ is normalized to unity. We have,

$$\langle 1S | r^j \frac{1}{H - E_{1S} + \hbar\omega} r^j | 1S \rangle = \frac{1}{\hbar\omega} \langle 1S | r^2 | 1S \rangle - \frac{3}{2m\hbar^2\omega^2} + O(\omega^{-3}). \tag{3.50}$$

We compute the expectation value

$$\begin{aligned}
\langle 1S | r^2 | 1S \rangle & = \int_0^\infty dr \, 2^2 \frac{1}{a_0^3} r^4 e^{-\frac{2r}{a_0}} = \frac{4a_0^2}{32} \int_0^\infty d \left(\frac{2r}{a_0} \right) \left(\frac{2r}{a_0} \right)^4 e^{-\frac{2r}{a_0}} = \frac{4a_0^2}{32} \Gamma(5) \\
& = \frac{3\hbar^2}{\alpha^2 m^2 c^2}, \tag{3.51}
\end{aligned}$$

whence

$$\begin{aligned}
P(1S, \omega) & = \frac{e^2}{3} \langle 1S | r^j \frac{1}{H - E_{1S} + \omega} r^j | 1S \rangle \\
& = \frac{3\hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar\omega} - \frac{3\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \tag{3.52}
\end{aligned}$$

Hence, we see that the coefficients in the large asymptotic expression (3.52) match those of the series expansion (3.46) of our result. This is a good way to check

the rather complicated expressions obtained when computing polarizabilities (for instance, expression (3.44)). We now substitute $t = (1 + 2\hbar\omega/\alpha^2 m c^2)^{-1/2}$ in Eq. (3.44) to get $P(1S, \omega)$.

3.4.2. 2S Matrix Element. For the $|2S\rangle$ state, the P-matrix element of the Schrödinger-Coulomb propagator $P(2S, t)$ is given by

$$P(2S, t) = \frac{e^2}{3} \langle 2S | x^j g_{\ell=1}(r_1, r_2, \nu = 2t) x^j | 2S \rangle, \quad (3.53)$$

where $t = (1 + 8\omega/(\alpha^2 m))^{-1/2}$ and $g_{\ell=1}(r_1, r_2, \nu = 2t)$ is the radial Green function given by Eq. (3.6). The wave function for the 2S state is

$$\Psi_{200}(r, \theta, \phi) = R_{20}(r) Y_{00}(\theta, \phi) = 2 \left(\frac{1}{2a_0} \right)^{3/2} \left(1 - \frac{r}{2a_0} \right) e^{-\frac{r}{2a_0}} Y_{00}(\theta, \phi). \quad (3.54)$$

Substituting $g_{\ell}(r_1, r_2, \nu = 2t)$ and $|2S\rangle$ in $P(2S, t)$ and integrating using the standard integral given in Eq. (3.37) we get,

$$P(2S, t) = \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{16t^2}{3(-1+t)^3(1+t)^8} \left(-21 - 105t - 162t^2 + 30t^3 + 340t^4 + 284t^5 - 46t^6 - 494t^7 - 239t^8 + 1181t^9 \right) - \frac{16384t^{10}(-1+4t^2)_2F_1\left(1, 2-2t; 3-2t; \left(\frac{-1+t}{1+t}\right)^2\right)}{3(-1+t)^3(1+t)^{10}} \right]. \quad (3.55)$$

We lower the arguments of Hypergeometric functions using the relations (3.41a) and (3.41b). After some algebra, $P(2S, t)$ becomes

$$P(2S, t) = \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{16t^2}{3(-1+t)^6(1+t)^4} \left(21 - 42t - 48t^2 + 138t^3 + 14t^4 - 166t^5 - 16t^6 - 314t^7 + 1181t^8 \right) - \frac{16384t^9(-1+4t^2)_2F_1\left(1, -2t; 1-2t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(-1+t)^6(1+t)^6} \right]. \quad (3.56)$$

For $t \rightarrow 1$, or, $\omega \rightarrow 0$, we have

$$\lim_{t \rightarrow 1} P(2S, t) = \frac{60 e^2 \hbar^2}{\alpha^4 m^3 c^4} + O(t - 1)^1. \quad (3.57)$$

For $t \rightarrow 0$ i.e. $\omega \rightarrow \infty$ we get the following series for $P(2S, t)$.

$$P(2S, \omega) = \frac{14 \hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar \omega} - \frac{\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \quad (3.58)$$

The Taylor series of the matrix element for large frequency is

$$\begin{aligned} P(2S, \omega) &= \frac{e^2}{3} \langle 2S | r^j \frac{1}{H - E_{2S} + \hbar \omega} r^j | 2S \rangle \\ &= \frac{e^2}{3} \left[\frac{1}{\hbar \omega} \langle 2S | r^2 | 2S \rangle - \frac{1}{\hbar^2 \omega^2} \langle 2S | r^j (H - E_{1S}) r^j | 2S \rangle \right] + O(\omega^{-3}) \\ &= \frac{e^2}{3 \hbar \omega} \langle 2S | r^2 | 2S \rangle - \frac{e^2 \hbar^2}{2m \hbar^2 \omega^2} + O(\omega^{-3}). \end{aligned} \quad (3.59)$$

We compute the expectation value

$$\begin{aligned} \langle 2S | r^2 | 2S \rangle &= \int_0^\infty dr \ 2^2 \left(\frac{\alpha m c}{2 \hbar} \right)^3 r^4 \left(1 - \frac{\alpha m c r}{2 \hbar} \right)^2 e^{-\alpha m c r / \hbar} \\ &= \frac{\alpha^3 m^3 c^3}{2 \hbar^3} \left[\int_0^\infty dr \ r^4 e^{-\alpha m c r / \hbar} - \frac{\alpha m c}{\hbar} \int_0^\infty dr \ r^5 e^{-\alpha m c r / \hbar} \right. \\ &\quad \left. + \frac{\alpha^2 m^2 c^2}{4 \hbar^2} \int_0^\infty dr \ r^6 e^{-\alpha m c r / \hbar} \right] \\ &= \frac{\alpha^3 m^3 c^3}{2 \hbar^3} \left[\frac{\hbar^5 \Gamma(5)}{\alpha^5 m^5 c^5} - \frac{\hbar^5 \Gamma(6)}{\alpha^5 m^5 c^5} + \frac{\hbar^5 \Gamma(7)}{4 \alpha^5 m^5 c^5} \right] \\ &= \frac{42 \hbar^2}{\alpha^2 m^2 c^2}. \end{aligned} \quad (3.60)$$

Substituting the value of $\langle 2S | r^2 | 2S \rangle$ from Eq. (3.60) in Eq. (3.59), we get

$$P(2S, \omega) = \frac{14 \hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar \omega} - \frac{\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \quad (3.61)$$

This is exactly what we have in (3.58).

Let's get back to the matrix element $P(2S, t)$. We want to exclude the 2P state from the sum over states in Eq.(3.56).

$$\begin{aligned} \frac{e^2}{3} \left\langle 2P \left| x^j \frac{1}{\hbar\omega} x^j \right| 2P \right\rangle &= \frac{e^2}{3\hbar} \frac{27a_0^2}{\omega} = \frac{e^2}{3\hbar} \frac{27\hbar^2}{\alpha^2 m^2 c^2 \omega} = \frac{9 e^2 \hbar}{\alpha^2 m^2 c^2} \frac{8\hbar}{\alpha^2 m c^2} \frac{t^2}{1-t^2} \\ &= \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \left[\frac{72t^2}{1-t^2} \right]. \end{aligned} \quad (3.62)$$

One needs to subtract right hand side of Eq. (3.62) from Eq. (3.56) to exclude the degenerate contribution of the 2P state to the matrix element $P(2S, \omega)$ which results

$$\begin{aligned} \tilde{P}(2S, t) &= \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \left[\frac{16t^2}{3(-1+t)^6(1+t)^4} \left(21 - 42t - 48t^2 + 138t^3 + 14t^4 - 166t^5 \right. \right. \\ &\quad \left. \left. - 16t^6 - 314t^7 + 1181t^8 \right) - \frac{16384t^9(-1+4t^2) {}_2F_1\left(1, -2t; 1-2t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(-1+t)^6(1+t)^6} \right. \\ &\quad \left. + \frac{72t^2}{t^2-1} \right], \quad \text{where } t = \left(1 + \frac{8\hbar\omega}{\alpha^2 m c^2} \right)^{-1/2}. \end{aligned} \quad (3.63)$$

$\tilde{P}(2S, t)$ in Eq. (3.63) is the nondegenerate contribution to the matrix element $P(2S, \omega)$.

3.4.3. 3S, 4S, and 5S Matrix Elements. For the 3S state of the hydrogen, the radial wave function is given as

$$R_{30}(r) = 2 \left(\frac{1}{3a_0} \right)^{3/2} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right) \exp\left(-\frac{r}{3a_0}\right). \quad (3.64)$$

Thus, the integral form of the P-matrix element takes

$$P(3S, \omega) = \frac{e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{30}(r_1) r_1 g_\ell(r_1, r_2, \nu = 3t) r_2 R_{30}(r_2). \quad (3.65)$$

After some algebra, the matrix element of Schrödinger Coulomb propagator for $3S$ state $P(3S, t)$ is given as

$$\begin{aligned}
P(3S, t) = & \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{54t^2}{(-1+t)^8(1+t)^6} \left(23 - 46t - 95t^2 + 236t^3 + 128t^4 - 492t^5 \right. \right. \\
& \left. \left. - 62t^6 + 40t^7 + 2871t^8 + 2090t^9 - 13283t^{10} - 2852t^{11} + 15538t^{12} \right) - \frac{972 t^2}{1-t^2} \right. \\
& \left. + \frac{6912 t^9 (-1+9t^2)(3-7t^2)^2 {}_2F_1 \left(1, -3t; 1-3t; \frac{(-1+t)^2}{(1+t)^2} \right)}{(-1+t)^8(1+t)^8} \right]; \\
\text{where } t = & \left(1 + \frac{18\hbar\omega}{\alpha^2 m c^2} \right)^{-1/2}. \tag{3.66}
\end{aligned}$$

We subtracted $\frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{972t^2}{(1-t^2)} \right]$ from $P(3S, t)$ to exclude the contribution of the degenerate $3P$ states. The series expansion of the matrix element $P(3S, t)$ for low frequency case *i.e.*, about $t = 1$ yields

$$P(3S, t) = \frac{2025}{4} \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} + O(t-1)^1. \tag{3.67}$$

On the other hand, the series expansion of the same matrix element $P(3S, t)$ for large frequency is

$$P(3S, \omega) = \frac{69 \hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar\omega} - \frac{\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \tag{3.68}$$

With the help of the Eq. (3.48), the matrix element

$$P(3S, \omega) = \frac{e^2}{3} \langle 3S | x^j \frac{1}{H - E_{3S} - \hbar\omega} x^j | 3S \rangle, \tag{3.69}$$

can be expanded for large ω to get

$$P(3S, \omega) = \frac{e^2 \langle 3S | r^2 | 3S \rangle}{3\hbar\omega} - \frac{e^2}{6\hbar^2 \omega^2} \langle 3S | r^j \left[(H - E_{3S}) + (H - E_{3S}) \right] r^j | 3S \rangle + O(\omega^{-3})$$

$$\begin{aligned}
&= \frac{e^2}{3\hbar\omega} \langle 3S|r^2|3S \rangle - \frac{e^2}{6\hbar^2\omega^2} \left(\langle 3S|r^j[(H - E_{3S}), r^j]|3S \rangle \right. \\
&\quad \left. + \langle 3S|[r^j, (H - E_{3S})]r^j|3S \rangle \right) + O(\omega^{-3}) \\
&= \frac{e^2}{3\hbar\omega} \langle 3S|r^2|3S \rangle - \frac{e^2}{6\hbar^2\omega^2} \left(\langle 3S|r^j(-i\hbar\frac{p^j}{m})|3S \rangle + \langle 3S|(i\hbar\frac{p^j}{m})r^j|3S \rangle \right) + O(\omega^{-3}) \\
&= \frac{e^2}{3\hbar\omega} \langle 3S|r^2|3S \rangle + \frac{i\hbar e^2}{6m\hbar^2\omega^2} \left(\langle 3S|[r^j, p^j]|3S \rangle \right) + O(\omega^{-3}) \\
&= \frac{e^2}{3\hbar\omega} \langle 3S|r^2|3S \rangle + \frac{i\hbar e^2}{6m\hbar^2\omega^2} \left(3i\hbar \langle 3S|3S \rangle \right) + O(\omega^{-3}) \\
&= \frac{e^2}{3\hbar\omega} \langle 3S|r^2|3S \rangle - \frac{\hbar^2 e^2}{2m\hbar^2\omega^2} + O(\omega^{-3}). \tag{3.70}
\end{aligned}$$

The expectation value $\langle 3S|r^2|3S \rangle$ amounts to be

$$\langle 3S|r^2|3S \rangle = \frac{207\hbar^2}{\alpha^2 m^2 c^2}. \tag{3.71}$$

Substituting the value of $\langle 3S|r^2|3S \rangle$ in the last line of Eq. (3.70), the series of the matrix element $P(3S, \omega)$ for large frequency gives

$$P(3S, \omega) = \frac{69 \hbar^2 e^2}{\alpha^2 m^2 c^2} \frac{1}{\hbar\omega} - \frac{\hbar^2 e^2}{2m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \tag{3.72}$$

This is exactly same to Eq. (3.68). This verifies our result (3.66) for matrix element $P(3S, \omega)$. Following the same steps what we did for $3S$ matrix element, the $4S$ matrix element and the $5S$ matrix element are given as

$$\begin{aligned}
P(4S, t) &= \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{256t^2}{27(t-1)^{10}(t+1)^8} \left(9293353t^{16} - 1252434t^{15} - 14419772t^{14} \right. \right. \\
&\quad \left. \left. + 1876682t^{13} + 7960532t^{12} - 963186t^{11} - 1841172t^{10} + 160410t^9 + 159222t^8 \right. \right. \\
&\quad \left. \left. + 37242t^7 - 12132t^6 - 31410t^5 + 10548t^4 + 10314t^3 - 4428t^2 - 1458t + 729 \right) \right. \\
&\quad \left. - \frac{5760t^2}{1-t^2} - \frac{1048576t^9 (16t^2 - 1) (23t^4 - 18t^2 + 3)^2 {}_2F_1 \left(1, -4t; 1 - 4t; \frac{(t-1)^2}{(t+1)^2} \right)}{27(t^2 - 1)^{10}} \right];
\end{aligned}$$

$$\text{where } t = \left(1 + \frac{32\hbar\omega}{\alpha^2 m c^2}\right)^{-1/2}, \quad (3.73)$$

$$P(5S, t) = \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{1250t^2}{27(t-1)^{12}(t+1)^{10}} \left[174886810t^{20} - 18533620t^{19} - 388092451t^{18} \right. \right. \\ \left. \left. + 40364922t^{17} + 339195951t^{16} - 34343064t^{15} - 148417204t^{14} + 14394688t^{13} \right. \right. \\ \left. \left. + 34111792t^{12} - 3002592t^{11} - 3909954t^{10} + 182820t^9 + 204834t^8 + 84312t^7 \right. \right. \\ \left. \left. - 28692t^6 - 41328t^5 + 15534t^4 + 10260t^3 - 4563t^2 - 1134t + 567 \right] - \frac{22500t^2}{1-t^2} \right. \\ \left. \frac{160000t^9(25t^2-1)(455t^6-509t^4+165t^2-15)^2 {}_2F_1\left(1, -5t; 1-5t; \frac{(t-1)^2}{(t+1)^2}\right)}{27(t^2-1)^{12}} \right];$$

$$\text{where } t = \left(1 + \frac{50\hbar\omega}{\alpha^2 m c^2}\right)^{-1/2}. \quad (3.74)$$

To exclude the contributions of the degenerate P -states, we subtracted $\frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{5760t^2}{(1-t^2)} \right]$ from $P(4S, t)$ and $\frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{22500t^2}{(1-t^2)} \right]$ from $P(5S, t)$.

4. DIRAC-DELTA PERTURBATION OF THE vdw ENERGY

4.1. HYPERFINE HAMILTONIAN AND DIRAC-DELTA POTENTIAL

Atomic nuclei have a small but non-zero magnetic moment. It is small in a sense that the magnetic moment of the nucleus is in the order of 10^3 times smaller than that of an electron. The interaction between the magnetic moment of the nucleus and the magnetic moment of the electron results in the hyperfine structure of spectral lines. The magnetic moment of the proton in a hydrogen atom is

$$\vec{\mu}_p = g_p \frac{e}{2M} \vec{S}_p, \quad (4.1)$$

where $g_p = 5.585\,694\,702$ is the g-factor of the proton. M and \vec{S}_p denote the mass of a proton and the proton spin vector. The proton of the hydrogen atom experiences the magnetic field due to the orbital angular momentum and the spin angular momentum of the electron revolving around it. The magnetic field due to the orbital motion of the electron is given by

$$\vec{B}_\ell = \frac{(-e)\vec{v} \times (-\vec{r})}{8\pi\epsilon_0 c^2 r^3} = -\frac{e}{8\pi\epsilon_0 c^2 m r^3} \vec{r} \times \vec{P} = -\frac{e}{8\pi\epsilon_0 c^2 m r^3} \vec{L}, \quad (4.2)$$

where $-\vec{r}$ is the relative position of the electron with respect to the proton. The electron is moving in a circular orbit around the proton with the velocity \vec{v} . In Eq. (4.2), we have used $\vec{v} = \vec{P}/m$ and $\vec{r} \times \vec{v} = \vec{L}$, where \vec{P} and \vec{L} are respectively the linear and the orbital angular momenta of the electron. The extra factor of $1/2$ comes from the so-called Thomas precession effect [44; 45] which is the relativistic effect as the electron does not move in a straight line.

The magnetic field experienced by the proton of the hydrogen atom associated with the spin angular momentum of the electron is given by [46]

$$\begin{aligned}\vec{B}_s &= \frac{1}{4\pi\epsilon_0 c^2 r^3} [3(\vec{\mu}_e \cdot \hat{r})\hat{r} - \vec{\mu}_e] + \frac{2}{3\epsilon_0 c^2} \vec{\mu}_e \delta^3(\vec{r}) \\ &= -\frac{e\hbar}{4\pi\epsilon_0 c^2 m r^3} \left[3(\vec{S}_e \cdot \hat{r})\hat{r} - \vec{S}_e \right] - \frac{2}{3\epsilon_0 c^2} \frac{e\hbar}{m} \vec{S}_e \delta^3(\vec{r}),\end{aligned}\quad (4.3)$$

where $\vec{\mu}_e = -\frac{e}{m}\vec{S}_e$ is the magnetic moment and $\vec{S}_e = \hbar S_e$ is the spin angular momentum of the electron. The total magnetic field on the proton is the sum

$$\begin{aligned}\vec{B} &= \vec{B}_\ell + \vec{B}_s \\ &= -\frac{e}{8\pi\epsilon_0 c^2 m r^3} \vec{L} - \frac{e}{4\pi\epsilon_0 c^2 m r^3} \left[3(\vec{S}_e \cdot \hat{r})\hat{r} - \vec{S}_e \right] - \frac{2}{3\epsilon_0 c^2} \frac{e}{m} \vec{S}_e \delta^3(\vec{r}).\end{aligned}\quad (4.4)$$

The total perturbation Hamiltonian due to the magnetic moment interaction of the electron and the proton is

$$H_{\text{hfs}} = -\vec{\mu}_p \cdot \vec{B} = -\frac{e g_p}{2M} \vec{S}_p \cdot \vec{B}. \quad (4.5)$$

Substituting the total magnetic field \vec{B} in Eq. (4.5) from Eq. (4.4), we obtain

$$\begin{aligned}H_{\text{hfs}} &= \frac{e^2 g_p}{16\pi\epsilon_0 c^2 m M r^3} \vec{S}_p \cdot \vec{L} + \frac{e^2 g_p}{8\pi\epsilon_0 c^2 m M r^3} \left[3(\vec{S}_e \cdot \hat{r})\hat{r} - \vec{S}_e \right] \cdot \vec{S}_p \\ &\quad + \frac{e^2 g_p}{3\epsilon_0 c^2 m M} (\vec{S}_p \cdot \vec{S}_e) \delta^3(\vec{r}) \\ &= \frac{\hbar \alpha g_p}{4m M c r^3} \vec{S}_p \cdot \vec{L} + \frac{\hbar \alpha g_p}{2m M c r^3} \left[3(\vec{S}_e \cdot \hat{r})(\hat{r} \cdot \vec{S}_p) - \vec{S}_e \cdot \vec{S}_p \right] \\ &\quad + \frac{4}{3} g_p (\vec{S}_p \cdot \vec{S}_e) \frac{\pi \hbar \alpha}{m M c} \delta^3(\vec{r}).\end{aligned}\quad (4.6)$$

In the first and the second lines of Eq. (4.6), we have used the value of e^2 in SI units i.e. $e^2 = 4\pi\epsilon_0 \hbar c \alpha$. For a pair of neutral hydrogen atoms a and b , the hyperfine

Hamiltonian is given by:

$$\begin{aligned}
H_{\text{hfs}} &= \frac{\hbar\alpha g_p}{4mMc} \sum_{j=a,b} \frac{\vec{S}_{pj} \cdot \vec{L}_j}{r_j^3} + \frac{\hbar\alpha g_p}{2mMc} \sum_{j=a,b} \frac{1}{r_j^3} \left[3(\vec{S}_{ej} \cdot \hat{r}_j)(\hat{r}_j \cdot \vec{S}_{pj}) - \vec{S}_{ej} \cdot \vec{S}_{pj} \right] \\
&+ \frac{4}{3} g_p \sum_{j=a,b} (\vec{S}_{pj} \cdot \vec{S}_{ej}) \frac{\pi\hbar\alpha}{mMc} \delta^3(\vec{r}_j). \tag{4.7}
\end{aligned}$$

The first summands in the right-hand side of Eq. (4.7) has zero contribution for S states as the orbital angular momentum quantum number for S states are zero. Let us now see $3(\vec{S}_{ej} \cdot \hat{r}_j)(\hat{r}_j \cdot \vec{S}_{pj})$ for S -states.

$$\begin{aligned}
\langle nS | \frac{3}{r_j^3} (\vec{S}_{ej} \cdot \hat{r}_j)(\hat{r}_j \cdot \vec{S}_{pj}) | nS \rangle &= 3 \int \frac{d^3r_j}{r_j^5} \langle nS | r_j^k | \vec{r}_j \rangle \langle \vec{r}_j | r_j^\ell | nS \rangle S_{ej}^k S_{pj}^\ell \\
&= 3 \int_0^\infty \frac{r_j^4}{r_j^5} dr_j |R_{n0}(r_j)|^2 \frac{\delta^{k\ell}}{3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{00}(\theta, \phi) Y_{00}(\theta, \phi) \\
&\quad \begin{bmatrix} \sin\theta & \cos\phi \\ \sin\theta & \sin\phi \\ \cos\theta \end{bmatrix}^m \begin{bmatrix} \sin\theta & \cos\phi \\ \sin\theta & \sin\phi \\ \cos\theta \end{bmatrix}^m S_{ej}^k S_{pj}^\ell \\
&= 3 \int_0^\infty \frac{1}{r_j} dr_j |R_{n0}(r_j)|^2 \frac{\delta^{k\ell}}{3} \int_0^\pi \sin\theta d\theta \frac{1}{4\pi} \begin{bmatrix} \pi \sin^2\theta \\ \pi \sin^2\theta \\ 2\pi \cos^2\theta \end{bmatrix}^m S_{ej}^k S_{pj}^\ell \\
&= \int_0^\infty \frac{1}{r_j} dr_j |R_{n0}(r_j)|^2 \delta^{k\ell} \frac{1}{4\pi} \left(\pi \frac{4}{3} + \pi \frac{4}{3} + 2\pi \left(\frac{2}{3}\right) \right) S_{ej}^k S_{pj}^\ell \\
&= \int_0^\infty \frac{1}{r_j} dr_j |R_{n0}(r_j)|^2 \delta^{k\ell} S_{ej}^k S_{pj}^\ell \\
&= \langle nS | \frac{\vec{S}_{ej} \cdot \vec{S}_{pj}}{r_j^3} | nS \rangle. \tag{4.8}
\end{aligned}$$

With the help of Eq. (4.8), it becomes evident that for S states the second summand in the right-hand side of Eq. (4.7) does not contribute anything which further leads us to the conclusion that a Dirac-delta type interaction depicts the hyperfine Hamiltonian

associated to S states of hydrogen atoms. More explicitly,

$$\begin{aligned}
 H_{\text{hfs}} &= \frac{4}{3} g_p \sum_{j=a,b} (\vec{S}_{pj} \cdot \vec{S}_{ej}) \frac{\pi \hbar \alpha}{m M c} \delta^3(\vec{r}_j) \quad \text{for S-states.} \\
 &= \frac{4}{3} g_p \sum_{j=a,b} \frac{m}{M} \left(\frac{\vec{S}_{pj}}{\hbar} \cdot \frac{\vec{S}_{ej}}{\hbar} \right) \alpha m c^2 \left(\frac{\hbar}{m c} \right)^3 \pi \delta^3(\vec{r}_j).
 \end{aligned} \tag{4.9}$$

4.2. WAVE FUNCTION PERTURBATION

Let us consider a small perturbation ‘ δV ’ on the Hamiltonian ‘ H ’ proportional to the Dirac- δ function as given below

$$\delta V = \alpha m c^2 \left(\frac{\hbar}{m c} \right)^3 \pi \delta^3(\vec{r}). \tag{4.10}$$

This potential is the so-called standard Dirac- δ potential. Suppose the perturbation δV changes the Hamiltonian, energy, and ket associated to the wave functions as

$$\begin{aligned}
 H &\rightarrow H + \delta V, \\
 E &\rightarrow E + \delta E = E + \langle nS | \delta V | nS \rangle, \\
 |nS\rangle &\rightarrow |nS\rangle + |\delta(nS)\rangle.
 \end{aligned} \tag{4.11}$$

This perturbation is weak enough. It is weak in the sense that the eigenstates and the eigenvalues do not deviate heavily from their corresponding values before the perturbation is applied. Applying this correction to the time-independent Schrodinger equation, we get the following equation

$$\left(H + \delta V \right) \left(|nS\rangle + |\delta(nS)\rangle \right) = \left(E_{nS} + \delta E \right) \left(|nS\rangle + |\delta(nS)\rangle \right). \tag{4.12}$$

In the zeroth order approximation, Eq. (4.12) takes the following form

$$H|nS\rangle = E_{nS}|nS\rangle, \quad (4.13)$$

and the eigenstates and eigenvalues reduce to their corresponding unperturbed values.

In first order approximation,

$$H|\delta(nS)\rangle + \delta V|nS\rangle = E_{nS}|\delta(nS)\rangle + \delta E|nS\rangle. \quad (4.14)$$

Rearranging Eq. (4.14), we get

$$\left(\delta V - \langle nS|\delta V|nS\rangle\right)|nS\rangle = \left(E_{nS} - H\right)|\delta(nS)\rangle. \quad (4.15)$$

This leads to the following modification on the wave functions

$$|\delta(nS)\rangle = \frac{1}{(E_{nS} - H)'}\delta V|nS\rangle. \quad (4.16)$$

As a result, the correction to the wave function reads

$$\delta\psi_{n00}(\vec{r}) = \langle \vec{r} | \frac{1}{(E_{nS} - H)'} \delta V | n00 \rangle = \frac{1}{\sqrt{4\pi}} \delta R_{n0}(r). \quad (4.17)$$

This correction to the wave function is orthonormal to the unperturbed wave function.

In Eq. (4.16), $1/(E_{nS} - H)'$ is a reduced Green function. We introduced the prime on the Green function to exclude nS states. Let us use the following form of the normalized radial wave function and calculate the energy shift due to δV :

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\frac{r}{na_0}} \left(\frac{r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right). \quad (4.18)$$

For S-states,

$$R_{n0}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-1)!}{2n(n!)}} e^{-\frac{r}{na_0}} L_{n-1}^{(1)}\left(\frac{2r}{na_0}\right). \quad (4.19)$$

Furthermore, $\langle r, \theta, \phi | nS \rangle = \Psi_{n00}(r, \theta, \phi)$ is the product of $R_{n0}(r)$ and $Y_{0,0}(\theta, \phi)$ i.e.

$$\Psi_{n00}(r, \theta, \phi) = R_{n0}(r) Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{(4\pi)}} R_{n0}(r). \quad (4.20)$$

The energy shift to the nS -state i.e. $\delta E = \langle nS | \delta V | nS \rangle$ is

$$\begin{aligned} \langle nS | \delta V | nS \rangle &= \frac{1}{4\pi} \left(\frac{2}{na_0}\right)^3 \frac{(n-1)!}{2n n!} \int d^3r e^{-\frac{2r}{na_0}} L_{n-1}^{(1)}\left(\frac{2r}{na_0}\right) \alpha mc^2 \\ &\times \left(\frac{\hbar}{mc}\right)^3 \pi \delta^3(\vec{r}) L_{n-1}^{(1)}\left(\frac{2r}{na_0}\right) \\ &= \frac{1}{4\pi} \left(\frac{2}{na_0}\right)^3 \frac{1}{2n^2} \frac{\alpha \pi \hbar^3}{m^2 c} \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi e^{-\frac{2r}{na_0}} L_{n-1}^{(1)}\left(\frac{2r}{na_0}\right) \\ &\times \frac{1}{r^2} \delta(r) \frac{1}{\sin \theta} \delta(\theta) \delta(\phi) L_{n-1}^{(1)}\left(\frac{2r}{na_0}\right) \\ &= \frac{1}{4\pi} \left(\frac{2}{na_0}\right)^3 \frac{1}{2n^2} \frac{\alpha \pi \hbar^3}{m^2 c} L_{n-1}^{(1)}(0) L_{n-1}^{(1)}(0) \\ &= \frac{1}{n^5} \alpha mc^2 \left(\frac{\hbar}{a_0 mc}\right)^3 L_{n-1}^{(1)}(0) L_{n-1}^{(1)}(0) \\ &= \frac{\alpha^4}{n^5} mc^2 \frac{\Gamma(n+1)}{\Gamma(n)} \frac{\Gamma(n+1)}{\Gamma(n)} \\ &= \frac{\alpha^4 mc^2}{n^3}. \end{aligned} \quad (4.21)$$

We may rewrite Eq. (4.16) as

$$(E_{nS} - H) \delta \Psi_{n00}(r, \theta, \phi) = \langle \delta V \rangle \Psi_{n00}(r, \theta, \phi). \quad (4.22)$$

Making use of Eqs. (4.17) and (4.20), one can show that the correction to the radial part of wave function $\delta R_{n0}(r)$ must satisfy the second order partial differential

equation as given below:

$$(E_{nS} - H) \delta R_{n0}(r) = \langle \delta V \rangle R_{n0}(r)$$

$$\text{or, } \left[E_{nS} - \left(-\frac{\hbar^2 \nabla_r^2}{2m} - \frac{\alpha \hbar c}{r} \right) \right] \delta R_{n0}(r) = \langle \delta V \rangle R_{n0}(r). \quad (4.23)$$

In the first line of Eq. (4.23), we have substituted $H = -\hbar^2 \nabla_r^2 / (2m) - \hbar c \alpha / r$. Rearranging Eq. (4.23), and substituting $\nabla_r^2 = \partial_r^2 + 2/r \partial_r$ and $E_{nS} = -\alpha^2 m c^2 / (2n^2)$, the differential equation takes the following form

$$\left[-\frac{\alpha^2 m^2 c^2}{n^2 \hbar^2} + \partial_r^2 + \frac{2}{r} \partial_r + \frac{2m c \alpha}{\hbar r} \right] \delta R_{n0}(r) = -\frac{2m^2 \alpha^4 c^2}{\hbar^2 n^3} R_{n0}(r). \quad (4.24)$$

To calculate the correction to the radial part of wave functions, we make the following ansatz:

$$\delta R_{10}(r) = \left(\frac{b_0}{r} + b_1 + b_2 r \right) e^{-r/a_0} + \ln \left(\frac{r}{a_0} \right) \left(b_3 \right) e^{-r/a_0}, \quad (4.25a)$$

$$\delta R_{20}(r) = \left(\frac{c_0}{r} + c_1 + c_2 r + c_3 r^2 \right) e^{-r/(2a_0)} + \ln \left(\frac{r}{2a_0} \right) \left(d_0 + d_1 r \right) e^{-r/(2a_0)}, \quad (4.25b)$$

$$\delta R_{30}(r) = \left(\frac{e_0}{r} + e_1 + e_2 r + e_3 r^2 + e_4 r^3 \right) e^{-r/(3a_0)} + \ln \left(\frac{r}{3a_0} \right) \left(f_0 + f_1 r + f_2 r^2 \right) e^{-r/(3a_0)}, \quad (4.25c)$$

$$\delta R_{40}(r) = \left(\frac{g_0}{r} + g_1 + g_2 r + g_3 r^2 + g_4 r^3 + g_5 r^4 \right) e^{-r/(4a_0)} + \ln \left(\frac{r}{4a_0} \right) \left(h_0 + h_1 r + h_2 r^2 + h_3 r^3 \right) e^{-r/(4a_0)}, \quad (4.25d)$$

$$\delta R_{50}(r) = \left(\frac{i_0}{r} + i_1 + i_2 r + i_3 r^2 + i_4 r^3 + i_5 r^4 + i_6 r^5 \right) e^{-r/(5a_0)} + \ln \left(\frac{r}{5a_0} \right) \left(j_0 + j_1 r + j_2 r^2 + j_3 r^3 + j_4 r^4 \right) e^{-r/(5a_0)}. \quad (4.25e)$$

The corresponding radial part of wave functions are listed below:

$$R_{10}(r) = 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}, \quad (4.26a)$$

$$R_{20}(r) = 2 \left(\frac{1}{2a_0} \right)^{3/2} e^{-r/(2a_0)} \left(1 - \frac{r}{2a_0} \right), \quad (4.26b)$$

$$R_{30}(r) = 2 \left(\frac{1}{3a_0} \right)^{3/2} e^{-r/(3a_0)} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right), \quad (4.26c)$$

$$R_{40}(r) = 2 \left(\frac{1}{4a_0} \right)^{3/2} e^{-r/(4a_0)} \left(1 - \frac{3r}{4a_0} + \frac{r^2}{8a_0^2} - \frac{r^3}{192a_0^3} \right), \quad (4.26d)$$

$$R_{50}(r) = 2 \left(\frac{1}{5a_0} \right)^{3/2} e^{-r/(5a_0)} \left(1 - \frac{4r}{5a_0} + \frac{4r^2}{25a_0^2} - \frac{4r^3}{375a_0^3} + \frac{2r^4}{9375a_0^4} \right). \quad (4.26e)$$

We first simplify the left-hand side of Eq. (4.24) for a given value of n and compare the coefficients of the various powers of r with the right-hand side of the expression. Using the fact that $|nS\rangle$ and $|\delta(nS)\rangle$ satisfy the orthogonality relation $\langle nS|\delta(nS)\rangle = 0$, we can uniquely determine all b_k , c_k , d_k , e_k , f_k , g_k , h_k , i_k , and j_k . The resulting corrections to the radial part of the wave functions are

$$\delta R_{10}(r) = \frac{\alpha^2}{a_0^{1/2}} \left[-\frac{1}{r} - \frac{5}{a_0} + \frac{2\gamma_E}{a_0} + \frac{2r}{a_0^2} + \frac{2 \ln\left(\frac{r}{a_0}\right)}{a_0} \right] e^{-r/a_0}, \quad (4.27a)$$

$$\delta R_{20}(r) = \frac{\alpha^2}{\sqrt{2}a_0^{1/2}} \left[-\frac{1}{2r} + \frac{\gamma_E}{a_0} - \frac{3}{4a_0} + \frac{13r}{8a_0^2} - \frac{\gamma_E r}{2a_0^2} - \frac{r^2}{8a_0^3} + \frac{\ln\left(\frac{r}{a_0}\right)}{a_0} - \frac{r \ln\left(\frac{r}{a_0}\right)}{2a_0^2} \right] e^{-r/(2a_0)}, \quad (4.27b)$$

$$\delta R_{30}(r) = \frac{\alpha^2}{\sqrt{3}a_0^{1/2}} \left[-\frac{1}{3r} + \frac{2\gamma_E}{3a_0} - \frac{4\gamma_E r}{9a_0^2} + \frac{8r}{9a_0^2} - \frac{16r^2}{81a_0^3} + \frac{4\gamma_E r^2}{81a_0^3} + \frac{4r^3}{729a_0^4} + \frac{2 \ln\left(\frac{2r}{3a_0}\right)}{3a_0} - \frac{4r \ln\left(\frac{2r}{3a_0}\right)}{9a_0^2} + \frac{4r^2 \ln\left(\frac{2r}{3a_0}\right)}{81a_0^3} \right] e^{-r/(3a_0)}, \quad (4.27c)$$

$$\begin{aligned}
\delta R_{40}(r) = & \frac{\alpha^2}{2a_0^{1/2}} \left[-\frac{1}{4r} + \frac{11}{48a_0} + \frac{\gamma_E}{2a_0} + \frac{33r}{64a_0^2} - \frac{3\gamma_E r}{8a_0^2} - \frac{11r^2}{64a_0^3} + \frac{\gamma_E r^2}{16a_0^3} \right. \\
& + \frac{113r^3}{9216a_0^4} - \frac{\gamma_E r^3}{384a_0^4} - \frac{r^4}{6144a_0^5} + \frac{\ln\left(\frac{r}{2a_0}\right)}{2a_0} - \frac{3r \ln\left(\frac{r}{2a_0}\right)}{8a_0^2} + \frac{r^2 \ln\left(\frac{r}{2a_0}\right)}{16a_0^3} \\
& \left. - \frac{r^3 \ln\left(\frac{r}{2a_0}\right)}{384a_0^4} \right] e^{-r/(4a_0)}, \tag{4.27d}
\end{aligned}$$

$$\begin{aligned}
\delta R_{50}(r) = & \frac{\alpha^2}{\sqrt{5} a_0^{1/2}} \left[-\frac{1}{5r} + \frac{47}{150a_0} + \frac{2\gamma_E}{5a_0} + \frac{116r}{375a_0^2} - \frac{8\gamma_E r}{25a_0^2} - \frac{86r^2}{625a_0^3} + \frac{8\gamma_E r^2}{125a_0^3} \right. \\
& + \frac{16r^3}{1125a_0^4} - \frac{8\gamma_E r^3}{1875a_0^4} - \frac{323r^4}{703125a_0^5} + \frac{4\gamma_E r^4}{46875a_0^5} + \frac{4r^5}{1171875a_0^6} + \frac{8r^2 \ln\left(\frac{2r}{5a_0}\right)}{125a_0^3} \\
& \left. - \frac{8r^3 \ln\left(\frac{2r}{5a_0}\right)}{1875a_0^4} + \frac{4r^4 \ln\left(\frac{2r}{5a_0}\right)}{46875a_0^5} + \frac{2 \ln\left(\frac{2r}{5a_0}\right)}{5a_0} - \frac{8r \ln\left(\frac{2r}{5a_0}\right)}{25a_0^2} \right] e^{-r/(5a_0)}. \tag{4.27e}
\end{aligned}$$

4.3. CALCULATION OF THE DIRAC-DELTA PERTURBATION TO E_{vdW}

Let us recall the fourth order energy shift $\Delta E_{a,b}^{(4)}(R)$ due to the interaction Hamiltonian between two atoms A and B .

$$\begin{aligned}
\Delta E_{a,b}^{(4)}(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_a(i\omega) \alpha_b(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \tag{4.28}
\end{aligned}$$

The interaction energy due to the presence of a Dirac-delta perturbation potential can be enunciated as

$$\begin{aligned}
\delta E_{a,b}(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \left[\delta\alpha_a(i\omega) \alpha_b(i\omega) + \alpha_a(i\omega) \delta\alpha_b(i\omega) \right] \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \tag{4.29}
\end{aligned}$$

where $\delta\alpha_a(i\omega)$ and $\delta\alpha_b(i\omega)$ are the perturbation of the Wick-rotated form of the polarizabilities of atoms A and B due to the potential δV . Each of them is the sum of the two contributions

$$\begin{aligned}\delta\alpha_a(i\omega) &= \delta\bar{\alpha}_a(i\omega) + \delta\tilde{\alpha}_a(i\omega), \\ \delta\alpha_b(i\omega) &= \delta\bar{\alpha}_b(i\omega) + \delta\tilde{\alpha}_b(i\omega),\end{aligned}\tag{4.30}$$

where $\delta\bar{\alpha}_a(i\omega)$ and $\delta\bar{\alpha}_b(i\omega)$ are degenerate contributions and $\delta\tilde{\alpha}_a(i\omega)$ and $\delta\tilde{\alpha}_b(i\omega)$ are nondegenerate contributions to the Wick-rotated polarizabilities.

In the vdW range of interatomic interaction, the exponential term in Eq. (4.29) does not suppress anymore, and the first four terms under the square bracket [] are insignificant in comparison to the fifth term $3/(\omega R)^4$. Thus the interaction energy, if the delta perturbation perturbs only atom A , can be estimated as

$$\delta E_6(a; b) \approx -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \delta\alpha_a(i\omega)\alpha_b(i\omega).\tag{4.31}$$

We can rewrite Eq. (4.31) as

$$\delta E_{a;b}(R) = -\frac{\delta D_6(a; b)}{R^6},\tag{4.32}$$

where $\delta D_6(a; b)$ is the direct vdW coefficient due to the Dirac-delta perturbation potential and given by

$$\delta D_6(a; b) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_a(i\omega)\alpha_b(i\omega).\tag{4.33}$$

The correction to the Wick-rotated form of the polarizability is the sum of perturbed P -matrix elements for ω and $-\omega$. For example for atom A , $\delta\alpha_a(i\omega)$ reads

$$\delta\alpha_a(i\omega) = \delta P_a(i\omega) + \delta P_a(-i\omega). \quad (4.34)$$

There are three sources for the Dirac delta modification of the P -matrix element, namely Hamiltonian, energy, and wave function. Let us first investigate how these components bring the modification to the P -matrix elements. In the investigation of the correction on the P -matrix element, we first consider the form of the matrix element without taking care of the Wick rotation. However, we definitely perform the Wick rotation before we calculate the integral. The Dirac delta perturbation on the Hamiltonian gives the following modification in the P -matrix.

$$\begin{aligned} & \langle nS | x^i \frac{1}{H + \delta V - E_{nS} + \hbar\omega} x^i | nS \rangle \\ &= \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} \left(1 + \frac{\delta V}{H - E_{nS} + \hbar\omega} \right)^{-1} x^i | nS \rangle \\ &= \langle nS | x^i \left[\frac{1}{H - E_{nS} + \hbar\omega} - \frac{1}{H - E_{nS} + \hbar\omega} \delta V \frac{1}{H - E_{nS} + \hbar\omega} + \dots \right] x^i | nS \rangle. \end{aligned} \quad (4.35)$$

To the first order,

$$\begin{aligned} \delta P_{nS}^H(\omega) &= -\frac{1}{3} \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} \delta V \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS \rangle \\ &= -\frac{1}{3} \alpha mc^2 \left(\frac{\hbar}{mc} \right)^3 \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} \delta^3(\vec{r}) \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS \rangle. \end{aligned} \quad (4.36)$$

The probability density of P -states vanishes at the origin. Thus, the Hamiltonian correction to the $\delta P(nS, \omega)$ is zero .

$$\delta P_{nS}^H(\omega) = 0. \quad (4.37)$$

We expect that the correction due to the energy brings the following modification on the matrix element

$$\begin{aligned} & \langle nS | x^i \frac{1}{H - E_{nS} - \delta E + \hbar\omega} x^i | nS \rangle \\ &= \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} \left(1 - \frac{\delta E}{H - E_{nS} + \hbar\omega} \right)^{-1} x^i | nS \rangle \\ &= \langle nS | x^i \left[\frac{1}{H - E_{nS} + \hbar\omega} + \frac{\delta E}{(H - E_{nS} + \hbar\omega)^2} + \dots \right] x^i | nS \rangle. \end{aligned} \quad (4.38)$$

To the first order,

$$\begin{aligned} \delta P_{nS}^E(\omega) &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \langle nS | x^i \frac{\delta E}{(H - E_{nS} + \hbar\omega)^2} x^i | nS \rangle \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \langle nS | x^i \left(- \frac{\partial}{\partial(\hbar\omega)} \frac{\delta E}{(H - E_{nS} + \hbar\omega)} \right) x^i | nS \rangle \\ &= - \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \frac{\partial}{\partial(\hbar\omega)} \langle nS | x^i \frac{1}{(H - E_{nS} + \hbar\omega)} x^i | nS \rangle \delta E \\ &= - \frac{\partial}{\partial(\hbar\omega)} \tilde{P}_{nS}(\omega) \langle nS | \delta V | nS \rangle. \end{aligned} \quad (4.39)$$

In terms of the parameter t , the frequency ω is given as

$$\hbar\omega = \frac{\alpha^2 m c^2}{2n^2} \frac{1 - t^2}{t^2}. \quad (4.40)$$

Hence the correction to the matrix element due to energy becomes

$$\delta P_{nS}^E(\omega) = - \left[-t^3 \frac{n^2}{\alpha^2 m c^2} \frac{\partial}{\partial t} \right] \tilde{P}(nS, t) \langle nS | \delta V | nS \rangle$$

$$= \frac{n^2 t^3}{\alpha^2 m c^2} \frac{\partial [\tilde{P}(nS, t)]}{\partial t} \langle nS | \delta V | nS \rangle. \quad (4.41)$$

Let us now replace $|nS\rangle$ by the corrected wave function $|nS + \delta(nS)\rangle$ in the P -matrix to examine the modification in the P -matrix element due to the wave function correction. It is corrected in the sense that it includes the effect of the Dirac delta modification on the wave function.

$$\begin{aligned} \langle nS + \delta(nS) | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS + \delta(nS) \rangle &= \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS \rangle \\ &+ \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | \delta(nS) \rangle + \langle \delta(nS) | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS \rangle \\ &+ \langle \delta(nS) | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | \delta(nS) \rangle. \end{aligned} \quad (4.42)$$

To the first order,

$$\begin{aligned} \delta P_{nS}^\psi(\omega) &= \frac{e^2}{3} \left[\langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | \delta(nS) \rangle + \langle \delta(nS) | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | nS \rangle \right] \\ &= \frac{2e^2}{3} \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i | \delta(nS) \rangle, \end{aligned} \quad (4.43)$$

where $|\delta(nS)\rangle$ is the modification of the wave function due to the delta perturbation potential. Substituting $|\delta(nS)\rangle$ in terms of the reduced Green function, from Eq. (4.16), Eq. (4.43) becomes

$$\delta P_{nS}^\psi(\omega) = \frac{2e^2}{3} \langle nS | x^i \frac{1}{H - E_{nS} + \hbar\omega} x^i \frac{1}{(H - E_{nS})'} \delta H | nS \rangle. \quad (4.44)$$

In general, the modification of the P -matrix element arising from the energy and the wave function is nonzero.

5. LONG-RANGE INTERACTION IN THE 1S-1S SYSTEM

5.1. CALCULATION OF $C_6(1S; 1S)$ IN THE vdW RANGE

As we already discussed in Sec. (2.2.2), the vdW coefficient for the interaction between two atoms a and b both being in the 1S state is

$$C_6(1S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \alpha_{1S}(i\omega). \quad (5.1)$$

The dipole polarizability for the 1S state, $\alpha_{1S}(i\omega)$, is the sum

$$\alpha_{1S}(i\omega) = P(1S, i\omega) + P(1S, -i\omega). \quad (5.2)$$

The matrix element $P(1S, i\omega)$ has been derived in Sec. (3.4.1). With the proper substitution of the variable, one can easily determine the dynamical polarizability $\alpha(1S, i\omega)$. In the static limit, the dipole polarizability [42] is given by

$$\alpha(1S, \omega = 0) = \frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4} = \frac{9e^2 a_0^2}{2E_h}. \quad (5.3)$$

where $E_h = \alpha^2 m c^2$ is the Hartree energy and $a_0 = \hbar/(\alpha m c)$ is the Bohr radius. The ground state of the hydrogen atom is a nondegenerate state. The calculation of the vdW coefficient $C_6(1S; 1S)$ is fairly easy as there are neither virtual P -states, nor mixing terms. The $C_6(1S; 1S)$ is calculated numerically which works out to

$$C_6(1S; 1S) = 6.499\,026\,705 E_h a_0^6. \quad (5.4)$$

5.2. CALCULATION OF $C_7(1S; 1S)$ IN THE LAMB SHIFT RANGE

If the interatomic distance, R , is very large, i.e., $R \gg \hbar c/\mathcal{L}$, the integrand in

$$E_{1S;1S}(R) = -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \quad (5.5)$$

is damped by oscillations in ω . The contribution of the non-vanishing frequencies in the polarizabilities is exponentially suppressed which yields

$$E_{1S;1S}(R) = -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{1S}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \quad (5.6)$$

Let us evaluate the following integral at first.

$$\begin{aligned} & \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ &= \frac{c^5}{R^7} \int_0^\infty d \left(\frac{\omega R}{c} \right) e^{-2\omega R/c} \left[\left(\frac{\omega R}{c} \right)^4 + 2 \left(\frac{\omega R}{c} \right)^3 + 5 \left(\frac{\omega R}{c} \right)^2 + 6 \left(\frac{\omega R}{c} \right) + 3 \right] \\ &= \frac{c^5}{R^7} \left[\frac{3}{4} + 2 \times \frac{3}{8} + 5 \times \frac{1}{4} + 6 \times \frac{1}{4} + 3 \times \frac{1}{2} \right] = \frac{23c^5}{4R^7}. \end{aligned} \quad (5.7)$$

With the help of Eq. (5.7), the interaction between two neutral atoms at ground states, at very large interatomic separation, reads

$$E_{1S;1S}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{1S}(0). \quad (5.8)$$

Note that, the interaction energy has the R^{-7} dependence in this range. Both hydrogen atoms are in the $1S$ -state which is the nondegenerate ground state. From

Eq. (5.6), the interaction energy $E_{1S;1S}(R)$ for the 1S-1S system can be written as

$$\begin{aligned}
E_{1S;1S}(R) &= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{1S}(0) \\
&= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \left(\frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4} \right)^2 \\
&= -\frac{1863}{16} \frac{E_h}{\alpha\pi} \left(\frac{a_0}{R} \right)^7, \tag{5.9}
\end{aligned}$$

which implies

$$C_7(1S; 1S) = \frac{1863}{16} \frac{E_h}{\alpha\pi} (a_0)^7. \tag{5.10}$$

5.3. CALCULATION OF THE 1S-1S DIRAC- δ PERTURBATION E_{vdW}

The perturbation of the CP energy for two neutral hydrogen atoms both in the ground state $|1S\rangle$ is computed using

$$\begin{aligned}
\delta E_{1S;1S}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{1S}(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \tag{5.11}
\end{aligned}$$

It should be noted that in the close range of the interatomic separation $a_0 \ll R \ll a_0/\alpha$, the fourth term under the square bracket [] i.e. $3(c/\omega R)^4$ dominates other terms and the exponential approaches unity. Thus, the Dirac delta perturbed energy $\delta E_{1S;1S}(R)$ obeys the power law R^{-6} such that

$$\delta E_{1S;1S}(R) = -\frac{\delta D_6(1S; 1S)}{R^6}, \tag{5.12}$$

where the Dirac-delta-perturbed vdW coefficient $\delta D_6(1S; 1S)$ is given by

$$\delta D_6(1S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{1S}(i\omega) \alpha_{1S}(i\omega). \quad (5.13)$$

The quantity $\delta\alpha_{1S}(i\omega)$ is the Wick-rotated Dirac-delta perturbed polarizability of the ground state hydrogen atom. Computation of the vdW coefficient becomes simpler if we separate the total contribution into two parts, namely the wave function contribution $\delta D_6^\psi(1S; 1S)$ and the energy contribution $\delta D_6^E(1S; 1S)$ which are respectively given by

$$\delta D_6^\psi(1S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{1S}^\psi(i\omega) \alpha_{1S}(i\omega), \quad (5.14)$$

$$\delta D_6^E(1S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{1S}^E(i\omega) \alpha_{1S}(i\omega). \quad (5.15)$$

Each of the wave function part and the energy part of the perturbed vdW coefficient has only the nondegenerate contribution as the ground state hydrogen atom does not have any degenerate neighbor.

5.3.1. $\delta D_6^\psi(1S; 1S)$ Coefficient. We first look at the modification on the P -matrix element due to the Dirac-delta perturbation potential action on the wave function.

$$\begin{aligned} \delta P_{1S}^\psi(t) &= \frac{2\alpha^4 m^3 c^4 e^2}{3\hbar^2} \langle 1S | x^i g_\ell(r_1, r_2, t) x^i | \delta(1S) \rangle \\ &= \frac{2e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{10}(r_1) r_1 g_\ell(r_1, r_2, t) r_2 \delta R_{10}(r_2). \end{aligned} \quad (5.16)$$

We first change the variables to their dimensionless forms and integrate using the standard integral (3.37). The perturbed P -matrix element due to the wave function

correction reads

$$\begin{aligned}
\delta P_{1S}^\psi(t) = & \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{t^2}{9(t-1)^6(t+1)^7} \left[609t^{11} + 2369t^{10} + 2561t^9 + 1569t^8 - 730t^7 \right. \right. \\
& - 570t^6 + 270t^5 + 366t^4 - 183t^3 - 183t^2 + 33t + 33 \left. \right] + \frac{128 t^9}{3(t-1)^5(t+1)^4} \ln \left(\frac{2t}{t+1} \right) \\
& + \frac{256}{3(t-1)(t+1)^9} F_{244}(t) - \frac{32t^7}{9(t-1)^6(t+1)^6} {}_2F_1 \left(1, -t; 1-t; \frac{(t-1)^2}{(t+1)^2} \right) \\
& \times \left[3 - 2t^2 + 95t^4 + 24(t^2-1)t^2 \ln \left(\frac{2t}{t+1} \right) \right] \\
& \left. + \frac{32t^7}{(t-1)^4(t+1)^4} {}_2F_1 \left(1, -t; 1-t; \frac{t-1}{t+1} \right) \right], \tag{5.17}
\end{aligned}$$

where the function $F_{244}(t)$

$$F_{244}(t) = \sum_{k=0}^{\infty} \frac{t^{10} \left(\frac{t-1}{t+1} \right)^k {}_2F_1^{(0,1,0,0)} \left(-k, 4, 4, \frac{2}{t+1} \right)}{k-t+2}, \tag{5.18}$$

can not be simplified to a closed-form expression. However, we can calculate this term numerically. In terms of the parameter t , the vdW coefficient $\delta D_6^\psi(1S; 1S)$ reduces to

$$\delta D_6^\psi(1S; 1S) = \frac{3\alpha^2 m c^2}{2\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt}{t^3} \delta\alpha_{1S}^\psi(t) \alpha_{1S}(t). \tag{5.19}$$

Let us say the parameter t before and after the Wick rotation is t and T_1 respectively.

Then, for the 1S state, T_1^\pm are given as

$$T_1^+ = \frac{t}{\sqrt{i + t^2(1-i)}} \quad \text{and} \quad T_1^- = \frac{t}{\sqrt{-i + t^2(1+i)}}. \tag{5.20}$$

In the new variables the integral (5.19) takes the following form

$$\begin{aligned} \delta D_6^\psi(1S; 1S) &= \frac{3\alpha^2 mc^2}{2\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt_1}{t_1^3} \left(\delta P_{1S}^\psi(T_1^+(t)) + \delta P_{1S}^\psi(T_1^-(t_1)) \right) \\ &\quad \times \left(P_{1S}(T_1^+(t)) + P_{1S}(T_1^-(t)) \right). \end{aligned} \quad (5.21)$$

We divide the integration into two different regions. (I) The non-asymptotic region for which t is close to 0 and (II) The asymptotic region for which t is close to 1. In the non-asymptotic region, we use the exact form of the expressions, however, in the asymptotic region, the exact expressions are replaced by the corresponding series. In the non-asymptotic region, the $F_{abc}(t)$ term converges very slowly. We compute this slowly convergent series using the convergence acceleration technique discussed in Ref. [47; 48]. We first take a general series $F_{abc}(t)$ which gives $F_{244}(t)$ as a special case. We first express $F_{abc}(t)$ as the following partial sums

$$F_{abc}(t, n) = \sum_{k=0}^n F_{abc}^s(t, k). \quad (5.22)$$

We perform the Van Wijngaarden transformation of the series as follows.

$$F_{abc}^{\text{VW}}(t, n) = \sum_{k=0}^n (-1)^k \sum_q^{\infty} 2^q F_{abc}^s(t, 2^q(k+1) - 1). \quad (5.23)$$

We now use the recursive Weniger transformation on $F_{abc}^{\text{VW}}(t, n)$. Let us define $g_{abc}(t, n, k, \beta)$ and $h_{abc}(t, n, k, \beta)$ as given below

$$g_{abc}(t, n, k, \beta) = \frac{F_{abc}^{\text{VW}}(t, n)}{R_{abc}^{\text{VW}}(t, n)}, \quad (5.24)$$

and

$$h_{abc}(t, n, k, \beta) = \frac{1}{R_{abc}^{\text{VW}}(t, n)}, \quad (5.25)$$

such that

$$F_{abc}^{\text{Wen}}(t, n, k, \beta) = \frac{g_{abc}(t, n, k, \beta)}{h_{abc}(t, n, k, \beta)}, \quad (5.26)$$

where $F_{abc}^{\text{Wen}}(t, n, k, \beta)$ stands for the series, we obtained from Weniger transformation. In Eq. (5.24), $R_{abc}^{\text{VW}}(t, n)$ is the remainder term. The remainder can be estimated as

$$R_{abc}^{\text{VW}}(t, n) = R_{abc}^{\text{VW}}(t, n + 1). \quad (5.27)$$

We use the following three terms recursion relations as explained in Ref. [49; 50]

$$\begin{aligned} h_{abc}(t, n, k, \beta) = & h_{abc}(t, n + 1, k - 1, \beta) \\ & - \frac{(\beta + n + k - 1)(\beta + n + k - 2)}{(\beta + n + 2k - 2)(\beta + n + 2k - 3)} h_{abc}(t, n, k - 1, \beta), \end{aligned} \quad (5.28)$$

$$\begin{aligned} g_{abc}(t, n, k, \beta) = & g_{abc}(t, n + 1, k - 1, \beta) \\ & - \frac{(\beta + n + k - 1)(\beta + n + k - 2)}{(\beta + n + 2k - 2)(\beta + n + 2k - 3)} g_{abc}(t, n, k - 1, \beta). \end{aligned} \quad (5.29)$$

In the asymptotic region, as $P(1S, t)$ and $\delta P(1S, t)$ contain $(-1 + t)$ in the denominator, they converge very slowly when the parameter t approaches to 1. To compute $P(1S, t)$ and $\delta P(1S, t)$ and hence the vdW coefficient in the asymptotic region, we replace all the condensed expressions by their corresponding series. Let us

now discuss the term containing $F_{244}(t)$ first:

$$\begin{aligned}\delta\check{P}(1S, t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{256 t^{10}}{3(t-1)(t+1)^9} F_{244}(t) \\ &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \sum_{k=0}^{\infty} \frac{256 t^{10} \left(\frac{t-1}{t+1}\right)^k {}_2F_1^{(0,1,0,0)}\left(-k, 4, 4, \frac{2}{t+1}\right)}{3(t-1)(t+1)^9(k-t+2)}.\end{aligned}\quad (5.30)$$

Here $\delta\check{P}(1S, t)$ denotes the term containing $F_{244}(t)$ in $\delta P(1S, t)$. Let us now calculate ${}_2F_1^{(0,1,0,0)}(-k, b; c; z)$ for a general case.

$$\begin{aligned}{}_2F_1^{(0,1,0,0)}(-k, b; c; z) &= \lim_{n \rightarrow \infty} \frac{\partial}{\partial b} \sum_{m=0}^n \frac{(-k)_m (b)_m z^m}{(c)_m m!} \\ &= \sum_{m=0}^k \frac{(-k)_m z^m}{(c)_m m!} \frac{\partial}{\partial b} \frac{\Gamma(b+m)}{\Gamma(b)} \\ &= \sum_{m=0}^k \frac{(-k)_m z^m}{(c)_m m!} \left[\frac{\Gamma'(b+m)}{\Gamma(b)} - \frac{\Gamma(b+m)}{\Gamma(b)} \frac{\Gamma'(b)}{\Gamma(b)} \right] \\ &= \sum_{m=0}^k \frac{(-k)_m z^m}{(c)_m m!} \frac{\Gamma(b+m)}{\Gamma(b)} \left[\frac{\Gamma'(b+m)}{\Gamma(b+m)} - \frac{\Gamma'(b)}{\Gamma(b)} \right].\end{aligned}\quad (5.31)$$

Let us use the following standard equation for the derivative of Gamma function:

$$\Gamma'(m) = -(m-1)! \left(\frac{1}{m} + \gamma_E - \sum_{j=1}^m \frac{1}{j} \right).\quad (5.32)$$

Then, Eq. (5.31) gives the following

$$\begin{aligned}{}_2F_1^{(0,1,0,0)}(-k, b; c; z) &= \sum_{m=0}^k \frac{(-k)_m z^m \Gamma(b+m)}{(c)_m m! \Gamma(b)} \left[- \left(\frac{1}{m+b} + \gamma_E - \sum_{j=1}^{m+b} \frac{1}{j} \right) \right. \\ &\quad \left. + \left(\frac{1}{b} + \gamma_E - \sum_{j=1}^b \frac{1}{j} \right) \right] \\ &= \sum_{m=0}^k \frac{(-k)_m (b)_m z^m}{(c)_m m!} \left[\frac{1}{b} - \frac{1}{b+m} - \sum_{j=1}^b \frac{1}{j} + \sum_{j=1}^{b+m} \frac{1}{j} \right]\end{aligned}$$

$$= \sum_{m=0}^k \frac{(-k)_m (b)_m}{(c)_m} \frac{z^m}{m!} \left[- \sum_{j=1}^{b-1} \frac{1}{j} + \sum_{j=1}^{b+m-1} \frac{1}{j} \right]. \quad (5.33)$$

For our special case

$$\begin{aligned} {}_2F_1^{(0,1,0,0)} \left(-k, 4; 4; \frac{2}{1+t} \right) &= \sum_{m=0}^k \frac{(-k)_m (4)_m}{(4)_m} \frac{1}{m!} \left(\frac{2}{1+t} \right)^m \left[- \sum_{j=1}^3 \frac{1}{j} + \sum_{j=1}^{3+m} \frac{1}{j} \right] \\ &= \sum_{m=1}^k (-1)^m \frac{k!}{(k-m)!} \frac{1}{m!} \left(\frac{2}{1+t} \right)^m \left[\sum_{j=4}^{3+m} \frac{1}{j} \right]. \end{aligned} \quad (5.34)$$

Substituting ${}_2F_1^{(0,1,0,0)} \left(-k, 4; 4; \frac{2}{1+t} \right)$ in Eq. (5.30), we get

$$\begin{aligned} \delta\check{P}(1S, t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \sum_{k=1}^N \sum_{m=1}^k \frac{256 t^{10}}{3(t-1)(t+1)^9} \left(\frac{-1+t}{1+t} \right)^k \left(\frac{2}{1+t} \right)^m \\ &\quad \times \frac{1}{k-t+2} \frac{k!}{(k-m)!} \frac{1}{m!} \left[\sum_{j=4}^{3+m} \frac{1}{j} \right]. \end{aligned} \quad (5.35)$$

We take $N = 50$ and expand the series about $t = 1$. This yields

$$\begin{aligned} \lim_{t \rightarrow 1} \delta\check{P}(1S, t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[-\frac{1}{96} - \frac{19(t-1)}{360} - \frac{691(t-1)^2}{6912} - \frac{1188151(t-1)^3}{14515200} \right. \\ &\quad \left. - \frac{20018237(t-1)^4}{870912000} - \frac{1496035033(t-1)^5}{365783040000} - \frac{1316337316397(t-1)^6}{153628876800000} \right] \\ &\quad + O(t-1)^7. \end{aligned} \quad (5.36)$$

We now numerically calculate the quantity $\delta P_6^\psi(1S; 1S)$ in both the asymptotic and non-asymptotic region and add them up which yields

$$\delta D_6^\psi(1S; 1S) = 27.286\,919\,180\,724 \alpha^2 E_h a_0^6. \quad (5.37)$$

5.3.2. $\delta D_6^E(1S; 1S)$ Coefficient. Let us recall the energy correction on the P -matrix element

$$\delta \tilde{P}_{nS}^E(t) = \frac{n^2 t^3}{\alpha^2 m c^2} \frac{\partial [\tilde{P}(nS, t)]}{\partial t} \langle nS | \delta V | nS \rangle. \quad (5.38)$$

For the $1S$ state, we have

$$\begin{aligned} \delta P_{1S}^E(t) &= \frac{t^3}{\alpha^2 m c^2} \frac{\partial [P(1S, t)]}{\partial t} \alpha^4 m c^2 = \alpha^2 t^3 \frac{\partial}{\partial t} P(1S, t) \\ &= \frac{4t^4}{3(t^2 - 1)^6} \left[3 - 18t^2 + 48t^4 - 118t^6 - 288t^7 - 171t^8 + 96t^9 + 64t^{10} - \right. \\ &192t^9 {}_2F_1 \left(1, -t; 1 - t; \frac{(t-1)^2}{(t+1)^2} \right) + 64t^8 (t^2 - 1) {}_2F_1^{(0,0,1,0)} \left(1, -t; 1 - t; \frac{(t-1)^2}{(t+1)^2} \right) + \\ &576t^7 {}_2F_1 \left(1, -t; 1 - t; \frac{(t-1)^2}{(t+1)^2} \right) + 64t^8 (t^2 - 1) {}_2F_1^{(0,1,0,0)} \left(1, -t; 1 - t; \frac{(t-1)^2}{(t+1)^2} \right) \left. \right]. \end{aligned} \quad (5.39)$$

The integral

$$\begin{aligned} \delta D_6^E(1S; 1S) &= \frac{3\alpha^2 m c^2}{2\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt_1}{t_1^3} \left(\delta P_{1S}^E(T_1^+(t)) + \delta P_{1S}^\psi(T_1^-(t)) \right) \\ &\quad \times \left(P_{1S}(T_1^+(t)) + P_{1S}(T_1^-(t)) \right), \end{aligned} \quad (5.40)$$

which measures the energy contribution to the delta perturbed vdW coefficient converges sufficiently fast for $t \rightarrow 0$. However, the convergence is slower as we approach $t = 1$. For $t \rightarrow 1$ we express the hypergeometric function and its derivatives in series. The series expansion of a hypergeometric function ${}_2F_1(a, b; c; z)$ is given by

$${}_2F_1(a, b; c; z) = \lim_{N \rightarrow \infty} \sum_{m=0}^N \frac{(a)_m (b)_m}{(c)_m} \frac{z^m}{m!}. \quad (5.41)$$

Moreover, the first order derivative of the hypergeometric function ${}_2F_1(a, b; c; z)$ with respect to its second and third arguments are given, in the series form, by the following formulas:

$${}_2F_1^{(0,1,0,0)}(a, b; c; z) = \lim_{N \rightarrow \infty} \sum_{m=0}^N \frac{(a)_m (b)_m}{(c)_m} \frac{z^m}{m!} \left[\sum_{j=b}^{n+b-1} \frac{1}{j} \right], \quad (5.42)$$

$${}_2F_1^{(0,0,1,0)}(a, b; c; z) = \lim_{N \rightarrow \infty} \sum_{m=0}^N \frac{(a)_m (b)_m}{(c)_m} \frac{z^m}{m!} \left[- \sum_{j=c}^{n+c-1} \frac{1}{j} \right]. \quad (5.43)$$

We now choose a finite value of N and substitute the corresponding arguments to get the respective series. At the end, we calculate the vdW coefficient $\delta D_6^E(1S; 1S)$ numerically which yields

$$\delta D_6^E(1S; 1S) = 7.398\,625\,218\,232 \alpha^2 E_h a_0^6. \quad (5.44)$$

The total Dirac delta perturbed van der Waals coefficient $D_6(1S; 1S)$ is the sum of the wave contribution and the energy contribution. More explicitly

$$\begin{aligned} \delta D_6(1S; 2S) &= \delta D_6^\psi(1S; 1S) + \delta D_6^E(1S; 1S) \\ &= 34.685\,544\,398\,957 \alpha^2 E_h a_0^6. \end{aligned} \quad (5.45)$$

5.4. CALCULATION OF $\delta C_7(1S; 1S)$ IN THE LAMB SHIRT RANGE

In the long-range interatomic distance, the contribution of the non-vanishing frequencies in the polarizabilities $\delta \alpha_{nS}(i\omega)$ is heavily repressed by the exponential term $e^{-2\omega R}$. Thus, in a good approximation, the Dirac-delta perturbed Wick-rotated

polarizability, $\delta\alpha_{nS}(i\omega)$, is given by

$$\delta\alpha_{nS}(i\omega) \approx \delta\alpha_{nS}(0). \quad (5.46)$$

In this work, in the long range, we are concentrating only on the $1S$ - $1S$ and $1S$ - $2S$ systems. The Dirac-delta perturbed interaction energy, in this range, reads

$$\begin{aligned} \delta E_{1S;nS}(R) \approx & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \delta\alpha_{nS}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ & \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (5.47)$$

Making use of the integral (8.81) and relation

$$\delta\alpha_{2S}(0) = \delta\alpha_{nS}^E(0) + \delta\alpha_{nS}^\psi(0), \quad (5.48)$$

equation (6.196) can be expressed as

$$\delta E_{1S;nS}(R) \approx -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \left(\delta\alpha_{nS}^E(0) + \delta\alpha_{nS}^\psi(0) \right). \quad (5.49)$$

For $1S$ - $1S$ system, Eq. (6.198) for interaction energy reads

$$\begin{aligned} \delta E_{1S;1S}(R) & \approx -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \left(\delta\alpha_{1S}^E(0) + \delta\alpha_{1S}^\psi(0) \right) \\ & = -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \delta\alpha_{1S}^E(0) - \frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \delta\alpha_{1S}^\psi(0) \\ & = \delta E_{1S;1S}^E(R) + \delta E_{1S;1S}^\psi(R). \end{aligned} \quad (5.50)$$

The energy type correction of δ -perturbed polarizability, $\delta\alpha_{1S}^E(0)$, and the wave function type correction of δ -perturbed polarizability, $\delta\alpha_{1S}^\psi(0)$, are

$$\delta\alpha_{1S}^E(0) = \frac{43 e^2 \hbar^2}{23 m^2 c^2}, \quad \text{and} \quad \delta\alpha_{1S}^\psi(0) = \frac{81 e^2 \hbar^2}{46 m^2 c^2}. \quad (5.51)$$

Hence, the interaction energy, $\delta E_{1S;1S}(R)$, becomes

$$\begin{aligned}
\delta E_{1S;1S}(R) &= -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \left(\delta\alpha_{1S}^E(0) + \delta\alpha_{1S}^\psi(0) \right) \\
&= -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \left(\frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4} \right) \left(\frac{43e^2\hbar^2}{23m^2 c^2} + \frac{81e^2\hbar^2}{46m^2 c^2} \right) \\
&= -\frac{1503}{16\pi} \left(\frac{e^2}{4\pi\epsilon_0\hbar c} \right)^2 \frac{1}{R^7} \left(\frac{\hbar}{\alpha mc} \right)^7 \alpha mc^2 \\
&= -\frac{1503}{16} \frac{\alpha}{\pi} E_h \left(\frac{a_0}{R} \right)^7.
\end{aligned} \tag{5.52}$$

From Eq. (5.52), the $\delta C_7(1S; 1S)$ coefficient is given by

$$\delta C_7(1S; 1S) = \frac{1503}{16} \frac{\alpha}{\pi} E_h a_0^7. \tag{5.53}$$

6. LONG-RANGE INTERACTION IN THE $2S$ - $1S$ SYSTEM

6.1. $2S$ - $1S$ SYSTEM IN THE vdW RANGE

Recall the vdW range of the interatomic distance. The interatomic distance, R , in the vdW range, satisfies the condition

$$a_0 \ll R \ll a_0/\alpha, \quad (6.1)$$

where a_0 is Bohr radius and a_0/α is the wavelength of the typical optical transition. As explained in Section 2, in the vdW range, the interaction energy $E_{2S;1S}(R)$ can be written as

$$E_{2S;1S}(R) = -\frac{(D_6(2S; 1S) \pm M_6(2S; 1S))}{R^6}, \quad (6.2)$$

where $D_6(2S; 1S)$ and $M_6(2S; 1S)$ are the direct and the mixing vdW coefficients of the $2S$ - $1S$ system.

6.1.1. Calculation of the $2S$ - $1S$ Direct vdW Coefficient. If one of the atoms is in the ground state and the other is in the first excited state, the $1S$ -state has none but the $2S$ -state has $2P$ -states as its quasi-degenerate neighbors as indicated in Figure 6.1. The dipole polarizability, in such cases, has two contributions, namely, (i) the Lamb shift \mathcal{L}_2 i.e. energy shift between $|2P_{1/2}\rangle$ and $|2S\rangle$ and fine-structure \mathcal{F}_2 i.e. energy shift between $|2P_{3/2}\rangle$ and $|2S\rangle$ [51].

$$\begin{aligned} E(2P_{1/2}) - E(2S_{1/2}) &\equiv \mathcal{L}_2 = 1.61 \times 10^{-7} E_h, \\ E(2S_{1/2}) - E(2P_{3/2}) &\equiv \mathcal{F}_2 = 1.51 \times 10^{-6} E_h \approx 10\mathcal{L}_2. \end{aligned} \quad (6.3)$$

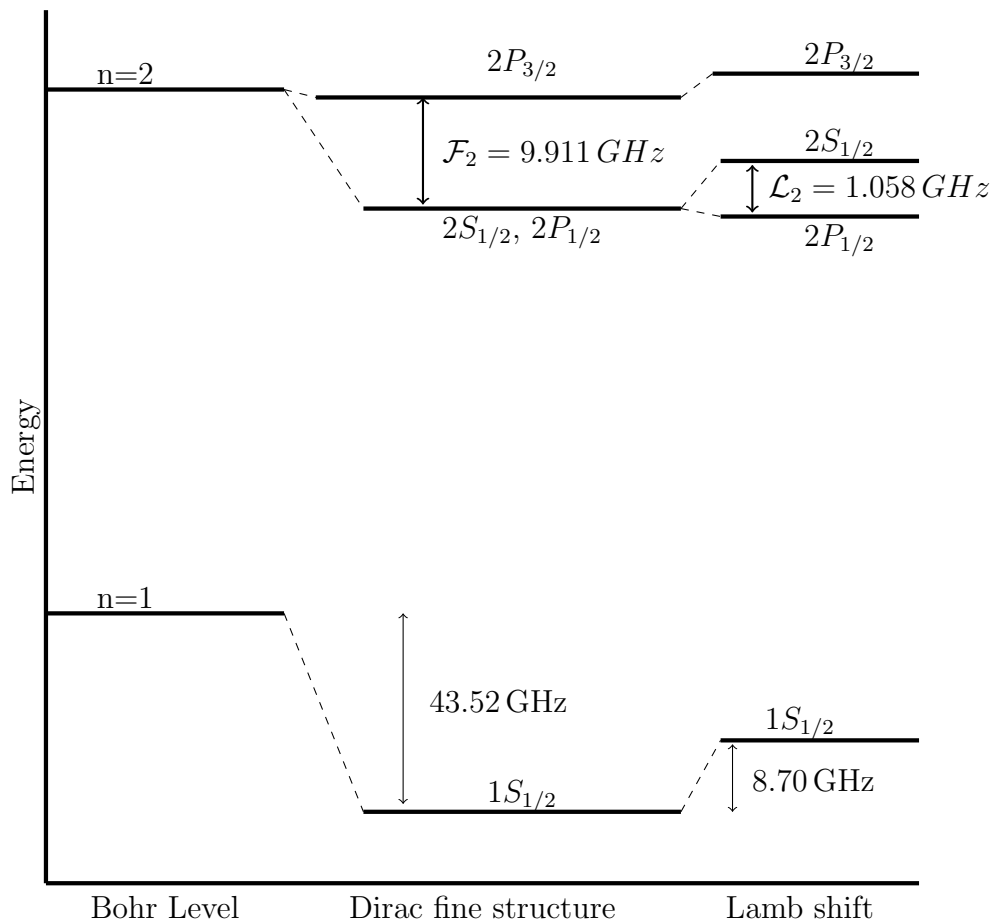


Figure 6.1: Energy levels of the hydrogen atom for $n=1$ and $n=2$. \mathcal{L}_2 and \mathcal{F}_2 stand for the Lamb shift energy and the fine structure respectively. The Dirac fine structure lowers the ground state energy and resolves the degeneracy corresponding to the first excited state. The degenerate $2S_{1/2}$ and $2P_{1/2}$ level is a low-lying energy level than $2P_{3/2}$ [1]. The degeneracy of the $2S_{1/2}$ and $2P_{1/2}$ levels is resolved by the Lamb shift, which is in the order of α^5 [2; 3].

where $E_h = \alpha^2 m c^2 = 4.35974434 \times 10^{-18} \text{J}$ is the Hartree energy. and (ii) the contributions due to nP states with principal quantum number $n \geq 3$.

The oscillator strength of $|2P_{1/2}\rangle$ and $|2P_{3/2}\rangle$ states with respect to $2S$ are distributed in a ratio $\frac{1}{3} \div \frac{2}{3}$ [52]. The dynamic polarizability is the sum of the contribution $\bar{\alpha}_{2S}(\omega)$ of the quasi-degenerate level and that $\tilde{\alpha}_{2S}(\omega)$ of the non-degenerate levels. Each $\alpha_{2S}(\omega)$ is the sum of the corresponding matrix elements for ω and $-\omega$

$$\begin{aligned}\alpha_{2S}(\omega) &= \bar{\alpha}_{2S}(\omega) + \tilde{\alpha}_{2S}(\omega), \\ \bar{\alpha}_{2S}(\omega) &= \bar{P}_{2S}(\omega) + \bar{P}_{2S}(-\omega), \\ \tilde{\alpha}_{2S}(\omega) &= \tilde{P}_{2S}(\omega) + \tilde{P}_{2S}(-\omega).\end{aligned}$$

The contribution of the quasi-degenerate levels to the P-matrix element corresponding to Schrödinger-Coulomb propagator for position operators is given as

$$\begin{aligned}\bar{P}_{2S}(\omega) &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2, 0, 0 | x^i | 2, \ell, m \rangle|^2}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2, 0, 0 | x^i | 2, \ell, m \rangle|^2}{\mathcal{F}_2 + \hbar\omega - i\epsilon} \\ &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2S | x^i | 2P(m = \mu) \rangle|^2}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2S | x^i | 2P(m = \mu) \rangle|^2}{\mathcal{F}_2 + \hbar\omega - i\epsilon}\end{aligned}\tag{6.4}$$

and the contribution of the non-degenerate level to the P-matrix element is

$$\tilde{P}_{2S}(\omega) = \frac{e^2}{3} \sum_{n \geq 3} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2S | x^i | nP(m = \mu) \rangle|^2}{E_n - E_2 + \hbar\omega - i\epsilon}.\tag{6.5}$$

All sums are taken over the nonrelativistic nP states with magnetic projection quantum numbers $\mu = -1, 0, 1$. Let us now evaluate $\bar{P}_{2S}(\omega)$.

We use the following form for $|2S\rangle$, $|2P(m = \mu)\rangle$ and x^j :

$$\Psi_{200} = \frac{1}{4\sqrt{2\pi}a_0^{3/2}} \left[2 - \frac{r}{a_0} \right] e^{-\frac{r}{2a_0}},$$

$$\begin{aligned}
\Psi_{210} &= \frac{1}{4\sqrt{2\pi}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta, \\
\Psi_{21\pm 1} &= \frac{1}{8\sqrt{\pi}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta e^{\pm i\phi}, \\
x^1 = x &= r\sin\theta \cos\phi, \quad x^2 = y = r\sin\theta \sin\phi, \quad x^3 = z = r\cos\theta.
\end{aligned} \tag{6.6}$$

Here,

$$\begin{aligned}
\langle 2S|x|2P(m=0)\rangle &= \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\frac{1}{4\sqrt{2\pi}a_0^{3/2}} \right)^2 \left(2 - \frac{r}{a_0} \right) \\
&\quad \times \left(\frac{r}{a_0} \right) \cos\theta r \sin\theta \cos\phi \\
&= \frac{1}{32\pi a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{a_0}} \int_0^\pi \sin^2\theta \cos\theta d\theta \int_0^{2\pi} \cos\phi d\phi,
\end{aligned} \tag{6.7}$$

and

$$\langle 2S|y|2P(m=0)\rangle = \frac{1}{32\pi a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{a_0}} \int_0^\pi \sin^2\theta \cos\theta d\theta \int_0^{2\pi} \sin\phi d\phi. \tag{6.8}$$

Both of these above integrals work out to zero as $\int_0^{2\pi} \cos\phi d\phi = 0$ and $\int_0^{2\pi} \sin\phi d\phi = 0$.

On the other hand

$$\langle 2S|z|2P(m=0)\rangle = \frac{1}{32\pi a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{a_0}} \int_0^\pi \sin\theta \cos^2\theta d\theta \int_0^{2\pi} d\phi. \tag{6.9}$$

The r -integral is

$$\begin{aligned}
\int_0^\infty dr r^4 \left(2 - \frac{r}{a_0} \right) e^{-\frac{r}{a_0}} &= 2 \int_0^\infty dr r^4 e^{-\frac{r}{a_0}} - \int_0^\infty dr r^4 \left(\frac{r}{a_0} \right) e^{-\frac{r}{a_0}} \\
&= 2a_0^5 \Gamma(5) - a_0^5 \Gamma(6) \\
&= -72a_0^5.
\end{aligned} \tag{6.10}$$

The θ -integral is given by

$$\int_0^\pi \sin\theta \cos^2\theta d\theta = \int_{-1}^1 d(\cos\theta) (\cos\theta)^2 = \frac{2}{3}. \quad (6.11)$$

While the ϕ -integral is given by $\int_0^{2\pi} d\phi = 2\pi$. Hence,

$$\langle 2S|z|2P(m=0)\rangle = \frac{1}{32\pi a_0^4} \times \left(-72a_0^5\right) \times \frac{2}{3} \times 2\pi = 3a_0. \quad (6.12)$$

Let us now evaluate $\langle 2S|x^j|2P(m=\mu)\rangle$ for $\mu = \pm 1$. Here,

$$\begin{aligned} \langle 2S|x|2P(m=\pm 1)\rangle &= \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\right) \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \\ &\times r \sin\theta \cos\phi \frac{1}{8\sqrt{\pi}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta e^{\pm i\phi} \\ &= \frac{1}{32\pi\sqrt{2}a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{a_0}} \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \cos\phi e^{\pm i\phi} d\phi \\ &= \frac{1}{32\pi\sqrt{2}a_0^4} \times \left(-72a_0^5\right) \times \left(\frac{4}{3}\right) \times \left(\pm\pi\right) = \mp \frac{3}{\sqrt{2}} a_0. \end{aligned} \quad (6.13)$$

Similarly,

$$\begin{aligned} \langle 2S|y|2P(m=\pm 1)\rangle &= \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\right) \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \\ &\times r \sin\theta \sin\phi \frac{1}{8\sqrt{\pi}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta e^{\pm i\phi} \\ &= \frac{1}{32\pi\sqrt{2}a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{a_0}} \int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} \sin\phi e^{\pm i\phi} d\phi \\ &= \frac{1}{32\pi\sqrt{2}a_0^4} \times \left(-72a_0^5\right) \times \left(\frac{4}{3}\right) \times \left(\pm i\pi\right) = \mp i \frac{3}{\sqrt{2}} a_0. \end{aligned} \quad (6.14)$$

Furthermore,

$$\langle 2S|z|2P(m=\pm 1)\rangle = \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left(\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\right) \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$\begin{aligned}
& \times r \cos\theta \frac{1}{8\sqrt{\pi}a_0^{3/2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta e^{\pm i\phi} \\
& = \frac{1}{32\pi\sqrt{2}a_0^4} \int_0^\infty dr r^4 \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{a_0}} \int_0^\pi \sin^2\theta \cos\theta d\theta \int_0^{2\pi} e^{\pm i\phi} d\phi = 0. \quad (6.15)
\end{aligned}$$

Hence,

$$\begin{aligned}
& \sum_{i=1}^3 \sum_{\mu} |\langle 2S|x^i|2P(m=\mu)\rangle|^2 \\
& = (3a_0)^2 + \left(\frac{3}{\sqrt{2}}a_0\right)^2 + \left(-\frac{3}{\sqrt{2}}a_0\right)^2 + \left|i\frac{3}{\sqrt{2}}a_0\right|^2 + \left|-i\frac{3}{\sqrt{2}}a_0\right|^2 \\
& = 27a_0^2, \quad (6.16)
\end{aligned}$$

and we can write

$$\begin{aligned}
\bar{P}_{2S}(\omega) & = \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2S|x^i|2P(m=\mu)\rangle|^2}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle 2S|x^i|2P(m=\mu)\rangle|^2}{\mathcal{F}_2 + \hbar\omega - i\epsilon} \\
& = \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} |\langle 2S|x^i|2P(m=\mu)\rangle|^2 \left(\frac{1}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + \hbar\omega - i\epsilon} \right) \\
& = \frac{e^2}{9} \left(27a_0^2\right) \left(\frac{1}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + \hbar\omega - i\epsilon} \right) \\
& = \frac{3\hbar^2 e^2}{\alpha^2 m^2 c^2} \left(\frac{1}{-\mathcal{L}_2 + \hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + \hbar\omega - i\epsilon} \right). \quad (6.17)
\end{aligned}$$

For the 2S-1S interaction, the vdW coefficient $D_6(2S; 1S)$ is given by

$$\begin{aligned}
D_6(2S; 1S) & = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S}(i\omega)\alpha_{1S}(i\omega) \\
& = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega [\bar{\alpha}_{2S}(i\omega) + \tilde{\alpha}_{2S}(i\omega)] \alpha_{1S}(i\omega) \\
& = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \bar{\alpha}_{2S}(i\omega)\alpha_{1S}(i\omega) + \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \tilde{\alpha}_{2S}(i\omega)\alpha_{1S}(i\omega) \\
& = \bar{D}_6(2S; 1S) + \tilde{D}_6(2S; 1S), \quad (6.18)
\end{aligned}$$

where

$$\bar{D}_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \bar{\alpha}_{2S}(i\omega)\alpha_{1S}(i\omega), \quad (6.19)$$

is the contribution due to degenerate states and

$$\tilde{D}_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \tilde{\alpha}_{2S}(i\omega)\alpha_{1S}(i\omega), \quad (6.20)$$

is the contribution due to non-degenerate states. Let us first evaluate $\bar{D}_6(2S; 1S)$.

$$\begin{aligned} \bar{D}_6(2S; 1S) &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \bar{\alpha}_{2S}(i\omega) \\ &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \left(\bar{P}_{2S}(i\omega) + \bar{P}_{2S}(-i\omega) \right) \\ &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \frac{3\hbar^2 e^2}{\alpha^2 m^2 c^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \left(\frac{1}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{1}{-\mathcal{L}_2 - i\hbar\omega - i\epsilon} \right. \\ &\quad \left. + \frac{2}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 - i\hbar\omega - i\epsilon} \right) \\ &= \frac{9\hbar a_0^2 e^2}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \left(\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} + \frac{4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right). \end{aligned} \quad (6.21)$$

Residue calculation at the poles of the integrand follows as given below. The first integrand $-2\mathcal{L}_2/[(-\mathcal{L}_2 - i\epsilon)^2 + (\omega)^2]$ has poles at $\hbar\omega = \pm i(-\mathcal{L}_2 - i\epsilon)$ and the second integrand $4\mathcal{F}_2/[(\mathcal{F}_2 - i\epsilon)^2 + (\omega)^2]$ has poles at $\hbar\omega = \pm i(\mathcal{F}_2 - i\epsilon)$. These poles lie in the first quadrant and the third quadrant. We close the contour in the upper half

plane and evaluate integrals.

$$\begin{aligned}
& \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \int_0^{\infty} d\omega \frac{-2\mathcal{L}_2 \alpha_{1S}(i\omega)}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} \\
&= \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\pi i \left(\frac{-2\mathcal{L}_2}{\hbar} \right) \operatorname{Res}_{\hbar\omega=i(-\mathcal{L}_2-i\epsilon)} \frac{\alpha_{1S}(i\omega)}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right) \\
&= \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\frac{-2\pi i \mathcal{L}_2}{\hbar} \frac{\alpha_{1S}(i\omega)}{i(-\mathcal{L}_2 - i\epsilon) + (\hbar\omega)} \Big|_{\hbar\omega=i(-\mathcal{L}_2-i\epsilon)} \right) \\
&= \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\frac{-2\pi \mathcal{L}_2}{\hbar} \frac{\alpha_{1S}(i\omega)}{2(-\mathcal{L}_2 - i\epsilon)} \right) \\
&= \frac{\pi}{\hbar} \alpha_{1S}(\omega = 0). \tag{6.22}
\end{aligned}$$

Likewise,

$$\begin{aligned}
& \lim_{\mathcal{F}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\int_0^{\infty} d\omega \frac{\alpha_{1S}(i\omega) 4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right) \\
&= \lim_{\mathcal{F}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left((\pi i) \left(\frac{4\mathcal{F}_2}{\hbar} \right) \operatorname{Res}_{\hbar\omega=i(\mathcal{F}_2-i\epsilon)} \frac{\alpha_{1S}(i\omega)}{(\mathcal{F}_2 - i\epsilon)^2 + (\omega)^2} \right) \\
&= \lim_{\mathcal{F}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\frac{4\pi i \mathcal{F}_2}{\hbar} \frac{\alpha_{1S}(i\omega)}{i(\mathcal{F}_2 - i\epsilon) + (\omega)} \Big|_{\hbar\omega=i(\mathcal{F}_2-i\epsilon)} \right) \\
&= \lim_{\mathcal{F}_2 \rightarrow 0} \lim_{\epsilon \rightarrow 0} \left(\frac{4\pi \mathcal{F}_2}{\hbar} \frac{\alpha_{1S}(i\omega)}{2(\mathcal{F}_2 - i\epsilon)} \right) \\
&= \frac{2\pi}{\hbar} \alpha_{1S}(\omega = 0). \tag{6.23}
\end{aligned}$$

Substituting Eqs. (6.22) and (6.23) in Eq. (6.21), we get the contribution of the degenerate part on the van der Waals coefficient,

$$\overline{D}_6(2S; 1S) = \frac{9 \hbar a_0^2 e^2}{\pi (4\pi\epsilon_0)^2} \left(\frac{\pi}{\hbar} + \frac{2\pi}{\hbar} \right) \alpha_{1S}(\omega = 0). \tag{6.24}$$

The ground state polarizability $\alpha_{1S}(i\omega)$ is given by

$$\alpha_{1S}(i\omega) = \frac{\hbar^2}{\alpha^4 m^3 c^4} \left(P(1S, i\omega) + P(1S, -i\omega) \right). \quad (6.25)$$

In the static limit, $\lim_{\omega \rightarrow 0} P(1S, \omega) = \lim_{\omega \rightarrow 0} P(1S, -\omega) = 9e^2/4$. Thus, the atomic polarizability in the static limit is given by

$$\alpha_{1S}(0) = \frac{9}{2} \left(\frac{\hbar}{\alpha mc} \right)^2 \frac{e^2}{\alpha^2 mc^2}. \quad (6.26)$$

Substituting $\alpha_{1S}(0)$ in $\bar{D}_6(2S; 1S)$ we get,

$$\begin{aligned} \bar{D}_6(2S; 1S) &= \frac{27 a_0^2 e^2}{(4\pi\epsilon_0)^2} \times \frac{9}{2} \left(\frac{\hbar}{\alpha mc} \right)^2 \frac{e^2}{\alpha^2 mc^2} \\ &= \frac{243}{2} a_0^4 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \left(\frac{\hbar}{\alpha mc} \right)^2 mc^2 \\ &= \frac{243}{2} a_0^6 \alpha^2 mc^2 = \frac{243}{2} a_0^6 E_h, \end{aligned} \quad (6.27)$$

where we have used the following expressions for the fine-structure constant α , the Bohr radius a_0 , and the Hartree energy E_h :

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}, \quad a_0 = \frac{\hbar}{\alpha mc}, \quad \text{and} \quad E_h = \alpha^2 mc^2. \quad (6.28)$$

The contribution of the non-degenerate states to $D_6(2S; 1S)$ reads

$$\tilde{D}_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \tilde{\alpha}_{2S}(i\omega) \alpha_{1S}(i\omega). \quad (6.29)$$

The dynamic polarizability due to the non-degenerate states $\tilde{\alpha}_{2S}(\omega)$ is

$$\tilde{\alpha}_{2S}(\omega) = \tilde{P}(2S, \omega) + \tilde{P}(2S, -\omega). \quad (6.30)$$

We substitute $t = \left(1 + 2i\hbar\omega/(\alpha^2 mc^2)\right)^{-1/2}$ in Eq. (3.44) to get $\tilde{P}(1S, i\omega)$. And $\tilde{P}(1S, -i\omega)$ is obtained through the relation $t = \left(1 - 2i\hbar\omega/(\alpha^2 mc^2)\right)^{-1/2}$. Similarly, substitution of $t = \left(1 + 8i\hbar\omega/(\alpha^2 mc^2)\right)^{-1/2}$ and $t = \left(1 - 8i\hbar\omega/(\alpha^2 mc^2)\right)^{-1/2}$ in $\tilde{P}(2S, t)$ gives $\tilde{P}(2S, i\omega)$ and $\tilde{P}(2S, -i\omega)$ respectively. We evaluate $\tilde{\alpha}_{2S}(i\omega)$ and $\tilde{\alpha}_{1S}(i\omega)$ using the following equations

$$\begin{aligned}\tilde{\alpha}_{2S}(i\omega) &= \tilde{P}(2S, i\omega) + \tilde{P}(2S, -i\omega), \\ \alpha_{1S}(i\omega) &= \tilde{P}(1S, i\omega) + \tilde{P}(1S, -i\omega).\end{aligned}\tag{6.31}$$

Now we evaluate $\tilde{D}_6(2S; 1S)$ numerically. A numerical integration of Eq. (6.29) then yields the following value for $\tilde{D}_6(2S; 1S)$,

$$\tilde{D}_6(2S; 1S) = 55.252\,266\,285 E_h a_0^6.\tag{6.32}$$

The total vdW coefficient D_6 for the 1S-2S interaction is thus

$$\begin{aligned}D_6(2S; 1S) &= \bar{D}_6(2S; 1S) + \tilde{D}_6(2S; 1S) \\ &= \left(\frac{243}{2} + 55.252266285\right) E_h a_0^6 \\ &= 176.752\,266\,285 E_h a_0^6.\end{aligned}\tag{6.33}$$

6.1.2. Calculation of the 2S-1S vdW Mixing Coefficient. We first determine the matrix element of the Schrödinger Coulomb propagator between the 1S state and the 2S state.

$$P(2S1S, \omega) = \frac{e^2}{3} \langle 1S | x^j \frac{1}{H_s - E_\nu + \hbar\omega} x^j | 2S \rangle.\tag{6.34}$$

E_ν in Eq. (6.34), given by $E_\nu = -\alpha^2 m c^2 / (2n_{\text{ref}}^2)$, is the energy of reference. The generalized quantum number ν depends on the selection of the reference energy. Namely, $\nu = t$ when $1S$ state is the reference state, and $\nu = 2t$ when $2S$ state is the reference state. The matrix element in (6.34) takes the following integral form

$$P(2S1S, \nu) = \frac{e^2}{3} \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 R_{10}(r_1) r_1 g_{\ell=1}(r_1, r_2, \nu) r_2 R_{20}(r_2). \quad (6.35)$$

We substitute the radial part of wave functions i.e. $R_{10}(r_1)$ and $R_{20}(r_2)$ for the $1S$ state and the $2S$ state respectively and the radial part of the reduced Green function $g_{\ell=1}(r_1, r_2, \nu)$ in Eq. (6.36). Then we integrate it which yields

$$P(2S1S, \nu) = \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \left[\frac{512 \sqrt{2} \nu^2}{729 (\nu - 2)^3 (\nu + 2)^2 (\nu^2 - 1)^2} (419 \nu^7 + 134 \nu^6 - 15 \nu^5 + 30 \nu^4 + 60 \nu^3 - 120 \nu^2 - 32 \nu + 64) - \frac{4096 \sqrt{2} \nu^9 {}_2F_1 \left(1, -\nu; 1 - \nu; \frac{\nu^2 - 3\nu + 2}{\nu^2 + 3\nu + 2} \right)}{3 (\nu^2 - 4)^3 (\nu^2 - 1)^2} \right]. \quad (6.36)$$

Taking $1S$ state as the reference state, the series expansion of the matrix element $P(2S1S, \nu)$ in terms of ω when ω is very large is

$$P(2S1S, \omega) = -\frac{512 \sqrt{2} e^2 \hbar^2}{729 \alpha^2 m^2 c^2 \hbar \omega} \frac{1}{\hbar \omega} + \frac{32 \sqrt{2} e^2 \hbar^2}{243 m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \quad (6.37)$$

One way of checking the expression (6.36) is expanding the matrix element $P(2S1S, \omega)$ for large ω and comparing the result with Eq. (6.37). For large ω , $(H - E_{1S})/(\hbar\omega) \ll 1$. Thus ,

$$\begin{aligned} P(2S1S, \omega) &= \frac{e^2}{3} \langle 1S | r^j \frac{1}{H - E_{1S} + \hbar\omega} r^j | 2S \rangle \\ &= \frac{e^2}{3 \hbar \omega} \langle 1S | r^j \left(1 + \frac{H - E_{1S}}{\hbar\omega} \right)^{-1} r^j | 2S \rangle \end{aligned}$$

$$\begin{aligned}
&= \frac{e^2}{3\hbar\omega} \langle 1S|r^2|2S \rangle - \frac{e^2}{3\hbar^2\omega^2} \langle 1S|r^j(H - E_{1S})r^j|2S \rangle + O\left(\omega^{-3}\right) \\
&= \frac{e^2}{3\hbar\omega} \langle 1S|r^2|2S \rangle - \frac{e^2}{3\hbar^2\omega^2} \langle 1S|r^j \left[(H - E_{1S}) + (E_{2S} - E_{1S}) \right. \\
&\quad \left. + (H - E_{2S}) \right] r^j|2S \rangle + O\left(\omega^{-3}\right) \\
&= \frac{e^2}{3\hbar\omega} \langle 1S|r^2|2S \rangle - \frac{e^2}{6\hbar^2\omega^2} \left((E_{2S} - E_{1S}) \langle 1S|r^2|2S \rangle \right. \\
&\quad \left. + \langle 1S|r^j[(H - E_{1S}), r^j]|2S \rangle + \langle 1S|r^j[(H - E_{2S}), r^j]|2S \rangle \right) + O\left(\omega^{-3}\right) \\
&= \frac{e^2}{3\hbar\omega} \langle 1S|r^2|2S \rangle - \frac{e^2}{6\hbar^2\omega^2} \left[(E_{2S} - E_{1S}) \langle 1S|r^2|2S \rangle \right. \\
&\quad \left. - \frac{i\hbar}{m} \left(\langle 1S|r_1p_1|2S \rangle + \langle 1S|r_2p_2|2S \rangle \right) \right] + O\left(\omega^{-3}\right). \tag{6.38}
\end{aligned}$$

The orthonormality condition of the wave functions requires that $\langle 1S|2S \rangle = 0$. Hence,

$$P(2S1S, \omega) = \frac{e^2}{3\hbar\omega} \langle 1S|r^2|2S \rangle - \frac{e^2}{6\hbar^2\omega^2} (E_{2S} - E_{1S}) \langle 1S|r^2|2S \rangle + O\left(\omega^{-3}\right). \tag{6.39}$$

Let us now evaluate $\langle 1S|r^2|2S \rangle$ and $(E_{2S} - E_{1S})$.

$$\begin{aligned}
\langle 1S|r^2|2S \rangle &= \int_0^\infty r^2 dr \, 2 \left(\frac{\alpha mc}{\hbar} \right)^{3/2} e^{-\alpha mc r/\hbar} r^2 \, 2 \left(\frac{\alpha mc}{2\hbar} \right)^{3/2} \left(1 - \frac{\alpha mc r}{2\hbar} \right) e^{-\frac{\alpha mc r}{2\hbar}} \\
&= \sqrt{2} \left(\frac{\alpha mc}{\hbar} \right)^3 \int_0^\infty r^4 dr \, e^{-\frac{3\alpha mc r}{2\hbar}} \left(1 - \frac{\alpha mc r}{2\hbar} \right) \\
&= \frac{2^5 \hbar^2 \sqrt{2}}{3^5 \alpha^2 m^2 c^2} \left(\int_0^\infty dx \, x^4 e^{-x} - \frac{1}{3} \int_0^\infty dx \, x^5 e^{-x} \right); \quad x = \frac{-3\alpha mc r}{2\hbar} \\
&= \frac{32\sqrt{2}}{243} \frac{\hbar^2}{\alpha^2 m^2 c^2} \left(\Gamma(5) - \frac{\Gamma(6)}{3} \right) = -\frac{512\sqrt{2}}{243} \frac{\hbar^2}{\alpha^2 m^2 c^2}. \tag{6.40}
\end{aligned}$$

And

$$E_{2S} - E_{1S} = -\frac{\alpha^2 mc^2}{8} + \frac{\alpha^2 mc^2}{2} = \frac{3\alpha^2 mc^2}{8}. \tag{6.41}$$

Substituting the values of $\langle 1S|r^2|2S\rangle$ and $(E_{2S} - E_{1S})$ in Eq. (6.39), we get

$$P(2S1S, \omega) = -\frac{512\sqrt{2} e^2 \hbar^2}{729 \alpha^2 m^2 c^2 \hbar \omega} \frac{1}{\hbar \omega} + \frac{32\sqrt{2} e^2 \hbar^2}{243 m} \frac{1}{\hbar^2 \omega^2} + O(\omega^{-3}). \quad (6.42)$$

This verifies our expression for $P(2S1S, \nu)$ given by Eq. (6.36).

Now we want to compute the $2S$ - $1S$ mixing vdW coefficient $M_6(2S; 1S)$. The total mixing vdW coefficient has two contributions, namely, the non-degenerate contribution and the degenerate contribution of mixing terms. The non-degenerate contribution to the vdW coefficient $\widetilde{M}_6(2S; 1S)$ is given by

$$\widetilde{M}_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \widetilde{\alpha}_{2S1S}(i\omega) \alpha_{2S1S}(i\omega), \quad (6.43)$$

where $\alpha_{2S1S}(i\omega)$ and $\widetilde{\alpha}_{2S1S}(i\omega)$ represent the Wick-rotated form of the non-degenerate polarizability $\widetilde{\alpha}_{2S1S}(\omega)$ when we take the energy level of the $1S$ state and the $2S$ state respectively as the reference level. We do not use the tilde $\alpha_{2S1S}(\omega)$ when the $1S$ -state is taken as the reference level as $1S$ -state does not have any degenerate neighbor. We numerically evaluate the expression (6.43) which gives

$$\widetilde{M}_6(2S; 1S) = -18.630786870 a_0^6 E_h. \quad (6.44)$$

Similarly, the degenerate contribution to the mixing vdW coefficient for $1S$ and $2S$ states is

$$\overline{M}_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \overline{\alpha}_{2S1S}(i\omega) \overline{\alpha}_{2S1S}(i\omega). \quad (6.45)$$

As in non-degenerate contribution, $\overline{\alpha}_{2S1S}(i\omega)$ refers to the Wick-rotated polarizability of $\overline{\alpha}_{2S1S}(\omega)$ when we take energy level of the $2S$ state as the reference level. Each

$\bar{\alpha}_{2S1S}(i\omega)$ is the sum of the two matrix elements $\sum_{\pm} \bar{P}_{2S1S}(\pm i\omega)$. Thus,

$$\bar{\alpha}_{2S1S}(i\omega) = \bar{P}_{2S1S}(i\omega) + \bar{P}_{2S1S}(-i\omega). \quad (6.46)$$

The mixing matrix element taking energy of the $2S$ state as the reference level, $\bar{P}_{2S1S}(i\omega)$, is given as

$$\begin{aligned} \bar{P}_{2S1S}(i\omega) &= \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu} \frac{\langle 2S|x^j|2P\rangle \langle 2P|x^j|1S\rangle}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{2e^2}{9} \sum_{j=1}^3 \sum_{\mu} \frac{\langle 2S|x^j|2P\rangle \langle 2P|x^j|1S\rangle}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} \\ &= \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu} \langle 2S|x^j|2P\rangle \langle 2P|x^j|1S\rangle \left(\frac{1}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} \right) \\ &= \frac{e^2}{9} \left(-\frac{128\sqrt{2}\hbar^2}{27\alpha^2 m^2 c^2} \right) \left(\frac{1}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} \right). \end{aligned} \quad (6.47)$$

Substituting the value of $\bar{P}_{2S1S}(i\omega)$ and $\bar{P}_{2S1S}(-i\omega)$ Eq. (6.46) follows

$$\begin{aligned} \bar{\alpha}_{2S1S}(i\omega) &= -\frac{128\sqrt{2}e^2\hbar^2}{243\alpha^2 m^2 c^2} \left(\frac{1}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{1}{-\mathcal{L}_2 - i\hbar\omega - i\epsilon} + \right. \\ &\quad \left. \frac{2}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 - i\hbar\omega - i\epsilon} \right) \\ &= -\frac{128\sqrt{2}e^2\hbar^2}{243\alpha^2 m^2 c^2} \left(\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} + \frac{-4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right). \end{aligned} \quad (6.48)$$

The degenerate contribution of the mixing term $\bar{M}_6(2S; 1S)$ is thus given as

$$\begin{aligned} \bar{M}_6(2S; 1S) &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^{\infty} d\omega \alpha_{2S1S}(\omega) \left(-\frac{128\sqrt{2}e^2\hbar^2}{243\alpha^2 m^2 c^2} \left(\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right. \right. \\ &\quad \left. \left. + \frac{-4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right) \right) \\ &= -\frac{384\sqrt{2}}{243\pi} \frac{e^2}{(4\pi\epsilon_0)^2} \frac{\hbar^2}{\alpha^2 m^2 c^2} \alpha_{2S1S}(\omega = 0) (\pi + 2\pi). \end{aligned} \quad (6.49)$$

In the static limit,

$$\alpha_{2S1S}(\omega = 0) = -\frac{3584\sqrt{2}e^2\hbar^2}{729\alpha^4m^3c^4}. \quad (6.50)$$

Substituting the value of $\alpha_{2S1S}(\omega = 0)$ in Eq. (6.49), we get

$$\begin{aligned} \overline{M}_6(2S; 1S) &= -\frac{384\sqrt{2}}{243\pi} \left(-\frac{3584\sqrt{2}}{729} \right) (3\pi) \left(\frac{\hbar}{\alpha mc} \right)^6 \alpha^2 mc^2 \\ &= 46.614\,032\,414\,a_0^6 E_h. \end{aligned} \quad (6.51)$$

The total contribution of the mixing term to the vdW coefficient is the sum

$$\begin{aligned} M_6(2S; 1S) &= \widetilde{M}_6(2S; 1S) + \overline{M}_6(2S; 1S) \\ &= -18.630\,786\,870\,a_0^6 E_h + 46.614\,032\,414\,a_0^6 E_h \\ &= 27.983\,245\,543\,a_0^6 E_h. \end{aligned} \quad (6.52)$$

Following calculation which follows the Chibisov approach [53] verifies the result we just calculated for $M_6(2S; 1S)$.

Let us now come back again to the Eq. (6.36). Take the average energy of the 1S level and 2S level as the reference energy. Calculate ν for this system as $\nu = n_{\text{ref}} t$, where n_{ref} is the effective quantum number associated with the reference energy level.

$$E_{\text{ref}} = -\frac{\alpha^2 mc^2}{2 n_{\text{ref}}^2} = \frac{E_1 + E_2}{2} = \frac{1}{2} \left(-\frac{\alpha^2 mc^2}{2} - \frac{\alpha^2 mc^2}{8} \right) = -\frac{5}{16} \alpha^2 mc^2. \quad (6.53)$$

Let us simplify Eq. (6.53) for n_{ref}

$$n_{\text{ref}} = \sqrt{\frac{8}{5}} \quad \text{Thus, } \nu = \sqrt{\frac{8}{5}} t. \quad (6.54)$$

We now calculate Wick-rotated $\alpha_{2S1S}(i\omega)$ using the sum.

$$\alpha_{2S1S}(i\omega) = P(2S1S, i\omega) + P(2S1S, -i\omega). \quad (6.55)$$

The mixing vdW coefficient $M_6(2S; 1S)$ is now calculated numerically using

$$M_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}(i\omega) \alpha_{2S1S}(i\omega), \quad (6.56)$$

which yields

$$M_6(2S; 1S) = 27.983\,245\,543 E_h a_0^6. \quad (6.57)$$

The total interaction energy in the vdW range can be written as

$$E_{2S;1S}(R) = - (176.752\,266\,285 \pm 27.983\,245\,543) E_h \left(\frac{a_0}{R}\right)^6. \quad (6.58)$$

The direct vdW coefficient for 2S-1S system is larger than that of the mixing one.

Thus the symmetry-dependent vdW coefficient

$$C_6(2S; 1S) = D_6(2S; 1S) \pm M_6(2S; 1S) \quad (6.59)$$

is positive and hence the interaction is attractive in nature.

6.2. 2S-1S SYSTEM IN THE INTERMEDIATE RANGE

The interatomic distance, R , in the intermediate range, satisfies

$$a_0/\alpha \ll R \ll \hbar c/\mathcal{L}. \quad (6.60)$$

Obviously, \mathcal{L} for $2S$ - $1S$ system is $\mathcal{L}_2 = E(2S_{1/2}) - E(2P_{1/2})$, the energy splitting between $|2S_{1/2}\rangle$ and $|2P_{1/2}\rangle$. The interaction energy of atoms, keeping in mind that the polarizability of the atom which is in $2S$ -state has two types of contributions which come from the non-degenerate state and the states degenerate to $2S$ -state, can be expressed as

$$\begin{aligned}
E_{2S;1S}^{(\text{direct})}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \tilde{\alpha}_{2S}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&\quad - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \bar{\alpha}_{2S}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&= \widetilde{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) + \overline{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R). \tag{6.61}
\end{aligned}$$

Here, the superscript ‘direct’ stands for the direct contribution. The contribution of the non-degenerate state to the interaction energy $\widetilde{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R)$ is exponentially suppressed in the CP region. Furthermore, we can approximate the polarizability due to the non-degenerate states by its static value. This leads us to the following general expression for the non-degenerate contribution to the interaction energy in the CP range

$$\begin{aligned}
\widetilde{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(\omega=0) \tilde{\alpha}_{2S}(\omega=0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(\omega=0) \tilde{\alpha}_{2S}(\omega=0). \tag{6.62}
\end{aligned}$$

In the last line of Eq. (6.62), we have used

$$\int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] = \frac{23c^5}{4R^7}. \quad (6.63)$$

The ground state static polarizability is $\alpha_{1S}(\omega = 0) = 9e^2\hbar^2/(2\alpha^4 m^3 c^4)$ and for the $2S$ state, the static polarizability α_{2S} is proportional to $e^2\hbar^2/(\alpha^4 m^3 c^4)$. This clearly indicates that

$$\widetilde{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) \sim \frac{E_h}{\alpha} \left(\frac{a_0}{R} \right)^7. \quad (6.64)$$

However, we can still approximate the degenerate contribution $\overline{\mathcal{W}}_{2S;1S}(R)$ of the interaction energy as

$$\begin{aligned} \overline{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) &= -\frac{3\alpha^2}{\pi R^6} \int_0^\infty d\omega \alpha_{1S}(i\omega) \overline{\alpha}_{2S}(i\omega) \\ &= -\frac{\overline{D}_6(2S; 1S)}{R^6}. \end{aligned} \quad (6.65)$$

In the CP region, the interatomic distance $R \gg a_0/\alpha \gg a_0$, thus the interaction energy $E_{2S;1S}(R)$ can be approximated as

$$E_{2S;1S}^{(\text{direct})}(R) = \overline{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) + \widetilde{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) \approx \overline{\mathcal{W}}_{2S;1S}^{(\text{direct})}(R) = -\frac{\overline{D}_6(2S; 1S)}{R^6}. \quad (6.66)$$

The behavior of the degenerate and the non-degenerate contributions to the interaction energy due to the mixing terms is similar to that of the direct terms in the CP region. More precisely,

$$E_{2S;1S}^{\text{mixing}}(R) = \overline{\mathcal{W}}_{2S;1S}^{(\text{mixing})}(R) + \widetilde{\mathcal{W}}_{2S;1S}^{(\text{mixing})}(R) \approx \overline{\mathcal{W}}_{2S;1S}^{(\text{mixing})}(R) = -\frac{\overline{M}_6(2S; 1S)}{R^6}. \quad (6.67)$$

Thus the $C_6(2S; 1S)$ coefficient, in the intermediate range, is given by

$$\begin{aligned} C_6(2S; 1S) &= \overline{C}_6(2S; 1S) = \overline{D}_6(2S; 1S) \pm \overline{M}_6(2S; 1S) \\ &= (243/2 \pm 46.614\,032\,413\,758) E_h a_0^6; \quad a_0/\alpha \ll R \ll \hbar c/\mathcal{L}. \end{aligned} \quad (6.68)$$

The interaction energy is thus reads

$$E_{2S;1S}(R) = - (243/2 \pm 46.614\,032\,413\,758) E_h \left(\frac{a_0}{R} \right)^6. \quad (6.69)$$

The negative sign in Eq. (6.69) indicates that the long-range interaction is of attractive nature. The long-range interaction fine-tune the $2S$ - $1S$ transition frequency and the $2S$ hyperfine splitting frequency [54].

6.3. $2S$ - $1S$ SYSTEM IN THE LAMB SHIFT RANGE

Here, by the Lamb shift range, we mean $R \gg \hbar c/\mathcal{L}$. In this range, the integrand in

$$\begin{aligned} E_{2S;1S}^{(\text{direct})}(R) &= - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \alpha_{nS}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (6.70)$$

is damped by oscillations in ω . The contribution of the non-vanishing frequencies in the polarizabilities is exponentially suppressed which yields

$$\begin{aligned} E_{2S;1S}^{(\text{direct})}(R) &= - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{2S}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (6.71)$$

Recall the already calculated value of the integral present in the Eq. (6.71) which we have done in section 5.1 and we got

$$\int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] = \frac{23c^5}{4R^7}, \quad (6.72)$$

which leads equation (6.71) to

$$E_{2S;1S}^{(\text{direct})}(R) = - \frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \alpha_{2S}(0). \quad (6.73)$$

Eq. (6.79) shows the R^{-7} dependence of the interaction energy, which depicts a much famous CP interaction. Recall that $\alpha_{2S}(0) = \bar{\alpha}_{2S}(0) + \tilde{\alpha}_{2S}(0)$. Substituting

$$\alpha_{1S}(0) = \frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4}, \quad \bar{\alpha}_{2S}(0) = 6e^2 \left(-\frac{1}{\mathcal{L}_2} + \frac{2}{\mathcal{F}_2} \right), \quad \tilde{\alpha}_{2S}(0) = \frac{120e^2\hbar^2}{\alpha^4 m^3 c^4}, \quad (6.74)$$

we get

$$E_{2S;1S}^{(\text{direct})}(R) = - \frac{621}{4\pi\alpha} \left(-\frac{E_h}{\mathcal{L}_2} + \frac{2E_h}{\mathcal{F}_2} \right) E_h \left(\frac{a_0}{R} \right)^7 - \frac{3105}{\pi\alpha R^7} E_h \left(\frac{a_0}{R} \right)^7. \quad (6.75)$$

However, there is also a R^{-2} dependent cosine pole term as discussed in Ref. [29]. AS explained in section 2.5, the direct pole term for $2S$ - $1S$ system reads

$$\begin{aligned} \mathcal{P}_{2S;1S}^{(\text{direct})}(R) = & - \frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} |\langle 2S | e \vec{r} | 2P(m = \mu) \rangle|^2 \alpha_{1S} \left(\frac{E_{2P,2S}}{\hbar} \right) \\ & \times \left\{ \cos \left(\frac{2E_{2P,2S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,2S}R}{\hbar c} \right)^2 + \left(\frac{E_{2P,2S}R}{\hbar c} \right)^4 \right] \right. \\ & \left. + \frac{2E_{2P,2S}R}{\hbar c} \sin \left(\frac{2E_{2P,2S}R}{\hbar c} \right) \left[3 - \left(\frac{2E_{2P,2S}R}{\hbar c} \right)^2 \right] \right\}. \quad (6.76) \end{aligned}$$

The interatomic distance, R , is sufficiently large, for example, a cruel approximation could be $R \rightarrow \infty$. So, $\cos(2E_{2P,2S}R/(\hbar c))$ cannot be approximated by unity, however,

$\cos(2E_{2P,2S}R/(\hbar c)) \times (E_{2P,2S}R/(\hbar c))^4$ is dominant to the other cosine and sine terms.

$$\begin{aligned} \mathcal{P}_{2S;1S}^{(\text{direct})}(R) \approx & -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} |\langle 2S|\vec{r}|2P(m=\mu)\rangle|^2 \alpha_{1S} \left(\frac{E_{2P,2S}}{\hbar} \right) \\ & \times \left\{ \cos \left(\frac{2E_{2P,2S}R}{\hbar c} \right) \left(\frac{E_{2P,2S}R}{\hbar c} \right)^4 \right\}. \end{aligned} \quad (6.77)$$

To a good approximation, $\alpha_{1S}(E_{2P,2S}/\hbar)$ can be replaced by the static value $\alpha_{1S}(0)$. Furthermore, considering that comparatively $|2P_{3/2}\rangle$ is displaced a lot than the $|2P_{1/2}\rangle$ from $|2S_{1/2}\rangle$, the energy shift $E_{2P,2S}$ can be approximated by the Lamb shift \mathcal{L}_2 .

$$\mathcal{P}_{2S;1S}^{(\text{direct})}(R) \approx -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^2} \alpha_{1S}(0) \left(\frac{\mathcal{L}_2}{\hbar c} \right)^4 \cos \left(\frac{2\mathcal{L}_2 R}{\hbar c} \right) \sum_{\mu} |\langle 2S|\vec{r}|2P(m=\mu)\rangle|^2. \quad (6.78)$$

Let us follow some parametric analysis of these two terms, namely CP and the pole terms with the very large interatomic distance. Let us recall $a_0 = \hbar/(\alpha mc)$ and $\mathcal{L} = \alpha^5 mc^2 \ln(\alpha^{-2})/(6\pi)$. Thus, at the transition $R/a_0 \sim \hbar c/\mathcal{L}_2 \sim \hbar c/(\alpha^5 mc^2) \sim a_0/\alpha^4$. Thus, keeping in mind that the dominant contribution on the polarizability $\alpha_{2S}(0)$ comes from the $2P$ -states which are quasi-degenerate with the $2S$ -state, i.e., $\alpha_{2S}(0) \approx \bar{\alpha}_{2S}(0)$, we have

$$E_{2S;1S}^{(\text{direct})}(R) \sim \frac{1}{R^7} \frac{(\hbar c)^3}{(4\pi\epsilon_0 \hbar c)^2} \frac{e^2 a_0^2}{E_h} \frac{e^2 a_0^2}{\mathcal{L}_2} \sim \frac{a_0^4}{R^7} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{\hbar^2 c^2}{\alpha^2 mc^2} \frac{\hbar c}{\mathcal{L}_2}. \quad (6.79)$$

Recognizing $e^2/(4\pi\epsilon_0 \hbar c) = \alpha$ and $\hbar/(\alpha mc) = a_0$, we get,

$$E_{2S;1S}^{(\text{direct})}(R) \sim \frac{a_0^4}{R^7} \alpha^2 mc^2 \left(\frac{\hbar}{\alpha mc} \right)^2 \frac{a_0}{\alpha^4} \sim \frac{E_h}{\alpha^4} \left(\frac{a_0}{R} \right)^7 \sim \alpha^{24} E_h. \quad (6.80)$$

On the other hand,

$$\begin{aligned}
\mathcal{P}_{2S;1S}^{(\text{direct})}(R) &\sim \frac{1}{R^2} \frac{e^2}{(4\pi\epsilon_0\hbar c)^2} \hbar^2 c^2 \frac{e^2 a_0^2}{E_h} \left(\frac{\mathcal{L}_2}{\hbar c}\right)^4 a_0^2 \\
&\sim \left(\frac{a_0}{R}\right)^2 \left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2 \frac{\hbar^2 c^2}{\alpha^2 m c^2} \left(\frac{\mathcal{L}_2}{\hbar c}\right)^4 a_0^2 \\
&\sim \left(\frac{a_0}{R}\right)^2 \alpha^2 m c^2 \left(\frac{\hbar}{\alpha m c}\right)^2 \left(\frac{\alpha^4}{a_0}\right)^4 a_0^2 \\
&\sim (\alpha^4)^2 E_h a_0^2 \frac{\alpha^{16}}{a_0^4} a_0^2 \sim \alpha^{24} E_h.
\end{aligned} \tag{6.81}$$

We can thus conclude that $E_{2S;1S}^{(\text{direct})}(R)$ and $\mathcal{P}_{2S;1S}^{(\text{direct})}(R)$ are on the same order. However, if the experimental relevance is concerned, the frequency shift in this region,

$$\nu \sim \frac{\alpha^{24} E_h}{h} \sim \frac{4.359 \times 10^{-18}}{(137)^{24} \times 6.626 \times 10^{-34}} \sim 10^{-36} \text{ Hz}, \tag{6.82}$$

is too small to consider.

Similar to the direct term contribution, the CP type mixing term contribution to the interaction energy $E_{2S;1S}^{(\text{mixing})}(R)$ also follows a R^{-7} power law and it can be expressed as

$$E_{2S;1S}^{(\text{mixing})}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{2S\underline{1S}}(0) \alpha_{\underline{2S}1S}(0). \tag{6.83}$$

Substituting the value of $\alpha_{2S\underline{1S}}(0)$ and $\alpha_{\underline{2S}1S}(0)$, we get

$$\begin{aligned}
E_{2S;1S}^{(\text{mixing})}(R) &= \frac{2^{16} \times 7 \times 23}{3^{11} \pi \alpha} \left(-\frac{E_h}{\mathcal{L}_2} + \frac{2E_h}{\mathcal{F}_2}\right) E_h \left(\frac{a_0}{R}\right)^7 \\
&\quad + \frac{2^{17} \times 5^2 \times 7 \times 23}{3^{12} \pi \alpha} E_h \left(\frac{a_0}{R}\right)^7.
\end{aligned} \tag{6.84}$$

The first term in Eq. (6.84) is the direct-type and the second term is the mixing-type contribution to $E_{2S;1S}^{(\text{mixing})}(R)$. And similar to the direct pole term, the mixing pole

term for the $2S$ - $1S$ system in the very large range of interatomic distance reads

$$\mathcal{P}_{2S;1S}^{(\text{mixing})}(R) \approx -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^2} \alpha_{2S1S}(0) \left(\frac{\mathcal{L}_2}{\hbar c}\right)^4 \cos\left(\frac{2\mathcal{L}_2 R}{\hbar c}\right) \sum_{\mu} \langle 1S|\vec{r}|2P(m=\mu)\rangle \langle 2P(m=\mu)|\vec{r}|2S\rangle. \quad (6.85)$$

where $E = E_{1S}$ in the polarizability indicates that we are taking $1S$ -state as the reference state. The parametric analysis for the mixing term contribution is same to that of the direct term contribution. We notice that

$$E_{2S;1S}^{(\text{mixing})}(R) \sim \mathcal{P}_{2S;1S}^{(\text{mixing})}(R) \sim \alpha^{24} E_h. \quad (6.86)$$

The frequency shift corresponding to them is in the order of 10^{-36} Hz, which is too small to consider in an experimental point of view.

6.4. $2S$ - $1S$ -DIRAC- δ PERTURBATION TO E_{vdW}

The perturbation of the CP energy for two neutral hydrogen atoms in which the atom A is at $|2S\rangle$ and the atom B is at $|1S\rangle$, reads

$$\delta E_{2S;1S}(R) = \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{2S}(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \times \left[1 + 2\left(\frac{c}{\omega R}\right) + 5\left(\frac{c}{\omega R}\right)^2 + 6\left(\frac{c}{\omega R}\right)^3 + 3\left(\frac{c}{\omega R}\right)^4 \right]. \quad (6.87)$$

The $2S$ - $1S$ -Dirac-delta-perturbed vdW coefficient in the vdW range of interatomic interaction can be evaluated using the integral

$$\delta D_6(2S;1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{2S}(i\omega) \alpha_{1S}(i\omega). \quad (6.88)$$

Let us concentrate on the detailed calculation of the contribution of the energy part and the wave function part on $\delta D_{2S;1S}(R)$.

6.4.1. $\delta D_6^E(2S; 1S)$ Coefficient. The correction to the van der Waals coefficient from the direct term due to the Dirac-delta perturbation to the energy can be approximated by

$$\delta D_6^E(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{2S}^E(i\omega) \alpha_{1S}(i\omega), \quad (6.89)$$

where $\delta\alpha_{2S}^E(i\omega)$ is the Wick-rotated energy correction on polarizability for $|2S\rangle$. For the 2S state, the modification of the P -matrix element can be deduced from Eq. (6.92) substituting $n = 2$ and using $\langle 2S|\delta V|2S\rangle = \alpha^4 m c^2/2^3$,

$$\begin{aligned} \delta P_{2S}^E(t) &= \frac{2^2 t^3}{\alpha^2 m c^2} \frac{\partial[\tilde{Q}(2S, t)]}{\partial t} \langle 2S|\delta V|2S\rangle \\ &= \frac{2^2 t^3}{\alpha^2 m c^2} \frac{\partial[\tilde{Q}(2S, t)]}{\partial t} \frac{\alpha^4 m}{2^3}. \end{aligned} \quad (6.90)$$

Differentiating $P(2S, t)$ derived in section 3.4.2 with respect to the parameter t , and substituting the result in Eq. (6.90), after some algebra, we get

$$\begin{aligned} \delta P_{2S}^E(t) &= \frac{8t^4 \hbar^2 e^2}{3\alpha^2 m^3 c^4 (t^2 - 1)^7} \left[8192t^{12} + 14336t^{11} - 9129t^{10} - 25088t^9 - 5947t^8 \right. \\ &\quad + 4608t^7 + 950t^6 - 294t^4 + 99t^2 - 15 + 2048(4t^4 - 5t^2 + 1)t^8 \\ &\quad \times {}_2F_1^{(0,0,1,0)} \left(1, -2t, 1 - 2t, \frac{(t-1)^2}{(t+1)^2} \right) \\ &\quad + 2048(4t^4 - 5t^2 + 1)t^8 {}_2F_1^{(0,1,0,0)} \left(1, -2t, 1 - 2t, \frac{(t-1)^2}{(t+1)^2} \right) \\ &\quad \left. - 1024(9 - 49t^2 + 28t^4) {}_2F_1 \left(1, -2t; 1 - 2t; \frac{(t-1)^2}{(t+1)^2} \right) \right]. \end{aligned} \quad (6.91)$$

In the above expression ${}_2F_1^{(0,1,0,0)}$ represents the first order derivative of ${}_2F_1$ with respect to its second argument and ${}_2F_1^{(0,0,1,0)}$ represents the first order derivative

with respect to its third argument.

Substituting the value of parameter t in terms of ω and expanding the series for large ω , Eq. (6.91) gives the following.

$$\delta P_{2S}^E(\omega) = \frac{7\alpha^6 m^2 c^4 e^2}{4\hbar^2 \omega^2} - \frac{\alpha^8 m^3 c^6 e^2}{8\hbar^3 \omega^3} + O(\omega^{-4}). \quad (6.92)$$

Let us now examine the large ω asymptotic behavior of the matrix element $Q_{2S}^E(\omega)$

$$\begin{aligned} \delta P_{2S}^E(\omega) &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \langle 2S | x^j \frac{\delta E}{(H - E_{2S} + \hbar\omega)^2} x^j | 2S \rangle \\ &= \frac{\alpha^4 m^3 c^4}{3\hbar^2} \delta E \langle 2S | x^j \frac{1}{\hbar^2 \omega^2 \left[1 + \frac{H - E_{2S}}{\hbar\omega}\right]^2} x^j | 2S \rangle \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \delta E \langle 2S | x^j \frac{1}{\hbar^2 \omega^2} \left[1 - \frac{2(H - E_{2S})}{\hbar\omega}\right] x^j | 2S \rangle + O(\omega^{-4}) \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \delta E \frac{\langle 2S | r^2 | 2S \rangle}{\hbar^2 \omega^2} - \frac{2\alpha^4 m^3 c^4 e^2}{3\hbar^2} \frac{\delta E}{\hbar^3 \omega^3} \langle 2S | x^j (H - E_{2S}) x^j | 2S \rangle + O(\omega^{-4}) \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \delta E \frac{\langle 2S | r^2 | 2S \rangle}{\hbar^2 \omega^2} + \frac{2\alpha^4 m^3 c^4 e^2}{3\hbar^5 \omega^3} \frac{i}{2m} [x^j, p^j] \delta E + O(\omega^{-4}) \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \delta E \frac{\langle 2S | r^2 | 2S \rangle}{\hbar^2 \omega^2} + i \frac{\alpha^4 m^2 c^4 e^2}{3\hbar^5 \omega^3} (3i) \delta E + O(\omega^{-4}) \\ &= \frac{\alpha^4 m^3 c^4 e^2}{3\hbar^2} \delta E \frac{\langle 2S | r^2 | 2S \rangle}{\hbar^2 \omega^2} - \frac{\alpha^4 m^2 c^4 e^2}{\hbar^5 \omega^3} \delta E + O(\omega^{-4}). \end{aligned} \quad (6.93)$$

Here,

$$\langle r^2 \rangle_{2S} = \langle 2S | r^2 | 2S \rangle = \int_0^\infty r^4 |R_{20}(r)|^2 dr = \frac{42 \hbar^2}{\alpha^2 m^2 c^2}, \quad (6.94)$$

and

$$\delta E = \langle \delta V \rangle = \frac{\alpha^4 m c^2}{8}. \quad (6.95)$$

Let us substitute Eqs. (6.94) and (6.95) in Eq. (6.93):

$$\delta P_{2S}^E(\omega) = \frac{7\alpha^6 m^2 c^4 e^2}{4\hbar^2 \omega^2} - \frac{\alpha^8 m^3 c^6 e^2}{8\hbar^3 \omega^3} + O(\omega^{-4}). \quad (6.96)$$

Eq. (6.96) is identical to equation (6.92). This confirms the expression for $\delta P_{2S}^E(t)$ given by Eq. (6.91). Thus, in terms of the parameter t , Eq. (6.91) takes the following form

$$\delta D_6^E(2S; 1S) = \frac{3\alpha^2 m c^2}{8\pi(4\pi\epsilon_0)^2} \int_0^1 dt \frac{1}{t^3} \delta\alpha_{2S}^E(t) \alpha_{1S}(t). \quad (6.97)$$

Taking the average energy, $(E_{1S} + E_{2S})/2$ as the reference state energy, the reference quantum number for the system is $2\sqrt{2}/\sqrt{5}$. Implementing the reference quantum number and integrating Eq. (6.97) numerically we get,

$$\delta D_6^E(2S; 1S) = 49.733\,193\,536 E_h a_0^6. \quad (6.98)$$

6.4.2. $\delta D_6^\psi(2S; 1S)$ Coefficient. In this section, we put the detailed calculation of the direct vdW coefficient arising from the modification of the wave function. The Dirac-delta perturbed interaction energy due to the wave function correction reads

$$\begin{aligned} \delta E_{2S;1S}^\psi(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \lim_{\eta \rightarrow 0} \int_0^\infty d\omega \delta\alpha_{2S}^\psi(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{2\omega R/c}}{R^2} \\ & \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (6.99)$$

As the polarizability is the sum of the non-degenerate and the degenerate polarizability, the wave function type correction to polarizability can be expressed as

$$\delta\alpha_{2S}^{\psi}(\omega) = \delta\bar{\alpha}_{2S}^{\psi}(\omega) + \delta\tilde{\alpha}_{2S}^{\psi}(\omega), \quad (6.100)$$

and hence the interaction energy can be written as

$$\delta E_{2S;1S}^{\psi}(R) = \delta\bar{E}_{2S;1S}^{\psi}(R) + \delta\tilde{E}_{2S;1S}^{\psi}(R), \quad (6.101)$$

where

$$\begin{aligned} \delta\tilde{E}_{2S;1S}^{\psi}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \lim_{\eta \rightarrow 0} \int_0^{\infty} d\omega \delta\tilde{\alpha}_{2S}^{\psi}(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{2\omega R/c}}{R^2} \\ &\times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \end{aligned} \quad (6.102)$$

is the non-degenerate contribution to $\delta E_6^{\psi}(2S; 1S)$ and

$$\begin{aligned} \delta\bar{E}_{2S;1S}^{\psi}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \lim_{\eta \rightarrow 0} \int_0^{\infty} d\omega \delta\bar{\alpha}_{2S}^{\psi}(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{2\omega R}}{R^2} \\ &\times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \end{aligned} \quad (6.103)$$

is the degenerate contribution. Let us first concentrate on the non-degenerate contribution to $\delta\tilde{D}_6^{\psi}(2S; 1S)$. In the vdW range of interaction, we can approximate Eq. (6.102) as

$$\delta\tilde{E}_{2S;1S}^{\psi}(R) \approx -\frac{\delta\tilde{D}_6^{\psi}(2S; 1S)}{R^6}. \quad (6.104)$$

Here, $\delta\tilde{D}_6^\psi(2S; 1S)$ is the non-degenerate contribution to the vdW coefficient due to the Dirac-delta perturbation potential on the wave function and is given by

$$\delta\tilde{D}_6^\psi(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\tilde{\alpha}_{2S}^\psi(i\omega) \alpha_{1S}(i\omega). \quad (6.105)$$

The wave function correction to the polarizability reads

$$\delta\tilde{\alpha}_{2S}^\psi(\omega) = \delta P_{2S}^\psi(\omega) + \delta P_{2S}^\psi(-\omega). \quad (6.106)$$

One can evaluate the modification in the matrix element $\delta P(2S, \omega)$ due to the wave function correction using the following relation:

$$\delta P_{2S}^\psi(\omega) = \frac{2e^2}{3} \langle 2S | x^i \frac{1}{H - E_{2S} + \hbar\omega} x^i | \delta(2S) \rangle, \quad (6.107)$$

where $\langle r, \theta, \phi | \delta(2S) \rangle = \frac{1}{\sqrt{4\pi}} \delta R_{20}(r)$. The radial part $\delta R_{20}(r)$ of the Dirac-delta-modified wave function $\delta\Psi_{200}(r, \theta, \phi)$ is given in Eq. (4.27b). Let us rewrite $\delta R_{20}(r)$ as a sum of six terms as follows.

$$\delta\varphi_1 = -\frac{\alpha^{5/2} m^{1/2} e^{-\alpha mr/2}}{2\sqrt{2} r}, \quad (6.108a)$$

$$\delta\varphi_2 = \frac{\gamma_E \alpha^{7/2} m^{3/2} e^{-\alpha mr/2}}{\sqrt{2}} - \frac{3\alpha^{7/2} m^{3/2} e^{-\alpha mr/2}}{4\sqrt{2}}, \quad (6.108b)$$

$$\delta\varphi_3 = \frac{13\alpha^{9/2} m^{5/2} r e^{-\alpha mr/2}}{8\sqrt{2}} - \frac{\gamma_E \alpha^{9/2} m^{5/2} r e^{-\alpha mr/2}}{2\sqrt{2}}, \quad (6.108c)$$

$$\delta\varphi_4 = -\frac{\alpha^{11/2} m^{7/2} r^2 e^{-\alpha mr/2}}{8\sqrt{2}}, \quad (6.108d)$$

$$\delta\varphi_5 = \frac{\alpha^{7/2} m^{3/2} e^{-\alpha mr/2} \ln(\alpha mr)}{\sqrt{2}}, \quad (6.108e)$$

$$\delta\varphi_6 = -\frac{\alpha^{9/2} m^{5/2} r e^{-\alpha mr/2} \ln(\alpha mr)}{2\sqrt{2}}. \quad (6.108f)$$

The contributions of $\delta\varphi_i$, $i = 1, 2, \dots, 6$ to the δP matrix element can be expressed as

$$\delta P_{2S}^{\delta(\varphi_i)}(t) = \frac{2e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{20}(r_1) r_1 g_\ell(r_1, r_2, t) r_2 \delta[\varphi_i(r_2)]. \quad (6.109)$$

We first change the variables to their dimensionless forms and integrate using standard integral (3.37). For $\delta\varphi_1$, $\delta\varphi_2$, $\delta\varphi_3$ and $\delta\varphi_4$, the matrix elements can be easily evaluated. We have,

$$\delta P_{2S}^{\delta(\varphi_1)}(t) = -\frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{8t^2 (305t^6 - 98t^5 - 19t^4 + 8t^3 - t^2 - 6t + 3)}{3(t-1)^5(t+1)^3} + \frac{2048t^7 (4t^2 - 1) {}_2F_1\left(1, -2t; 1 - 2t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(t^2 - 1)^5} \right], \quad (6.110a)$$

$$\delta P_{2S}^{\delta(\varphi_2)}(t) = \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{24(4\gamma_E - 3)t^2}{t^2 - 1}, \quad (6.110b)$$

$$\delta P_{2S}^{\delta(\varphi_3)}(t) = -\frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{8192(4\gamma_E - 13)t^9 (4t^2 - 1) \alpha^2 {}_2F_1\left(1, -2t; 1 - 2t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(t^2 - 1)^6} + \frac{16(4\gamma_E - 13)t^2}{3(t-1)^6(t+1)^4} \left(586t^8 - 148t^7 + t^6 - 110t^5 + 7t^4 + 96t^3 - 33t^2 - 30t + 15 \right) \right], \quad (6.110c)$$

$$\delta P_{2S}^{\delta(\varphi_4)}(t) = -\frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{65536\alpha^2 e^2 t^{11} (4t^2 - 1) {}_2F_1\left(1, -2t; 1 - 2t; \left(\frac{1-t}{1+t}\right)^2\right)}{3(t^2 - 1)^7} + \frac{8t^2}{3(t-1)^7(t+1)^5} (9331t^{10} - 2278t^9 + 331t^8 - 2480t^7 - 338t^6 + 3156t^5 - 618t^4 - 1920t^3 + 735t^2 + 450t - 225) \right]. \quad (6.110d)$$

Fifth and sixth terms contain the natural logarithm of r along with the Laguerre polynomial and exponential of r . These terms require special consideration. The replica trick helps us to handle them. The replica trick refers to the following identity:

$$\ln(mr\alpha) = \lim_{\epsilon \rightarrow 0} \frac{(mr\alpha)^\epsilon - 1}{\epsilon} = \left. \frac{d(mr\alpha)^\epsilon}{d\epsilon} \right|_{\epsilon=0}. \quad (6.111)$$

As suggested by the replica trick [55], at first, we differentiate the expression with respect to ϵ , and then we take the limit $\epsilon \rightarrow 0$. Besides the simpler looking terms, $\delta P_{2S}^{\delta(\varphi_5)}(t)$ contains ${}_2F_1^{(0,1,0,0)}(-k, 5; 4; 2/(1+t))$ and $\delta P_{2S}^{\delta(\varphi_6)}(t)$ contains ${}_2F_1^{(0,1,0,0)}(-k, 6; 4; 2/(1+t))$. We now use the following identity for the hypergeometric function Ref. [43].

$${}_2F_1(a, b; c; z) = \frac{(b-c-1){}_2F_1(a, b-2; c; z)}{(b-1)(z-1)} + \frac{(-az+bz-2b+c-z+2){}_2F_1(a, b-1; c; z)}{(b-1)(z-1)}. \quad (6.112)$$

We use the derivative of this identity with respect to the second argument, b , of the hypergeometric function. This lowers the second arguments of the hypergeometric functions and simplifies

$${}_2F_1^{(0,1,0,0)}(-k, 5; 4; 2/(1+t)) \quad \text{and} \quad {}_2F_1^{(0,1,0,0)}(-k, 6; 4; 2/(1+t)) \quad (6.113)$$

in terms of ${}_2F_1^{(0,1,0,0)}(-k, 4; 4; 2/(1+t))$ and some simpler algebraic terms containing t and k . $\delta P_{2S}^{\delta(\phi_5)}(t)$ contains two types of terms.

1. Terms *free* from the hypergeometric function.
2. Terms containing the derivative of the hypergeometric function with respect to its second argument on the numerator.

The terms free from the hypergeometric function can be easily summed over k and simplified. The terms containing the derivative of the hypergeometric function with respect to its second argument in the numerator appear in the following form

$$\sum_{k=0}^{\infty} k^q \left(\frac{-1+t}{1+t} \right)^k {}_2F_1^{(0,1,0,0)}\left(-k, 4; 4; \frac{2}{t+1}\right); \quad q = 1, 2, \dots, 5. \quad (6.114)$$

All the terms which do not contain the derivative of the hypergeometric function can be summed over k using the following identity.

$$\sum_{k=0}^{\infty} k^n \frac{s^k}{a+k} = \frac{1}{a} \sum_{j=0}^n \left\{ \begin{matrix} n \\ j \end{matrix} \right\} s^j \frac{\partial^j {}_2F_1(1, a : a+1 : s)}{\partial s^j}, \quad (6.115)$$

where $\left\{ \begin{matrix} n \\ j \end{matrix} \right\}$ is the Stirling number of the second kind which can be computed using the following formula:

$$\left\{ \begin{matrix} n \\ j \end{matrix} \right\} = \frac{1}{j!} \sum_{q=0}^j (-1)^{j-q} \binom{j}{q}, \quad (6.116)$$

where $\binom{j}{q}$ is a binomial coefficient. For terms which contain the derivative of the hypergeometric function, we use the following identity

$$\sum_{k=0}^{\infty} k^n \xi^k {}_2F_1(-k, b; c; z) = \sum_{j=0}^n \left\{ \begin{matrix} n \\ j \end{matrix} \right\} \xi^j \frac{\partial^j}{\partial \xi^j} \left[\frac{{}_2F_1(1, b; c; -\frac{\xi z}{1-\xi})}{1-\xi} \right], \quad (6.117)$$

which is obtained from the following identity discussed in Ref. [42].

$$\sum_{k=0}^{\infty} \xi^k {}_2F_1(-k, b; c; z) = \frac{{}_2F_1\left(1, b; c; -\frac{\xi z}{1-\xi}\right)}{1-\xi}. \quad (6.118)$$

Substituting the corresponding sums, the result will be the sum of a number of terms of the form ${}_2F_1^{(0,1,0,0)}\left(a, 4; 4; \frac{1-t}{1+t}\right)$ where $a = 4, 5$ and 6 . We calculate the first order derivative of hypergeometric function with respect to its second argument as follows:

$${}_2F_1^{(0,1,0,0)}\left(a, 4; 4; \frac{1-t}{1+t}\right) = \lim_{\epsilon \rightarrow 0} \frac{{}_2F_1\left(a, 4+\epsilon; 4; \frac{1-t}{1+t}\right) - {}_2F_1\left(a, 4-\epsilon; 4; \frac{1-t}{1+t}\right)}{2\epsilon}. \quad (6.119)$$

To get rid of the indeterminate form which arises if we take the limit $\epsilon \rightarrow 0$, we make use of the L'Hospital rule:

$$\lim_{\epsilon \rightarrow 0} \frac{g(\epsilon)}{h(\epsilon)} = \lim_{\epsilon \rightarrow 0} \frac{g'(\epsilon)}{h'(\epsilon)}. \quad (6.120)$$

In Eq. (6.120), $g(\epsilon)$ and $h(\epsilon)$ represent the numerator and the denominator of the right-hand side of Eq. (6.119) and the prime denotes their first order derivative with respect to ϵ . In Eq. (6.120), we first calculate the derivative of the numerator and the denominator and determine their ratio. Only then we substitute $\epsilon = 0$.

The contribution of $\delta\varphi_5$ to the matrix element is found to be

$$\begin{aligned} \delta P_{2S}^{\delta(\varphi_5)}(t) = & -\frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{8t^2}{3(t^2-1)^6} \left(-3715t^{10} - 6400t^9 - 189t^8 + 3328t^7 + 242t^6 + 950t^4 \right. \right. \\ & \left. \left. - 447t^2 + 87 \right) - \frac{8\gamma_E t^2 (36t^{10} - 180t^8 + 360t^6 - 360t^4 + 180t^2 - 36)}{3(t^2-1)^6} \right. \\ & - \frac{8t^2 (-384t^9 + 768t^7 - 384t^5)}{3(t^2-1)^6} {}_2F_1 \left(1, -2t; 1-2t; \frac{t-1}{t+1} \right) \\ & \left. - \frac{8t^2 (13184t^9 - 7424t^7 + 384t^5)}{3(t^2-1)^6} {}_2F_1 \left(1, -2t; 1-2t; \frac{(t-1)^2}{(t+1)^2} \right) \right]. \quad (6.121) \end{aligned}$$

In contrast to the first five $\delta P_{2S}^{\delta(\varphi_i)}(t)$, the $\delta P_{2S}^{\delta(\varphi_6)}(t)$ not only contains the derivative of hypergeometric function with respect to its second argument on the numerator but also contains $(2+k-2t)$ on the denominator which appear in the following form

$$t^{10} \sum_{k=0}^{\infty} \frac{\xi^k {}_2F_1^{(0,1,0,0)} \left(-k, 4; 4; \frac{2}{t+1} \right)}{2+k-2t}. \quad (6.122)$$

and can not be simplified to a closed-form expression. We denote this function as $F_{244}(t)$ and evaluate it numerically. The total expression is

$$\delta P_{2S}^{\delta(\varphi_6)}(t) = \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{16}{9(t-1)^7(t+1)^8} \left(7185t^{15} + 36625t^{14} + 1275t^{13} - 43525t^{12} \right. \right.$$

$$\begin{aligned}
& -62622t^{11} - 926t^{10} + 24470t^9 + 10902t^8 - 7515t^7 - 7515t^6 + 2847t^5 \\
& + 2847t^4 - 456t^3 - 456t^2) - \frac{64\gamma_E}{3(t-1)^6(t+1)^4} \left(586t^{10} - 148t^9 + t^8 - 110t^7 \right. \\
& \left. + 7t^6 + 96t^5 - 33t^4 - 30t^3 + 15t^2 \right) + \frac{2048 {}_2F_1 \left(1, -2t; 1 - 2t; \frac{(t-1)^2}{(t+1)^2} \right)}{9(t-1)^7(t+1)^7} \\
& \times \left[192\gamma_E t^{13} - 283t^{13} - 240\gamma_E t^{11} + 566t^{11} + 48\gamma_E t^9 - 139t^9 \right. \\
& \left. - 48(4t^4 - 5t^2 + 1)t^9 \ln\left(\frac{2t}{t+1}\right) \right] - \frac{2048t^9 {}_2F_1 \left(1, -2t; 1 - 2t; \frac{t-1}{t+1} \right)}{(t-1)^5(t+1)^5} \\
& \left. + \frac{8192(7t^{11} + t^{10} - 2t^9) \ln\left(\frac{2t}{t+1}\right)}{3(t-1)^6(t+1)^5} + \frac{65536(4t^2 - 1) F_{244}(t)}{3(t-1)^2(t+1)^{10}} \right]. \quad (6.123)
\end{aligned}$$

We now add all these six terms to get the total correction due to the wave function:

$$\delta P_{2S}^\psi(t) = \delta P_{2S}^{\delta(\varphi_1)}(t) + \delta P_{2S}^{\delta(\varphi_2)}(t) + \delta P_{2S}^{\delta(\varphi_3)}(t) + \delta P_{2S}^{\delta(\varphi_4)}(t) + \delta P_{2S}^{\delta(\varphi_5)}(t) + \delta P_{2S}^{\delta(\varphi_6)}(t). \quad (6.124)$$

After a bit of work, Eq. (6.124) simplifies to

$$\begin{aligned}
\delta P_{2S}^\psi(t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{8}{9(t-1)^7(t+1)^{10}} \left\{ 12288(4t^2 - 1)(t-1)^5 F_{244}(t) + t^2(t+1)^2 \right. \\
&\times \left[-123 - 123t + 801t^2 + 801t^3 - 2124t^4 - 1932t^5 + 4002t^6 + 11234t^7 \right. \\
&+ 3661t^8 - 20979t^9 + 2285t^{10} + 9645t^{11} + 26314t^{12} + 3402t^{13} - 576(t-1)^2 t^5 (t+1)^3 \\
&\times (t^2 + 1) {}_2F_1 \left(1, -2t; 1 - 2t; \frac{t-1}{t+1} \right) + 3072t^7 \ln\left(\frac{2t}{t+1}\right) + 4608t^8 \ln\left(\frac{2t}{t+1}\right) \\
&- 13824t^9 \ln\left(\frac{2t}{t+1}\right) - 27648t^{10} \ln\left(\frac{2t}{t+1}\right) + 23040t^{12} \ln\left(\frac{2t}{t+1}\right) \\
&+ 10752t^{13} \ln\left(\frac{2t}{t+1}\right) - 64t^5(t+1) {}_2F_1 \left(1, -2t; 1 - 2t; \frac{(t-1)^2}{(t+1)^2} \right) \\
&\left. \times \left[371t^6 - 193t^4 + 113t^2 + 96(4t^6 - 5t^4 + t^2) \ln\left(\frac{2t}{t+1}\right) - 3 \right] \right\}. \quad (6.125)
\end{aligned}$$

Let us now compare the coefficients of leading terms for large ω . Substituting t in terms of ω in the final result obtained from Eq. (6.125), we get

$$\delta P_{2S}^\psi(\omega) = \frac{41}{m^2} \frac{1}{\omega} - \frac{21\alpha^2}{8m} \frac{1}{\omega^2} + \dots \quad (6.126)$$

For large ω , we can expand the P -matrix element as given below

$$\begin{aligned} \langle 2S | r^j \frac{1}{(H - E_{2S} + \hbar\omega)} r^j | \delta(2S) \rangle \\ = \frac{1}{\hbar\omega} \langle 2S | r^2 | \delta(2S) \rangle + \frac{i}{m\hbar^2\omega^2} \langle 2S | [i p^j r^j] | \delta(2S) \rangle + O(\omega^{-3}) \end{aligned} \quad (6.127)$$

$$= A_1 \frac{1}{\hbar\omega} + A_2 \frac{1}{\hbar^2\omega^2} + O(\omega^{-3}), \quad (\text{say}). \quad (6.128)$$

The coefficient of $(\hbar\omega)^{-1}$ is

$$A_1 = \int_0^\infty r^2 dr R_{20}(r) r^2 \delta R_{20}(r). \quad (6.129)$$

We use the following expressions for $R_{20}(r)$ and $\delta R_{20}(r)$:

$$R_{20}(r) = \frac{(\alpha m)^{3/2} e^{-\alpha m r/2} \left(1 - \frac{1}{2} \alpha m r\right)}{\sqrt{2}}, \quad (6.130)$$

$$\begin{aligned} \delta R_{20}(r) = & -\frac{\alpha^{5/2} m^{1/2} e^{-\alpha m r/2}}{2\sqrt{2} r} + \frac{\gamma_E \alpha^{7/2} m^{3/2} e^{-\alpha m r/2}}{\sqrt{2}} - \frac{3\alpha^{7/2} m^{3/2} e^{-\alpha m r/2}}{4\sqrt{2}} \\ & + \frac{13\alpha^{9/2} m^{5/2} r e^{-\alpha m r/2}}{8\sqrt{2}} - \frac{\gamma_E \alpha^{9/2} m^{5/2} r e^{-\alpha m r/2}}{2\sqrt{2}} - \frac{\alpha^{11/2} m^{7/2} r^2 e^{-\alpha m r/2}}{8\sqrt{2}} \\ & + \frac{\alpha^{7/2} m^{3/2} e^{-\alpha m r/2} \ln(\alpha m r)}{\sqrt{2}} - \frac{\alpha^{9/2} m^{5/2} r e^{-\alpha m r/2} \ln(\alpha m r)}{2\sqrt{2}}. \end{aligned} \quad (6.131)$$

The right-hand side of the Eq. (6.129) works out to $41/m^2$. i.e.

$$A_1 = \frac{41}{m^2}. \quad (6.132)$$

We now calculate coefficient of $(\omega)^{-2}$

$$A_2 = \frac{i}{m} \int_0^\infty r^2 dr i \left(\frac{\partial R_{20}(r)}{\partial r} \right) r \delta R_{20}(r). \quad (6.133)$$

We first differentiate Eq. (6.130) with respect to r and then substitute the result and the corrected wave function given by Eq. (6.131) in Eq. (6.133). Eq. (6.133) simplifies to

$$A_2 = -\frac{21\alpha^2}{8m}. \quad (6.134)$$

These coefficients verify the Eq. (6.126). We now replace ω by $i\omega$ to find the Wick-rotated form of the perturbed P -matrix.

In terms of the parameter t , Eq. (6.105) takes the following form

$$\delta \tilde{D}_6^\psi(2S; 1S) = \frac{3\alpha^2 mc^2}{8\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt}{t^3} \delta \tilde{\alpha}_{2S}^\psi(t) \alpha_{1S}(t). \quad (6.135)$$

Let us say the parameter t before and after the Wick rotation are t_n and T_n respectively. Then, for 1S state, T_n are given as

$$T_1^+ = \frac{t_1}{\sqrt{i + t_1^2(1 - i)}} \quad \text{and} \quad T_1^- = \frac{t_n}{\sqrt{-i + t_1^2(1 + i)}}. \quad (6.136)$$

Similarly for $n = 2$, we get the following

$$T_2^+ = \frac{t_2}{\sqrt{i + t_2^2(1 - i)}} \sqrt{\frac{-1 + (1 + i)t_2^2}{-4 + (4 + i)t_2^2}}, \quad T_2^- = \frac{t_2}{\sqrt{-i + t_2^2(1 + i)}} \sqrt{\frac{-i + (1 + i)t_2^2}{-4i + (4i + 1)t_2^2}}. \quad (6.137)$$

In the new variables the integral (6.135) takes the following form

$$\begin{aligned} \delta\tilde{D}_6^\psi(2S; 1S) &= \frac{3\alpha^2 mc^2}{8\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt_1}{t_1^3} \left(\delta\tilde{P}_{2S}^\psi(T_2^+(t_1)) + \delta\tilde{P}_{2S}^\psi(T_2^-(t_1)) \right) \\ &\quad \times \left(P_{1S}(T_1^+(t_1)) + P_{1S}(T_1^-(t_1)) \right). \end{aligned} \quad (6.138)$$

Following the same procedure we followed for $\delta D_6^\psi(1S; 1S)$, we now numerically calculate $\delta\tilde{D}_6^\psi(2S; 1S)$ in both the asymptotic and non-asymptotic regions and add them up. The total non-degenerate wave function contribution to the perturbed vdW coefficient is found to be

$$\delta\tilde{D}_6^\psi(2S; 1S) = 297.931\,412\,174\,718\,\alpha^2 E_h a_0^6. \quad (6.139)$$

We now consider the degenerate contribution on $\delta\bar{D}_6(2S; 1S)$ due to the wave function correction. The degenerate contribution $\delta D_6^\psi(2S; 1S)$ comes from the quasi degenerate 2P states. Let us recall the degenerate contribution on perturbation energy due to the wave function correction $\delta E_6^\psi(2S; 1S)$ of CP interaction.

$$\begin{aligned} \delta\bar{E}_{2S;1S}^\psi(R) &= -\frac{\hbar}{\pi(4\pi\epsilon_0)^2} \lim_{\eta \rightarrow 0} \int_0^\infty d\omega \delta\bar{\alpha}_{2S}^\psi(i\omega) \alpha_{1S}(i\omega) \frac{\omega^4 e^{2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (6.140)$$

The P -matrix element for degenerate states in terms of frequencies in its Wick-rotated form reads as below.

$$\bar{P}_{2S}(\pm i\omega) = \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^i|2P(m=\mu)\rangle|^2 \left(\frac{1}{-\mathcal{L}_2 \pm i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 \pm i\hbar\omega - i\epsilon} \right), \quad (6.141)$$

where \mathcal{L}_2 and \mathcal{F}_2 stand for the Lamb-shift energy and the fine structure interaction respectively between $2S$ and $2P$ states. The Lamb shift energy \mathcal{L}_2 is in the order of 10^{-7} times Hartree energy and the fine-structure energy \mathcal{F}_2 is in order of 10^{-6} times Hartree energy. To the first order approximation, the ket associated to wave function corresponding to the nS -state can be expressed as $|nS\rangle \rightarrow |nS + \delta(nS)\rangle$. The P -matrix element also gets modified.

$$\begin{aligned}
\delta\bar{P}_{2S}^\psi(\pm i\omega) &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu=1,0,-1} \left(\langle \delta(2S)|x^i|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^i|2S\rangle + \right. \\
&\quad \left. \times \langle 2S|x^i|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^i|\delta(2S)\rangle \right) \left(\frac{1}{-\mathcal{L}_2 \pm i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 \pm i\hbar\omega - i\epsilon} \right) \\
&= \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu=1,0,-1} \langle 2S|x^i|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^i|\delta(2S)\rangle \\
&\quad \times \left(\frac{1}{-\mathcal{L}_2 \pm i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 \pm i\hbar\omega - i\epsilon} \right). \tag{6.142}
\end{aligned}$$

The wave function correction to the polarizability, $\delta\bar{\alpha}_{2S}^\psi(\omega)$ is the sum

$$\delta\bar{\alpha}_{2S}^\psi(\omega) = \delta\bar{P}_{2S}^\psi(\omega) + \delta\bar{P}_{2S}^\psi(-\omega). \tag{6.143}$$

Thus, we have

$$\begin{aligned}
\delta\bar{\alpha}_{2S}^\psi(i\omega) &= \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu=1,0,-1} \langle 2S|x^i|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^i|\delta(2S)\rangle \\
&\quad \times \left(\frac{1}{-\mathcal{L}_2 + i\hbar\omega - i\epsilon} + \frac{1}{-\mathcal{L}_2 - i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 + i\hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_2 - i\hbar\omega - i\epsilon} \right) \\
&= \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu=1,0,-1} \langle 2S|x^i|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^i|\delta(2S)\rangle \\
&\quad \times \left(\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + \hbar^2\omega^2} + \frac{4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + \hbar^2\omega^2} \right). \tag{6.144}
\end{aligned}$$

With the help of equations (6.140) and (6.144), we can evaluate $\delta\bar{E}_{2S;1S}^\psi(R)$ as

$$\begin{aligned}
\delta\bar{E}_{2S;1S}^\psi(R) &= -\frac{\hbar}{\pi(4\pi\epsilon_0)^2}\alpha_{1S}(0)\frac{2e^2}{9}\sum_{i=1}^3\sum_{\mu=1,0,-1}\langle 2S|x^i|2P(m=\mu)\rangle \\
&\times \langle 2P(m=\mu)|x^i|\delta(2S)\rangle \lim_{\epsilon\rightarrow 0}\lim_{\mathcal{L}\rightarrow 0}\lim_{\mathcal{F}\rightarrow 0}\int_0^\infty d\omega\frac{\omega^4 e^{2\omega R/c}}{R^2}\left(\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2-i\epsilon)^2+(\hbar\omega)^2}\right. \\
&+ \left.\frac{4\mathcal{F}_2}{(\mathcal{F}_2-i\epsilon)^2+(\hbar\omega)^2}\right)\left[1+2\left(\frac{c}{\omega R}\right)+5\left(\frac{c}{\omega R}\right)^2+6\left(\frac{c}{\omega R}\right)^3+3\left(\frac{c}{\omega R}\right)^4\right] \\
&\approx -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6}\alpha_{1S}(0)\frac{2e^2}{9}\sum_{i=1}^3\sum_{\mu=1,0,-1}\langle 2S|x^i|2P(m=\mu)\rangle \\
&\times \langle 2P(m=\mu)|x^i|\delta(2S)\rangle\left(\frac{\pi}{\hbar}+\frac{2\pi}{\hbar}\right) \\
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6}\alpha_{1S}(0)\sum_{i=1}^3\sum_{\mu=1,0,-1}\int_0^\infty r_1^2 dr_1\int_0^\infty r_2^2 dr_2\langle 2S|\vec{r}_1\rangle\langle \vec{r}_1|x^i|2P(m=\mu)\rangle \\
&\times \langle 2P(m=\mu)|x^i|\vec{r}_2\rangle\langle \vec{r}_2|\delta(2S)\rangle \\
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6}\alpha_{1S}(0)\int_0^\infty r_1^2 dr_1\int_0^\infty r_2^2 dr_2 R_{20}(r_1)r_1 R_{21}(r_1)R_{21}(r_2)r_2\delta R_{20}(r_2) \\
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6}\alpha_{1S}(0)\int_0^\infty dr_1 r_1^3 R_{20}(r_1)R_{21}(r_1)\int_0^\infty dr_2 r_2^3 R_{21}(r_2)\delta R_{20}(r_2).
\end{aligned} \tag{6.145}$$

The integration (6.145) evaluates to $\frac{9}{4}\alpha^2 a_0^2$ so that

$$\delta\bar{E}_{2S;1S}^\psi(R) = -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6}\frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4}\frac{9}{4}\alpha^2 a_0^2 = -\frac{81}{4}\alpha^2 E_h \frac{a_0^6}{R^6}. \tag{6.146}$$

Comparing Eq. (6.146) with

$$\delta\bar{E}_{2S;1S}^\psi(R) = -\frac{\delta\bar{D}_{2S;1S}^\psi(R)}{R^6}, \tag{6.147}$$

we see that the vdW coefficient $\delta\bar{D}_{2S;1S}^\psi(R)$ is

$$\delta\bar{D}_{2S;1S}^\psi(R) = \frac{81}{4}\alpha^2 E_h a_0^6. \tag{6.148}$$

The non-degenerate and the degenerate contributions of the wave function add up to give the total wave function contribution to the direct vdW coefficient due to the Dirac delta perturbation potential.

$$\begin{aligned}
\delta D_6^\psi(2S; 1S) &= \delta \tilde{D}_6^\psi(2S; 1S) + \delta \bar{D}_6^\psi(2S; 1S) \\
&= (297.931\,412\,174\,718 + \frac{81}{4}) \alpha^2 E_h a_0^6 \\
&= 318.181\,412\,174\,718 \alpha^2 E_h a_0^6.
\end{aligned} \tag{6.149}$$

The δ -perturbed direct vdW coefficient is the sum of the energy type contribution, $\delta D_6^E(2S; 1S)$ and the wave function type contribution, $\delta D_6^\psi(2S; 1S)$, i.e.,

$$\delta D_6(2S; 1S) = \delta D_6^\psi(2S; 1S) + \delta D_6^E(2S; 1S) = 367.914\,605\,710 \alpha^2 E_h a_0^6. \tag{6.150}$$

Note that, in the vdW range, the wave function type contribution is dominant over the energy type contribution.

6.5. 2S-1S-DIRAC- δ MIXING PERTURBATION TO E_{vdW}

For $n = 2$, the mixing vdW coefficient can be written as

$$M_6(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}(i\omega) \alpha_{2S1S}(i\omega). \tag{6.151}$$

The Wick-rotated polarizability $\alpha_{2S1S}(i\omega)$ is the the sum of the mixing matrix elements

$$\alpha_{2S1S}(i\omega) = P(2S1S, i\omega) + P(2S1S, -i\omega). \tag{6.152}$$

The probability density of P -states features by lobes emanated from the origin which vanishes for $r = 0$. Thus, the modification to the Hamiltonian due to the Dirac-delta

perturbation potential does not give any contribution to the mixing vdW coefficient. However, the modification to the energy and the wave function, in general, have non-vanishing contribution to the mixing vdW coefficient. Let $\delta M_6^E(2S;1S)$ and $\delta M_6^\psi(2S;1S)$ be the contributions due to the modification to the energy and the modification to the wave function respectively in the presence of the Dirac-delta perturbation potential.

Only the $2S$ state is perturbed. However, both E_{1S} and E_{2S} energy levels can serve as the reference energy level. For the sake of simplicity, we take the average of E_{1S} and E_{2S} as the reference energy level. The reference quantum number associated with the reference energy level is given as

$$\frac{1}{-2n_{\text{ref}}^2} = \frac{1}{2} \left(-\frac{1}{2} - \frac{1}{8} \right) \quad \implies \quad n_{\text{ref}} = 2\sqrt{\frac{2}{5}}. \quad (6.153)$$

The energy and the wave function parts of the perturbed vdW coefficient can be written as

$$\delta M_6^E(2S;1S) = \frac{6\hbar e^2}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}(i\omega) \delta\alpha_{2S1S}^E(i\omega), \quad (6.154)$$

and

$$\delta M_6^\psi(2S;1S) = \frac{6\hbar e^2}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}(i\omega) \delta\alpha_{2S1S}^\psi(i\omega). \quad (6.155)$$

The energy correction to the polarizability due to the Dirac-delta perturbation potential can be expressed as

$$\delta\alpha_{2S1S}^E(i\omega) = \sum_{\pm} \delta P_{2S1S}^E(\pm i\omega) = - \sum_{\pm} \frac{\partial}{\partial\omega} P(2S1S, i\omega) \frac{\delta E}{2}. \quad (6.156)$$

where $\delta P_{2S1S}^E(i\omega)$ is the modification to the P -matrix element due to the Dirac-delta perturbation. In terms of the parameter t , the perturbed P - mixing matrix element due to the energy correction is given as

$$\begin{aligned}
\delta P_{2S1S}^E(t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{t^3 n_{\text{ref}}^2}{2^3} \frac{\partial}{\partial t} P(2S1S, t) \frac{\delta E}{2} \\
&= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{64\sqrt{2} n_{\text{ref}}^4 t^4}{729 (n_{\text{ref}}^2 t^2 - 4)^4 (n_{\text{ref}}^2 t^2 - 1)^3} \left[972 n_{\text{ref}}^{12} t^{12} + 2430 n_{\text{ref}}^{11} t^{11} - 6119 n_{\text{ref}}^{10} t^{10} \right. \\
&\quad - 17010 n_{\text{ref}}^9 t^9 + 1975 n_{\text{ref}}^8 t^8 + 17496 n_{\text{ref}}^7 t^7 + 4384 n_{\text{ref}}^6 t^6 + 656 n_{\text{ref}}^4 t^4 - 1408 n_{\text{ref}}^2 t^2 + 512 \\
&\quad - 972 n_{\text{ref}}^7 t^7 (5 n_{\text{ref}}^4 t^4 - 35 n_{\text{ref}}^2 t^2 + 36) {}_2F_1 \left(1, -n_{\text{ref}} t; 1 - n_{\text{ref}} t; \frac{n_{\text{ref}}^2 t^2 - 3 n_{\text{ref}} t + 2}{n_{\text{ref}}^2 t^2 + 3 n_{\text{ref}} t + 2} \right) \\
&\quad + 972 n_{\text{ref}}^8 t^8 (n_{\text{ref}}^4 t^4 - 5 n_{\text{ref}}^2 t^2 + 4) {}_2F_1^{(0,0,1,0)} \left(1, -n_{\text{ref}} t; 1 - n_{\text{ref}} t; \frac{n_{\text{ref}}^2 t^2 - 3 n_{\text{ref}} t + 2}{n_{\text{ref}}^2 t^2 + 3 n_{\text{ref}} t + 2} \right) \\
&\quad \left. + 972 n_{\text{ref}}^8 t^8 (n_{\text{ref}}^4 t^4 - 5 n_{\text{ref}}^2 t^2 + 4) {}_2F_1^{(0,1,0,0)} \left(1, -n_{\text{ref}} t; 1 - n_{\text{ref}} t; \frac{n_{\text{ref}}^2 t^2 - 3 n_{\text{ref}} t + 2}{n_{\text{ref}}^2 t^2 + 3 n_{\text{ref}} t + 2} \right) \right]. \tag{6.157}
\end{aligned}$$

The $P(2S1S, \nu)$ mixed-matrix element is given by

$$\begin{aligned}
P_{2S1S}(t) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \frac{512\sqrt{2} n_{\text{ref}}^2 t^2}{729 (n_{\text{ref}} t - 2)^3 (n_{\text{ref}} t + 2)^2 (n_{\text{ref}}^2 t^2 - 1)^2} \left(419 n_{\text{ref}}^7 t^7 + 134 n_{\text{ref}}^6 t^6 \right. \\
&\quad \left. - 15 n_{\text{ref}}^5 t^5 + 30 n_{\text{ref}}^4 t^4 + 60 n_{\text{ref}}^3 t^3 - 120 n_{\text{ref}}^2 t^2 - 32 n_{\text{ref}} t + 64 \right) \\
&\quad - \frac{4096\sqrt{2} n_{\text{ref}}^9 t^9 {}_2F_1 \left(1, -n_{\text{ref}} t; 1 - n_{\text{ref}} t; \frac{n_{\text{ref}}^2 t^2 - 3 n_{\text{ref}} t + 2}{n_{\text{ref}}^2 t^2 + 3 n_{\text{ref}} t + 2} \right)}{3 (n_{\text{ref}}^2 t^2 - 4)^3 (n_{\text{ref}}^2 t^2 - 1)^2}. \tag{6.158}
\end{aligned}$$

In terms of the variable t , taking the average of E_{1S} and E_{2S} as the reference energy, the Dirac delta perturbed mixing vdW coefficient $\delta M_6^E(2S; 1S)$ is given by

$$\begin{aligned}
\delta M_6^E(2S; 1S) &= \frac{3 \alpha^2 m c^2}{4\pi (4\pi \epsilon_0)^2} \int_0^1 \frac{dt}{t^3} \left(\delta P_{2S1S}^E(T_{n_{\text{ref}}}^+(t)) + \delta P_{2S1S}^E(T_{n_{\text{ref}}}^-(t)) \right) \\
&\quad \times \left(P_{2S1S}(T_{n_{\text{ref}}}^+(t)) + P_{2S1S}(T_{n_{\text{ref}}}^-(t)) \right). \tag{6.159}
\end{aligned}$$

The numerical evaluation of the integral (6.159) yields

$$\delta M_6^E(2S; 1S) = 12.556\,663\,546\,763\,\alpha^2 E_h a_0^6. \quad (6.160)$$

The wave function correction on the P -mixed matrix element due to the Dirac-delta perturbation potential acting on the $2S$ - $1S$ system is

$$\begin{aligned} \delta P_{2S1S}^\psi(\nu) &= \frac{2e^2}{3} \langle 1S | r^j g_{\ell=1}(r_1, r_2, \nu) r^j | \delta(2S) \rangle \\ &= \frac{2e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{10}(r_1) r_1 g_{\ell=1}(r_1, r_2, \nu) r_2 \delta R_{20}(r). \end{aligned} \quad (6.161)$$

where $\nu = n_{\text{ref}} t$ is the generalized principal quantum number. For the $2S$ - $1S$ system, the reference quantum number is $n_{\text{ref}} = 2\sqrt{2}/\sqrt{5}$. We obtain

$$\begin{aligned} \delta P_{2S1S}^\psi(\nu) &= \frac{\hbar^2 e^2}{\alpha^2 m^3 c^4} \left[\frac{4194304\sqrt{2} F_{244}(\nu)}{3(\nu-2)(\nu+1)^4(\nu+2)^5} + \frac{32\sqrt{2}\nu^2}{2187(\nu^2-4)^4(\nu^2-1)^3} \left[12503\nu^{12} \right. \right. \\ &+ 86994\nu^{11} - 107796\nu^{10} + 49572\nu^9 - 283245\nu^8 + 451008\nu^7 + 235472\nu^6 + 46656\nu^5 \\ &- 213216\nu^4 + 155904\nu^2 - 40192 \left. \right] - \frac{32\sqrt{2}\nu^7(\nu^2+4) {}_2F_1\left(1, -\nu; 1-\nu; \frac{\nu-1}{\nu+1}\right)}{(\nu-2)^2(\nu-1)^3(\nu+1)^3(\nu+2)^2} \\ &- \frac{32\sqrt{2}\nu^7 {}_2F_1\left(1, -\nu; 1-\nu; \frac{\nu^2-3\nu+2}{\nu^2+3\nu+2}\right)}{9(\nu-2)^4(\nu-1)^3(\nu+1)^3(\nu+2)^4} \left[371\nu^6 - 772\nu^4 + 1808\nu^2 - 192 + \right. \\ &384(\nu^4 - 5\nu^2 + 4)\nu^2 \ln\left(\frac{2\nu}{\nu+2}\right) \left. \right] + \frac{512\sqrt{2}\nu^2 \ln(81)}{243(\nu^2-4)} + \frac{2048\sqrt{2}\nu^2 \ln\left(\frac{\nu}{\nu+2}\right)}{243(\nu^2-4)} + \\ &\frac{512\sqrt{2}\nu^2(419\nu^7 + 134\nu^6 - 15\nu^5 + 30\nu^4 + 60\nu^3 - 120\nu^2 - 32\nu + 64) \ln\left(\frac{2\nu}{\nu+2}\right)}{729(\nu-2)^3(\nu+2)^2(\nu^2-1)^2} \\ &- \left. \frac{128\sqrt{2}\nu^2(23\nu^8 - 128\nu^6 + 1020\nu^4 - 992\nu^2 + 320) \ln\left(\frac{3\nu}{\nu+2}\right)}{729(\nu^2-4)^2(\nu^2-1)^3} \right], \end{aligned} \quad (6.162)$$

where

$$F_{244}(\nu) = \sum_{k=0}^{\infty} \frac{\nu^{10} \left(\frac{\nu-1}{\nu+1}\right)^k {}_2F_1^{(0,1,0,0)}\left(-k, 4, 4, \frac{4}{\nu+2}\right)}{1024(k-\nu+2)}, \quad (6.163)$$

is a term containing sum over k which does not take a closed form expression. The series convergence is extremely slow around $\nu = 0$. We use the convergence acceleration technique as discussed above in the Sec. 5.3.1.

Keeping in mind that n_{ref} is the reference quantum number, the wave function correction to the mixing matrix element $\delta P_{2S1S}^{\psi}(\nu)$ can be expressed in terms of the parameter t just by the substitution of $\nu = n_{\text{ref}} t$. We now use the following formula for the Delta perturbed mixing vdW coefficient due to the wave function correction

$$\begin{aligned} \delta M_6^{\psi}(2S; 1S) &= \frac{3\alpha^2 mc^2}{4\pi(4\pi\epsilon_0)^2} \int_0^1 \frac{dt}{t^3} \left(\delta P_{2S1S}^{\psi}(T_{n_{\text{ref}}}^+(t)) + \delta P_{2S1S}^{\psi}(T_{n_{\text{ref}}}^-(t)) \right) \\ &\quad \times \left(P_{2S1S}(T_{n_{\text{ref}}}^+(t)) + P_{2S1S}(T_{n_{\text{ref}}}^-(t)) \right), \end{aligned} \quad (6.164)$$

and evaluate the integral numerically which yields

$$\delta M_6^{\psi}(2S; 1S) = -70.652\,014\,640\,246 \alpha^2 E_h a_0^6. \quad (6.165)$$

The total mixing vdW coefficient in the presence of the Dirac delta perturbation potential is the sum

$$\begin{aligned} \delta M_6(2S; 1S) &= \delta M_6^{\psi}(2S; 1S) + \delta M_6^E(2S; 1S) \\ &= -58.095\,351\,093\,483 \alpha^2 E_h a_0^6. \end{aligned} \quad (6.166)$$

The total δ -perturbed vdW coefficient $\delta C_6(2S; 1S)$ is the sum

$$\begin{aligned} \delta C_6(2S; 1S) &= \delta D_6(2S; 1S) \pm \delta M_6(2S; 1S) \\ &= (367.914\,605\,710 \mp 58.095\,351\,093) \alpha^2 E_h a_0^6. \end{aligned} \quad (6.167)$$

Notice that, in the vdW range, the direct term contribution to the symmetry-dependent $\delta C_6(2S; 1S)$ coefficient is dominant over mixing term contribution.

6.6. DIRAC- δ INTERACTION FOR 2S-1S SYSTEM IN THE CP RANGE

The Dirac delta perturbation potential has very interesting impacts on the interaction energy. The perturbation potential gives rise to both the energy type and the wave function type corrections. Both the energy and the wave function corrections have contributions from the degenerate term and the non-degenerate term. If we concentrate only on the non-degenerate part of the contribution, the interaction potential would be proportional to R^{-7} . However, the degenerate contribution is expected to be in the order of R^{-6} . In the CP range, the degenerate contribution is dominant over the non-degenerate contribution. Let us separate the degenerate contributions on the Dirac-delta perturbed interaction energy into two different categories, namely, wave function contribution and the energy contribution.

6.6.1. Wave Function Contribution. If we concentrate on the Dirac-delta perturbed interaction energy due to the presence of the $2P$ -states which are degenerate with the $2S$ -state, the following expression provides the wave function type contributions:

$$\begin{aligned} \delta \bar{E}^\psi(2S; 1S) &= -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha_{1S}(i\omega) \delta \bar{\alpha}_{2S}^\psi(i\omega) \\ &= -\frac{\delta \bar{D}_6^\psi(2S; 1S)}{R^6}. \end{aligned} \quad (6.168)$$

As we already calculated in Section 4, the $\delta \bar{D}_6^\psi(2S; 1S)$ coefficient is given by

$$\delta \bar{D}_6^\psi(2S; 1S) = \frac{81}{4} \alpha^2 E_h a_0^6. \quad (6.169)$$

On the other hand, the mixing terms contribution $\delta\bar{E}^{\psi,\text{mixing}}(2S; 1S)$ reads

$$\begin{aligned} \delta\bar{E}^{\psi,\text{mixing}}(2S; 1S) = & -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \left[\alpha_{2S1S}^{E=E_{1S}}(i\omega) \delta\bar{\alpha}_{2S1S}^{\psi,E=E_{2S}}(i\omega) \right. \\ & \left. + \delta\alpha_{2S1S}^{E=E_{1S}}(i\omega) \bar{\alpha}_{2S1S}^{\psi,E=E_{2S}}(i\omega) \right]. \end{aligned} \quad (6.170)$$

where $\alpha_{2S1S}^{E=E_{1S}}(i\omega)$ and $\alpha_{2S1S}^{E=E_{2S}}(i\omega)$ are Wick-rotated polarizabilities taking $1S$ and $2S$ as the reference state respectively. Here, ψ in the superscript indicates the wave function contribution. Recognizing that Eq. (6.170) is in the usual mathematical form for CP interaction,

$$\delta\bar{E}^{\psi,\text{mixing}}(2S; 1S) = -\frac{\delta\bar{M}_6^\psi(2S; 1S)}{R^6}, \quad (6.171)$$

the mixing coefficient $\delta\bar{M}_6^\psi(2S; 1S)$ can be written as

$$\begin{aligned} \delta\bar{M}_6^\psi(2S; 1S) = & \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \delta\bar{\alpha}_{2S1S}^{\psi,E=E_{2S}}(i\omega) \\ & + \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{2S1S}^{E=E_{1S}}(i\omega) \bar{\alpha}_{2S1S}^{\psi,E=E_{2S}}(i\omega) \\ = & \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle \delta(2S) | x^j | 2P(m=\mu) \rangle \\ & \times \langle 2P(m=\mu) | x^j | 1S \rangle \left[\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + \hbar^2\omega^2} + \frac{4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + \hbar^2\omega^2} \right] \\ & + \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \delta\alpha_{2S1S}^{E=E_{1S}}(i\omega) e^2 \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 2S | x^j | 2P(m=\mu) \rangle \\ & \times \langle 2P(m=\mu) | x^j | 1S \rangle \left[\frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + \hbar^2\omega^2} + \frac{4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + \hbar^2\omega^2} \right]. \end{aligned} \quad (6.172)$$

The integrands have poles of order one at $\omega = \pm(-\mathcal{L}_2 - i\epsilon)$ and $\omega = \pm(\mathcal{F}_2 - i\epsilon)$. We complete the contour in the upper half of the complex plane such that the contributing poles will be $\omega = -(-\mathcal{L}_2 - i\epsilon)$ and $\omega = -(\mathcal{F}_2 - i\epsilon)$. We now calculate residues about

the poles enclosed by the contours and then take limits $\lim_{\mathcal{L}_2 \rightarrow 0}$ and $\lim_{\mathcal{F}_2 \rightarrow 0}$ which yields

$$\begin{aligned}
\delta \bar{M}_6^\psi(2S; 1S) &= \frac{\hbar e^2}{3\pi(4\pi\epsilon_0)^2} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle \delta(2S)|x^j|2P(m=\mu) \rangle \\
&\quad \times \langle 2P(m=\mu)|x^j|1S \rangle \left(\frac{\pi}{\hbar} + \frac{2\pi}{\hbar} \right) + \frac{\hbar e^2}{3\pi(4\pi\epsilon_0)^2} \delta \alpha_{2S1S}^{E=E_{1S}}(0) \\
&\quad \times \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 2S|x^j|2P(m=\mu) \rangle \langle 2P(m=\mu)|x^j|1S \rangle \left(\frac{\pi}{\hbar} + \frac{2\pi}{\hbar} \right) \\
&= \frac{e^2}{(4\pi\epsilon_0)^2} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle \delta(2S)|x^j|2P(m=\mu) \rangle \langle 2P(m=\mu)|x^j|1S \rangle \\
&\quad + \frac{e^2}{(4\pi\epsilon_0)^2} \delta \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 2S|x^j|2P(m=\mu) \rangle \langle 2P(m=\mu)|x^j|1S \rangle. \quad (6.173)
\end{aligned}$$

For the $2S$ - $1S$ system, the perturbed mixing vdW coefficient arising from the wave function correction due to the degenerate level reads

$$\begin{aligned}
\delta \bar{M}_6^\psi(2S; 1S) &= \frac{e^2}{(4\pi\epsilon_0)^2} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle \delta(2S)|x^j|2P(m=\mu) \rangle \langle 2P(m=\mu)|x^j|1S \rangle \\
&\quad + \frac{e^2}{(4\pi\epsilon_0)^2} \delta \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 2S|x^j|2P(m=\mu) \rangle \langle 2P(m=\mu)|x^j|1S \rangle \\
&= \frac{e^2}{(4\pi\epsilon_0)^2} \left(-\frac{3584\sqrt{2}\hbar^2 e^2}{729\alpha^4 m^3 c^4} \right) \left(-\frac{32\sqrt{2}\alpha^2 \hbar^2}{81\alpha^2 m^2 c^2} \right) \\
&\quad + \frac{e^2}{(4\pi\epsilon_0)^2} \left(\frac{9.295\,890\,768\,1811\hbar^2 e^2 \alpha^2}{\alpha^4 m^3 c^4} \right) \left(-\frac{128\sqrt{2}\hbar^2}{81\alpha^2 m^2 c^2} \right) \\
&= -58.439\,051\,900\,100\alpha^2 E_h a_0^6. \quad (6.174)
\end{aligned}$$

6.6.2. Energy Contribution. The Dirac-delta perturbed interaction energy due to the degenerate levels that come from the modification of the energy reads

$$\delta \bar{E}^E(2S; 1S) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha_{1S}(i\omega) \bar{\alpha}_{2S}^E(i\omega). \quad (6.175)$$

Recognizing that the right-hand side of Eq. (6.175) is in the form $-\delta\bar{D}_6^E(2S; 1S)/R^6$, the direct term contribution of the vdW coefficient $\delta\bar{E}^\psi(2S; 1S)$ can be expressed as

$$\delta\bar{D}_6^E(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \delta\bar{\alpha}_{2S}^E(i\omega). \quad (6.176)$$

Substituting the value of $\delta\bar{\alpha}_{2S}^E(i\omega)$, we get

$$\begin{aligned} \delta\bar{D}_6^E(2S; 1S) &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \\ &\times \langle 2S|\delta V|2S\rangle \left[\frac{2(\mathcal{L}_2^2 - \hbar^2\omega^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} + \frac{4(\mathcal{F}_2^2 - \hbar^2\omega^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right] \\ &= \frac{\hbar e^2}{3\pi(4\pi\epsilon_0)^2} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \langle 2S|\delta V|2S\rangle \\ &\times \int_0^\infty d\omega \alpha_{1S}(i\omega) \left[\frac{\partial}{\partial\mathcal{L}_2} \frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} + \frac{\partial}{\partial\mathcal{F}_2} \frac{-4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right] \\ &= \frac{\alpha^2}{3\pi} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \langle 2S|\delta V|2S\rangle \\ &\times \left[\alpha_{1S}(\mathcal{L}_2) \frac{\partial}{\partial\mathcal{L}_2} \left(\frac{\pi}{\hbar} \right) + \alpha_{1S}(\mathcal{F}_2) \frac{\partial}{\partial\mathcal{F}_2} \left(\frac{2\pi}{\hbar} \right) \right] = 0. \end{aligned} \quad (6.177)$$

Let us now investigate contribution of the energy modification of the mixing coefficient $\delta\bar{M}_6^E(2S; 1S)$ which reads

$$\delta\bar{M}_6^E(2S; 1S) = \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \delta\bar{\alpha}_{2S1S}^{E, E=E_{2S}}(i\omega). \quad (6.178)$$

The superscript E in $\delta\bar{M}_6^E(2S; 1S)$ and $\delta\bar{\alpha}_{2S1S}^{E=E_{1S}}$ indicate that these contributions are of the energy type and the $E = E_{2S}$ in the superscript tells us that we are taking E_{2S} as a reference energy level. Substituting the value for the Wick-rotated form of the

perturbed mixing polarizability, we can rewrite Eq. (6.178) as

$$\begin{aligned}
\delta\overline{M}_6^E(2S;1S) &= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \delta\overline{\alpha}_{2S1S}^{E,E=E_{2S}}(i\omega) \\
&= \frac{3\hbar}{\pi(4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu)\rangle \\
&\quad \times \langle 2P(m=\mu)|x^j|2S\rangle \langle 2S|\delta V|2S\rangle \left[\frac{2(\mathcal{L}_2^2 - \hbar^2\omega^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right. \\
&\quad \left. + \frac{4(\mathcal{F}_2^2 - \hbar^2\omega^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right] \\
&= \frac{\hbar e^2}{3\pi(4\pi\epsilon_0)^2} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^j|2S\rangle \langle 2S|\delta V|2S\rangle \\
&\quad \times \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \left[\frac{\partial}{\partial\mathcal{L}_2} \frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} + \frac{\partial}{\partial\mathcal{F}_2} \frac{-4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \right] \\
&= \frac{\alpha^2}{3\pi} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^j|2S\rangle \langle 2S|\delta V|2S\rangle \\
&\quad \times \left[\alpha_{2S1S}^{E=E_{1S}}(\mathcal{L}_2) \frac{\partial}{\partial\mathcal{L}_2} \left(\frac{\pi}{\hbar} \right) + \alpha_{2S1S}^{E=E_{1S}}(\mathcal{F}_2) \frac{\partial}{\partial\mathcal{F}_2} \left(\frac{2\pi}{\hbar} \right) \right] = 0. \tag{6.179}
\end{aligned}$$

We conclude that not only the direct $\delta\overline{D}_6^E(2S;1S)$ but also the mixing $\delta\overline{M}_6^E(2S;1S)$ term vanishes. Let us take a step back from the R^{-6} paradigm and go to the more general expression. To the first order approximation, the modification of the P -matrix due to the Dirac-delta perturbation on energy is

$$\begin{aligned}
\delta\overline{P}_{2S}^E(\pm i\omega) &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^i|2P(m=\mu)\rangle|^2 \\
&\quad \times \left(\frac{1}{[-\mathcal{L}_2 \pm i\hbar\omega - i\epsilon]^2} + \frac{2}{[\mathcal{F}_2 \pm i\hbar\omega - i\epsilon]^2} \right) \delta E. \tag{6.180}
\end{aligned}$$

The Wick-rotated perturbed polarizability $\delta\bar{\alpha}_{2S}^E(i\omega)$ which is the sum $\sum_{\pm} \delta\bar{P}_{2S}^E(\pm i\omega)$ is given by

$$\begin{aligned} \delta\bar{\alpha}_{2S}^E(i\omega) = & \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \left(\frac{2(\mathcal{L}_2^2 - (\hbar\omega)^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right. \\ & \left. + \frac{4(\mathcal{F}_2^2 - (\hbar\omega)^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right) \langle 2S|\delta V|2S\rangle. \end{aligned} \quad (6.181)$$

The perturbed interaction energy due to the modification of the energy which comes from nP -states which are degenerate with nS -state can be written as

$$\begin{aligned} \delta\bar{E}_{2S;1S}^E(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \lim_{\epsilon \rightarrow 0} \lim_{\eta \rightarrow 0} \int_0^{\infty} d\omega \alpha_{1S}(i\omega) \bar{\alpha}_{2S}^E(i\omega, \eta) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ & \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right], \end{aligned} \quad (6.182)$$

where η stands for the lamb shift \mathcal{L}_2 or the fine structure \mathcal{F}_2 . We can approximate the ground state atomic polarizability by its static value. This is because in the range $R \ll 1/\eta$, the degenerate polarizability $\bar{\alpha}_{2S}(i\omega, \eta)$ varies very rapidly over the range $\omega \sim \eta$ and is suppressed for $\omega \gg \eta$. The dominant contribution comes from the frequency range $\omega \sim \eta \ll 1/R$, where we can approximate the non-degenerate polarizability by its static value i.e. $\omega = 0$. This infers that the ground state polarizability $\alpha_{1S}(i\omega)$ can be approximated by its static value $\alpha_{1S}(0)$ in the range $R \ll 1/\eta$. Thus, the energy correction to the Dirac-delta perturbed interaction energy can be written as

$$\begin{aligned} \delta\bar{E}_{2S;1S}^E(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=1,0,-1} |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \langle 2S|\delta V|2S\rangle \\ & \times \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \int_0^{\infty} d\omega \alpha_{1S}(0) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{2(\mathcal{L}_2^2 - (\hbar\omega)^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} + \frac{4(\mathcal{F}_2^2 - (\hbar\omega)^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \right) \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
= & - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=1,0,-1} |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \langle 2S|\delta V|2S\rangle \\
& \times \left[\lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \int_0^\infty d\omega \frac{2(\mathcal{L}_2^2 - (\hbar\omega)^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \right. \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
& + \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \int_0^\infty d\omega \frac{4(\mathcal{F}_2^2 - (\hbar\omega)^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
= & - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=1,0,-1} |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \\
& \times \langle 2S|\delta V|2S\rangle \left[\textcircled{\text{I}} + \textcircled{\text{II}} \right]. \tag{6.183}
\end{aligned}$$

where the integral

$$\begin{aligned}
\textcircled{\text{I}} & = \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \int_0^\infty d\omega \frac{2(\mathcal{L}_2^2 - (\hbar\omega)^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
& = \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \frac{\partial}{\partial \mathcal{L}_2} \int_0^\infty d\omega \frac{-2\mathcal{L}_2}{(-\mathcal{L}_2 - i\epsilon)^2 + (\hbar\omega)^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
& = \frac{11c^3}{2\hbar^2 R^5}, \tag{6.184}
\end{aligned}$$

and the integral

$$\begin{aligned}
\textcircled{\text{II}} &= \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \int_0^{\infty} d\omega \frac{4(\mathcal{F}_2^2 - (\hbar\omega)^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2]^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&= \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \frac{\partial}{\partial \mathcal{F}_2} \int_0^{\infty} d\omega \frac{-4\mathcal{F}_2}{(\mathcal{F}_2 - i\epsilon)^2 + (\hbar\omega)^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&= \frac{11c^3}{\hbar^2 R^5}. \tag{6.185}
\end{aligned}$$

In the above calculation of the terms $\textcircled{\text{I}}$ and $\textcircled{\text{II}}$, we first integrate the above expressions over ω , then we carry out the respective derivatives. Only then we do set $\lim_{\epsilon \rightarrow 0}$, $\lim_{\mathcal{L}_2 \rightarrow 0}$ and $\lim_{\mathcal{F}_2 \rightarrow 0}$ which yields the above results. Substituting the values for $\textcircled{\text{I}}$ and $\textcircled{\text{II}}$ from Eqs. (6.184) and (6.185), we find a R^{-5} dependence of the degenerate energy contribution on the interaction energy which is a distinct feature of Dirac-delta perturbed interaction energy.

$$\begin{aligned}
\delta \bar{E}_{2S;1S}^E(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=1,0,-1} |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \\
&\quad \times \langle 2S|\delta V|2S\rangle \left[\frac{11c^3}{2\hbar^2 R^5} + \frac{11c^3}{\hbar^2 R^5} \right] \\
&= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \frac{9\hbar^2 e^2}{2\alpha^4 m^3 c^4} \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=1,0,-1} |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \frac{\alpha^4 m c^2}{2^3} \frac{33c^3}{2\hbar^2 R^5} \\
&= -\frac{33}{32\pi R^5} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{\hbar^3}{\alpha^4 m^3 c^3} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \alpha^2 E_h \\
&= -\frac{33}{32\pi R^5} \alpha^2 \left(\frac{a_0^3}{\alpha} \right) \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 \alpha^2 E_h. \tag{6.186}
\end{aligned}$$

Substituting $\sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 2S|x^j|2P(m=\mu)\rangle|^2 = 27a_0^2$ in Eq. (6.186), we get

$$\delta \bar{E}_{2S;1S}^E(R) = -\frac{33}{32\pi R^5} \alpha^3 E_h a_0^3 (27a_0^2) = -\frac{891}{32\pi} \alpha^3 E_h \left(\frac{a_0}{R}\right)^5. \quad (6.187)$$

The Eq. (6.186) is in the form

$$\delta \bar{E}_{2S;1S}^E(R) = -\frac{\bar{D}_5^E(2S;1S)}{R^5}, \quad (6.188)$$

where the $\bar{D}_5^E(2S;1S)$ coefficient is given by

$$\bar{D}_5^E(2S;1S) = \frac{891}{32\pi} \alpha^3 E_h (a_0)^5. \quad (6.189)$$

Interestingly, the interaction energy $\delta E_{a;b}^E(R)$ has vanishing $1/R^6$ but non-vanishing $1/R^5$ dependence. This situation motivates us to present a model integral for the energy type correction on the δ -perturbed interaction energy. We can model the interaction energy $\delta E_{a;b}^E(R)$ as

$$K(a, \eta, R) \equiv \int_0^\infty dx \frac{a}{(a-i\epsilon)^2 + x^2} \frac{\partial}{\partial \eta} \frac{(-\eta)}{(-\eta-i\epsilon)^2 + x^2} \frac{x^4 e^{-2Rx}}{R^2} \\ \times \left[1 + \frac{2}{Rx} + \frac{5}{(Rx)^2} + \frac{3}{(Rx)^3} + \frac{3}{(Rx)^4} \right]. \quad (6.190)$$

We choose the following numerical values for the parameters:

$$a = 1, \quad \eta = 10^{-3}, \quad \epsilon = 10^{-6}. \quad (6.191)$$

In Figure 6.2, we present a numerical model for energy type modification of the interaction energy in three different interatomic ranges. The blue curve overlaps with $1/R^6$ red-dashed curve in the vdW range, $1/R^5$ orange-dashed in the CP range and $1/R^7$ green-dashed curve in the Lamb shift range.

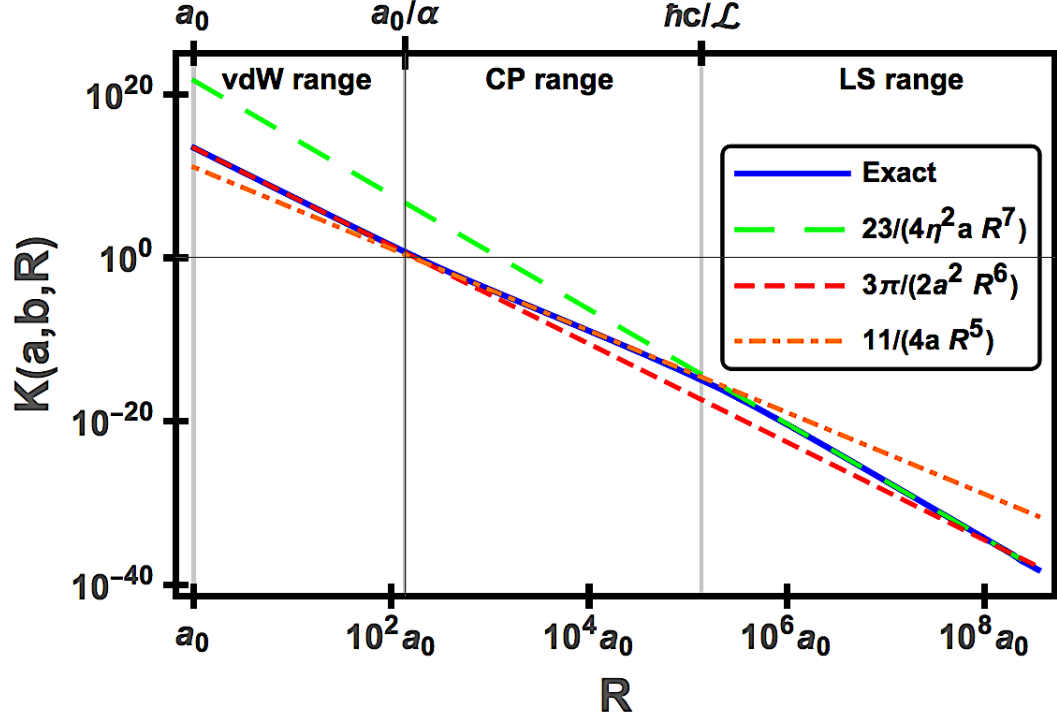


Figure 6.2: Asymptotics of the modification of the interaction energy due to the energy type correction in all three ranges. The interaction energy follows the $1/R^6$ power law in the vdW range, and the $1/R^7$ power law in the Lamb shift range. However, it follows the peculiar $1/R^5$ power law in the CP range.

Let us now examine the mixing terms contribution $\overline{M}_5^E(2S;1S)$ due to the modification of the energy. The energy type correction to the interaction energy arising from the degenerate $2S - 2P$ levels can be expressed as

$$\begin{aligned}
\delta \overline{E}_{2S;1S}^{E,\text{mixing}}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega) \delta \overline{\alpha}_{2S1S}^{E,E=E_{2S}}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
&\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
&= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \frac{e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S | x^j | 2P(m=\mu) \rangle \langle 2P(m=\mu) | x^j | 2S \rangle \\
&\quad \times \langle 2S | \delta V | 2S \rangle \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \int_0^\infty d\omega \alpha_{2S1S}^{E=E_{1S}}(i\omega)
\end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{2(\mathcal{L}_2^2 - \hbar^2\omega^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + \hbar^2\omega^2]^2} + \frac{4(\mathcal{F}_2^2 - \hbar^2\omega^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + \hbar^2\omega^2]^2} \right) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
& = - \frac{\hbar e^2}{9\pi c^4 (4\pi\epsilon_0)^2} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu) \rangle \\
& \times \langle 2P(m=\mu)|x^j|2S \rangle \langle 2S|\delta V|2S \rangle \\
& \times \left\{ \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_2 \rightarrow 0} \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \frac{2(\mathcal{L}_2^2 - \hbar^2\omega^2)}{[(-\mathcal{L}_2 - i\epsilon)^2 + \hbar^2\omega^2]^2} \right. \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\
& + \lim_{\epsilon \rightarrow 0} \lim_{\mathcal{F}_2 \rightarrow 0} \int_0^\infty d\omega \frac{4(\mathcal{F}_2^2 - \hbar^2\omega^2)}{[(\mathcal{F}_2 - i\epsilon)^2 + \hbar^2\omega^2]^2} \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\
& \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \left. \right\} \\
& = - \frac{\hbar e^2}{9\pi c^4 (4\pi\epsilon_0)^2} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu) \rangle \\
& \times \langle 2P(m=\mu)|x^j|2S \rangle \langle 2S|\delta V|2S \rangle \left\{ \textcircled{\text{I}} + \textcircled{\text{II}} \right\}. \tag{6.192}
\end{aligned}$$

Substituting the values of $\textcircled{\text{I}}$ and $\textcircled{\text{II}}$ in Eq. (6.192), $\delta \overline{E}_{2S;1S}^{E,\text{mixing}}(R)$ is given by

$$\begin{aligned}
\delta \overline{E}_{2S;1S}^{E,\text{mixing}}(R) &= - \frac{33}{18\pi R^5} \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right) \frac{1}{4\pi\epsilon_0} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu) \rangle \\
& \times \langle 2P(m=\mu)|x^j|2S \rangle \langle 2S|\delta V|2S \rangle \\
& = - \frac{33\alpha}{18\pi(4\pi\epsilon_0)R^5} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu) \rangle \\
& \times \langle 2P(m=\mu)|x^j|2S \rangle \frac{\alpha^4 m c^2}{2^3} \\
& = - \frac{33\alpha^3 E_h}{144\pi R^5} \frac{\alpha_{2S1S}^{E=E_{1S}}(0)}{(4\pi\epsilon_0)} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu) \rangle \\
& \times \langle 2P(m=\mu)|x^j|2S \rangle,
\end{aligned}$$

which is in the form

$$\delta \overline{E}_{2S;1S}^{E,\text{mixing}}(R) = - \frac{\delta \overline{M}_5^E(2S;1S)}{R^5}, \quad (6.193)$$

where the perturbed mixing vdW coefficient $\delta \overline{M}_5^E(2S;1S)$ is

$$\begin{aligned} \overline{M}_5^E(2S;1S) &= \frac{11\alpha^3 E_h}{48\pi(4\pi\epsilon_0)} \alpha_{2S1S}^{E=E_{1S}}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|2P(m=\mu)\rangle \langle 2P(m=\mu)|x^j|2S\rangle \\ &= \frac{11\alpha^3 E_h}{48\pi(4\pi\epsilon_0)} \left(-\frac{128\sqrt{2}}{27} \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \right) \left(-\frac{3584\sqrt{2}}{729} \frac{\hbar^2}{\alpha^2 m^2 c^2} \right) \\ &= 10.682\,382\,428\,153 \frac{\alpha^3}{\pi} E_h a_0^5. \end{aligned} \quad (6.194)$$

Above calculation leads us to the conclusion that for the CP regime, the energy type contribution follows the R^{-5} asymptotic.

6.7. $\delta \mathbf{E}_{2S,1S}(\mathbf{R})$ IN THE LAMB SHIFT RANGE

For $R \gg \hbar c/\mathcal{L}$, the contribution of the non-vanishing frequencies in the polarizabilities $\delta\alpha_{2S}(i\omega)$ is heavily repressed by the exponential term $e^{-2\omega R}$. Thus, in a good approximation, the Dirac-delta perturbed Wick-rotated polarizability, $\delta\alpha_{2S}(i\omega)$, is given by

$$\delta\alpha_{2S}(i\omega) \approx \delta\alpha_{2S}(0). \quad (6.195)$$

The Dirac-delta perturbed interaction energy for the $2S$ - $1S$ system, in this range, reads

$$\begin{aligned} \delta E_{2S;1S}^{\text{direct}}(R) &\approx - \frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \delta\alpha_{2S}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (6.196)$$

Making use of the integral (8.81) and relation

$$\delta\alpha_{2S}(0) = \delta\alpha_{2S}^E(0) + \delta\alpha_{2S}^\psi(0), \quad (6.197)$$

equation (6.196) can be expressed as

$$\delta E_{2S;1S}^{\text{direct}}(R) \approx -\frac{23}{4\pi} \frac{\hbar c}{(4\pi\epsilon_0)^2 R^7} \alpha_{1S}(0) \left(\delta\alpha_{2S}^E(0) + \delta\alpha_{2S}^\psi(0) \right). \quad (6.198)$$

The δ -perturbed polarizability has two contributions, namely, the non-degenerate and the degenerate contributions. However, the most dominant contribution on the polarizability comes from the degenerate $2S$ state. Thus, $\delta\alpha_{2S}(0)$ can be approximated as

$$\delta\alpha_{2S}(0) = \delta\alpha_{2S}^E(0) + \delta\alpha_{2S}^\psi(0) \approx \delta\bar{\alpha}_{2S}^E(0) + \delta\bar{\alpha}_{2S}^\psi(0). \quad (6.199)$$

As,

$$\delta\bar{\alpha}_{2S}^E(0) \sim |\langle 2S|e\vec{r}|2P\rangle|^2 \left[\frac{1}{\mathcal{L}_2^2} - \frac{2}{\mathcal{F}_2^2} \right] \langle 2S|\delta V|2S\rangle, \quad (6.200)$$

$$\delta\bar{\alpha}_{2S}^\psi(0) \sim \langle 2S|e\vec{r}|2P\rangle \langle 2P|e\vec{r}|\delta(2S)\rangle \left[-\frac{1}{\mathcal{L}_2} + \frac{2}{\mathcal{F}_2} \right], \quad (6.201)$$

and the energy type contribution dominates over the wave function type contribution, the frequency shift does not exceed $\frac{1}{\mathcal{L}_2} \langle 2S|\delta V|2S\rangle \times 10^{-36}$ Hz, which is too small to measure from the experimental point of view.

7. HYPERFINE-RESOLVED $2S$ - $2S$ SYSTEM

7.1. ORIENTATION

In Ref. [56], S. Jonsell et al. studied the long-range interaction between two hydrogen atoms when each atom is in the first excited state. They treated the difference between the total Hamiltonian of the $2S$ - $2S$ hydrogen system and the sum of the Hamiltonians of the atoms as a perturbation. They mentioned the necessity of including further effects like the spin-orbit interaction and the Lamb shift in the $2S$ - $2S$ interaction. However, we have noticed that no work has been done yet in this regard. On the other hand, the hyperfine correction has been taken into account in the vdW interaction between two atoms in Refs. [57; 58; 59; 60]. In these works, the authors investigated the hyperfine pressure shift and vdW Interactions in the hydrogen-helium, nitrogen-helium, and hydrogen-rare-gas systems. In 2003, Hänsch's group at the Max-Planck Institute of Quantum Optics in Garching, Germany measured the $2S$ hyperfine splitting frequency in hydrogen atom using an optical method [61]. In 2009, Hänsch's group measured the $2S$ hyperfine frequency again using an ultra-stable optical frequency reference [5; 62]. This optical measurement of the $2S$ hyperfine frequency interval boosted up our motivation to investigate the hyperfine resolved $2S$ - $2S$ system.

The $2S$ - $2S$ interaction is fascinating as each of the $2S$ -state couples with their quasi-degenerate neighbors ($2P$ -states). We first write down the total Hamiltonian of the system. The vdW, the Lamb shift, and the hyperfine energy splits are on same order for $R > 100a_0$. However, the fine structure splitting energy is much larger than them for $R > 100a_0$. Assuming that fine structure levels are sufficiently apart, we do not take the fine structure splitting Hamiltonian into account. Thus, the total

Hamiltonian of the system is the sum of the vdW, the Lamb shift, and the hyperfine splitting Hamiltonians. More explicitly,

$$H = H_{\text{LS}} + H_{\text{HFS}} + H_{\text{vdW}}, \quad (7.1)$$

where H_{LS} is the Lamb shift, H_{HFS} is the hyperfine splitting, and H_{vdW} is the vdW Hamiltonians. If A and B are the two hydrogen atoms, at the first excited states, interacting with each other, the Lamb shift Hamiltonian is given as

$$H_{\text{LS}} = H_{\text{LS},A} + H_{\text{LS},B} = \frac{4}{3}\alpha^2 mc^2 \left(\frac{\hbar}{mc}\right)^3 \ln\left(\frac{1}{\alpha^2}\right) \sum_{j=A,B} \delta^3(\vec{r}_j), \quad (7.2)$$

where α is the fine-structure constant, m is the mass of an electron, and \vec{r}_j is the relative distance of an electron in an atom with respect to its nucleus. The Lamb shift energy E_{LS} shifts the $nS_{1/2}$ state upwards relative to the Dirac position for the corresponding $j = 1/2$ level, thereby splitting the $nS_{1/2}$ and the $nP_{1/2}$ states, which are otherwise degenerate according to the Dirac theory of the hydrogen atom. It is believed that the origin of the Lamb shift is the interactions of the electron and the quantum vacuum fluctuations of the electromagnetic field within the atom [63]. The H_{HFS} in Eq. (7.1) represents the hyperfine splitting Hamiltonian given by

$$\begin{aligned} H_{\text{HFS}} &= H_{\text{HFS},A} + H_{\text{HFS},B} \\ &= \frac{\hbar\alpha g_p}{4mMc} \sum_{j=A,B} \frac{\vec{S}_{pj} \cdot \vec{L}_j}{r_j^3} + \frac{\hbar\alpha g_p}{2mMc} \sum_{j=A,B} \frac{1}{r_j^3} \left[3(\vec{S}_{ej} \cdot \hat{r}_j)(\hat{r}_j \cdot \vec{S}_{pj}) - \vec{S}_{ej} \cdot \vec{S}_{pj} \right] \\ &\quad + \frac{4}{3}g_p \sum_{j=A,B} (\vec{S}_{pj} \cdot \vec{S}_{ej}) \frac{\pi\hbar\alpha}{mMc} \delta^3(\vec{r}_j), \end{aligned} \quad (7.3)$$

where \vec{S}_{ej} and \vec{S}_{pj} are the spin angular momenta of the electron and the proton of the atoms A or B . M and $g_p = 5.585694702$ are the mass and the g -factor of the proton. \vec{L}_j is the orbital angular momentum of the electron. The first term on the

right-hand side of Eq. (7.3) has a zero contribution for S states as $l = 0$ for S -states and the second term is zero for S -states as

$$\left\langle nS \left| \frac{3}{r_j^3} (\vec{S}_{ej} \cdot \hat{r}_j) (\hat{r}_j \cdot \vec{S}_{pj}) \right| nS \right\rangle = \left\langle nS \left| \frac{\vec{S}_{ej} \cdot \vec{S}_{pj}}{r_j^3} \right| nS \right\rangle. \quad (7.4)$$

Thus for S -states, the hyperfine splitting Hamiltonian is also the Dirac- δ type as given below:

$$H_{\text{HFS}} = \frac{4}{3} g_p \sum_{j=A,B} (\vec{S}_{pj} \cdot \vec{S}_{ej}) \frac{\pi \hbar \alpha}{m M c} \delta^3(\vec{r}_j) \quad (7.5)$$

$$= \frac{4}{3} g_p \sum_{j=A,B} \frac{m}{M} \left(\frac{\vec{S}_{pj}}{\hbar} \cdot \frac{\vec{S}_{ej}}{\hbar} \right) \alpha m c^2 \left(\frac{\hbar}{m c} \right)^3 \pi \delta^3(\vec{r}_j). \quad (7.6)$$

H_{vdW} in Eq. (7.1) denotes vdW hamiltonian of the system. Recalling the electrostatic interaction between two hydrogen atoms, as discussed in Section2, we have

$$\hat{H}_{\text{vdW}} \approx \frac{e^2}{4\pi\epsilon_0} \sum_{ij} \beta_{ij} \frac{r_i^{(A)} r_j^{(B)}}{R^3}, \quad (7.7)$$

where β_{ij} is a second rank tensor given by

$$\beta_{ij} = \delta_{ij} - \frac{3R_i R_j}{R^2}. \quad (7.8)$$

Eq. (7.7) can equivalently be written as

$$\hat{H}_{\text{vdW}} \approx \frac{e^2}{4\pi\epsilon_0} \left(\frac{\vec{r}_A \cdot \vec{r}_B}{R^3} - \frac{3 \vec{r}_A \cdot \vec{R} \vec{r}_B \cdot \vec{R}}{R^5} \right). \quad (7.9)$$

Let us assume that the atomic separation \vec{R} is along the quantization axis of the system i.e., z -axis, we obtain

$$\begin{aligned} H_{\text{vdW}} &\approx \frac{e^2}{4\pi\epsilon_0} \left(\frac{(x_A x_B + y_A y_B + z_A z_B)}{R^3} - \frac{3(z_A z_B R^2)}{R^5} \right) \\ &= \alpha\hbar c \frac{(x_A x_B + y_A y_B - 2z_A z_B)}{R^3}. \end{aligned} \quad (7.10)$$

7.2. CONSERVED QUANTITY

The total angular momentum of the system is the sum of the total angular momentum of the atoms A and B .

$$\vec{F} = \vec{F}_A + \vec{F}_B. \quad (7.11)$$

The total angular momentum of each atom is defined by the sum

$$\vec{F} = \vec{L} + \vec{S}_e + \vec{S}_p, \quad (7.12)$$

where \vec{L} is the orbital angular momentum, \vec{S} is the spin angular momentum of the electron, and \vec{S}_p is the spin angular momentum of the proton. The z -component of the total angular momentum is thus given by

$$F_z = L_{z,A} + L_{z,B} + S_{ez,A} + S_{ez,B} + S_{pz,A} + S_{pz,B}. \quad (7.13)$$

We are interested in the commutation relation $[F_z, H]$.

Let us first compute the commutator $[L_{z,A} + L_{z,B}, H]$:

$$[L_{z,A} + L_{z,B}, H] = [L_{z,A} + L_{z,B}, H_{\text{LS}}] + [L_{z,A} + L_{z,B}, H_{\text{HFS}}] + [L_{z,A} + L_{z,B}, H_{\text{vdW}}], \quad (7.14)$$

where

$$[L_{z,A} + L_{z,B}, H_{\text{LS}}] = \frac{4}{3}\alpha^2 mc^2 \left(\frac{\hbar}{mc}\right)^3 \ln\left(\frac{1}{\alpha^2}\right) \left[L_{z,A} + L_{z,B}, \sum_{j=A,B} \delta^3(\vec{r}_j) \right]. \quad (7.15)$$

The spatial distribution of the electron of an electrically neutral hydrogen atom in its S -states is spherically symmetric. The position operator \vec{r} of the electron in such a spherically symmetric distribution commutes with the orbital angular momentum operator of the same electron. This implies

$$[L_{z,A} + L_{z,B}, H_{\text{LS}}] = 0. \quad (7.16)$$

Furthermore,

$$[L_{z,A} + L_{z,B}, H_{\text{HFS}}] = \frac{4}{3}g_p \frac{\pi\hbar\alpha}{mMc} \left[L_{z,A} + L_{z,B}, \sum_{j=A,B} (\vec{S}_{pj} \cdot \vec{S}_{ej}) \delta^3(\vec{r}_j) \right]. \quad (7.17)$$

As explained earlier for commutation relation (7.15), the orbital angular momentum commutes with the position operator. Moreover, the orbital angular momentum and the spin commutes. Thus, we have

$$[L_{z,A} + L_{z,B}, H_{\text{HFS}}] = 0. \quad (7.18)$$

Let us now examine the commutator of $L_{z,A} + L_{z,B}$ with H_{vdW} :

$$\begin{aligned} [L_{z,A} + L_{z,B}, H_{\text{vdW}}] &= \left[L_{z,A} + L_{z,B}, \alpha\hbar c \frac{(x_A x_B + y_A y_B - 2z_A z_B)}{R^3} \right] \\ &= \frac{\alpha\hbar c}{R^3} [L_{z,A} + L_{z,B}, x_A x_B + y_A y_B - 2z_A z_B] \\ &= \frac{\alpha\hbar c}{R^3} \left([L_{z,A}, x_A x_B + y_A y_B] + [L_{z,B}, x_A x_B + y_A y_B] \right) \\ &= \frac{\alpha\hbar c}{R^3} \left([x_A P_{y,A} - y_A P_{x,A}, x_A x_B + y_A y_B] \right) \end{aligned}$$

$$\begin{aligned}
& + [x_B P_{y,B} - y_B P_{x,B}, x_A x_B + y_A y_B] \Big) \\
& = \frac{\alpha \hbar c}{R^3} \left(x_A (-i \hbar y_B) - y_A (-i \hbar x_B) - y_A (-i \hbar x_B) - x_A (-i \hbar y_B) \right) = 0. \quad (7.19)
\end{aligned}$$

To get the third line of Eq. (7.19), we have used the fact that $[L_z, z] = 0$. In the fourth line, we have expressed the z -component of the orbital angular momentum in terms of position components and the linear momenta as

$$L_z = x P_y - y P_x. \quad (7.20)$$

To get the fifth line of Eq. (7.19), we have made use of the following commutation relations:

$$[r_i, r_i] = 0, \quad [P_i, P_i] = 0, \quad [r_i, P_j] = i \hbar \delta_{ij}, \quad \text{and} \quad [A, B] = -[B, A]. \quad (7.21)$$

The spin angular momentum commutes with the spherically symmetric function of the position operator. Thus, we have

$$[S_{ez,A} + S_{ez,B}, H_{\text{LS}}] = 0, \quad (7.22a)$$

$$[S_{ez,A} + S_{ez,B}, H_{\text{HFS}}] = 0, \quad (7.22b)$$

$$[S_{ez,A} + S_{ez,B}, H_{\text{vdW}}] = 0, \quad (7.22c)$$

$$[S_{pz,A} + S_{pz,B}, H_{\text{LS}}] = 0, \quad (7.22d)$$

$$[S_{pz,A} + S_{pz,B}, H_{\text{HFS}}] = 0, \quad (7.22e)$$

$$[S_{pz,A} + S_{pz,B}, H_{\text{vdW}}] = 0. \quad (7.22f)$$

From Eqs. (7.16), (7.18), (7.19), and (7.22a)-(7.22f), we can conclude that the total angular momentum of the system containing two electrically neutral hydrogen atoms

commutes with the total Hamiltonian of the system i.e.

$$[F_z, H] = 0. \quad (7.23)$$

This clearly states that the total angular momentum F_z is a constant of motion [64].

7.3. HYPERFINE-RESOLVED BASIS STATES

The Hyperfine splitting and the Lamb shift are of the same order to the vdW interaction for $R > 100a_0$, where R is the interatomic distance. However, the fine structure energy shift E_{FS} is

$$E_{FS} = E(2P_{3/2}) - E(2S_{1/2}) \approx 10 \times E_{LS}. \quad (7.24)$$

In comparison to the $2P_{1/2}$ -state, the $2P_{3/2}$ -state is heavily displaced from the $2S_{1/2}$ -state (see Figure 7.1). Thus, we can neglect the influence of the $2P_{3/2}$ -state. In other words, we concentrate only on the effects of the hyperfine splitting, the fine structure, and the vdW interaction on the $2S$ - $2S$ system.

If ℓ , j , and F are the orbital angular momentum quantum number, the total electronic angular quantum number, and the total atomic quantum number, j is $\frac{1}{2}$ and ℓ takes value $\ell = 0$ for the $2S_{1/2}$ and $\ell = 1$ for the $2P_{1/2}$. However, F holds

$$\left| \frac{1}{2} - \frac{1}{2} \right| \leq F \leq \left| \frac{1}{2} + \frac{1}{2} \right|, \quad (7.25)$$

which indicates that F takes either 0 or 1. By the definition of the multiplicity,

$$g_F = 2F + 1, \quad (7.26)$$

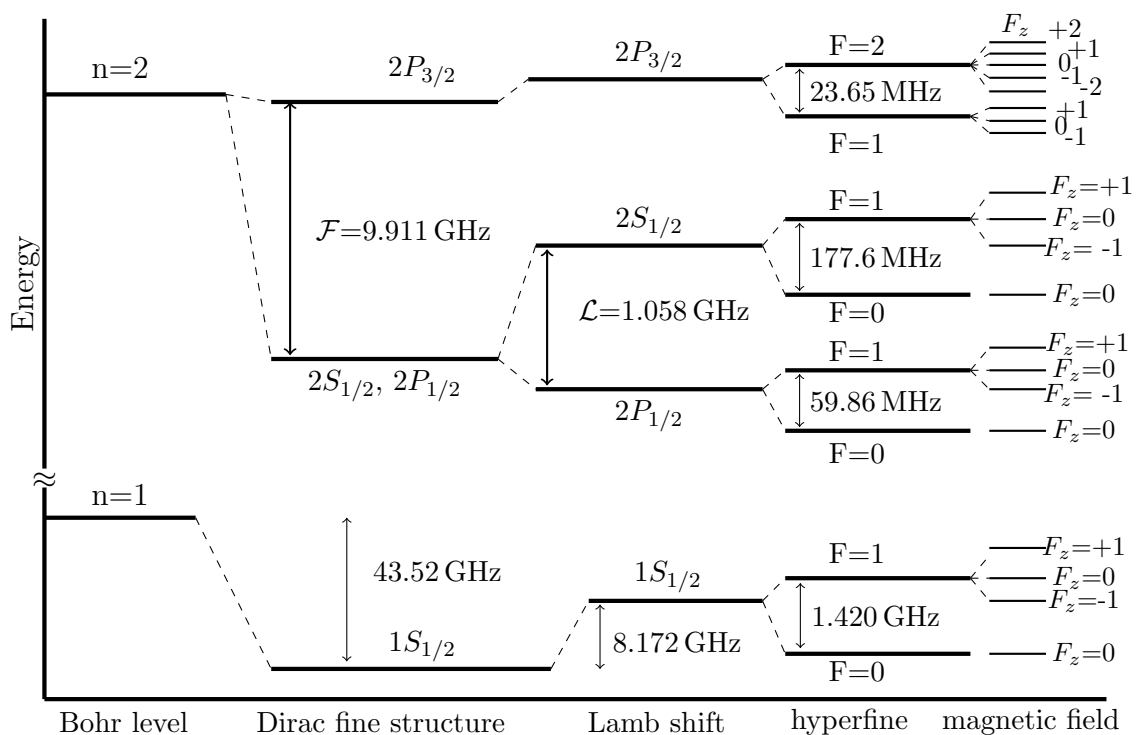


Figure 7.1: Fine and hyperfine levels of the hydrogen atom for $n=1, 2$. Here, \mathcal{L} and \mathcal{F} represent the Lamb shift and fine structure, F stands for the hyperfine quantum number and F_z indicates the z -component of the hyperfine quantum number, where z -axis is the axis of quantization. The numerical values presented in this figure are taken from Refs. [4; 5; 6; 7; 8; 9]. The spacing between the levels is not well scaled. In other words, some closed levels are also spaced widely for better visibility.

the ($F = 0$)-state is a singlet and the ($F = 1$)-state is a triplet. There are 8 states per atoms, viz. one state corresponding to the $2S_{1/2}$ -state with $F = 0$, three states corresponding to the $2S_{1/2}$ -state with $F = 1$, one state corresponding to the $2P_{1/2}$ -state with $F = 0$, and three states corresponding to the $2P_{1/2}$ -state with $F = 1$. For the two-hydrogen atoms system, there are $8 \times 8 = 64$ states. Let $F_z = F_{z,A} + F_{z,B}$ be the total hyperfine quantum number of the 64-dimensional Hilbert space. As F_z of either atom can have values 1, 0, or -1 , the total hyperfine quantum number takes values

$$F_z = -2, -1, 0, +1, +2. \quad (7.27)$$

Let us denote the eigenstates of the unperturbed Hamiltonian

$$H_0 = H_{\text{HFS},A} + H_{\text{HFS},B} + H_{\text{LS},A} + H_{\text{LS},B}, \quad (7.28)$$

of the system as $|\ell, F, F_z\rangle$. Let us first analyze the basis sets considering only the electronic contribution. The total angular quantum number j and the total magnetic projection quantum number μ are given by

$$j = \ell + \frac{1}{2} \quad \text{and} \quad \mu = m \pm \frac{1}{2}, \quad (7.29)$$

where ℓ is 0 for S -state and 1 for P -state. The magnetic projection quantum number m ranges from $-\ell$ to ℓ . Let us denote the electronic basis state by $|j, \ell, \mu\rangle$ which can be expressed in terms of the orbital angular momentum and the spin angular momentum with the help of Clebsch-Gordan coefficients as

$$|j, \ell, \mu\rangle = \sum_{m=-\ell}^{\ell} \sum_{\sigma=\pm\frac{1}{2}} C_{\ell m \frac{1}{2}\sigma}^{\frac{1}{2}\mu} |\ell, m\rangle |\frac{1}{2}, \sigma\rangle. \quad (7.30)$$

As we ignore the influence of the $2P_{3/2}$ -state, we consider only the value $j = \frac{1}{2}$. We then have

$$|\frac{1}{2}, \ell, \mu\rangle = \sum_{m=-\ell}^{\ell} \sum_{\sigma=\pm\frac{1}{2}} C_{\ell m \frac{1}{2} \sigma}^{\frac{1}{2} \mu} |\ell, m\rangle |\frac{1}{2}, \sigma\rangle. \quad (7.31)$$

For $\ell = 0$, the total magnetic projection number μ can take either $+\frac{1}{2}$ or $-\frac{1}{2}$.

$$|\frac{1}{2}, 0, \frac{1}{2}\rangle = C_{00\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} |0, 0\rangle |\frac{1}{2}, \frac{1}{2}\rangle = |0, 0\rangle |\frac{1}{2}, \frac{1}{2}\rangle \equiv |0, 0\rangle_e |+\rangle_e. \quad (7.32a)$$

$$|\frac{1}{2}, 0, -\frac{1}{2}\rangle = C_{00\frac{1}{2}-\frac{1}{2}}^{\frac{1}{2}-\frac{1}{2}} |0, 0\rangle |\frac{1}{2}, -\frac{1}{2}\rangle = |0, 0\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \equiv |0, 0\rangle_e |-\rangle_e. \quad (7.32b)$$

For $\ell = 1$, m can have any one value of 1, 0, or -1. However, the condition $m \pm \frac{1}{2} = \mu$ is satisfied.

$$\begin{aligned} |\frac{1}{2}, 1, \frac{1}{2}\rangle &= \sum_{m=-1}^1 C_{1m\frac{1}{2}\sigma}^{\frac{1}{2}\frac{1}{2}} |1, m\rangle |\frac{1}{2}, \sigma\rangle \\ &= C_{10\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} |1, 0\rangle |\frac{1}{2}, \frac{1}{2}\rangle + C_{11\frac{1}{2}-\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}} |1, 1\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \\ &= -\frac{1}{\sqrt{3}} |1, 0\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |1, 1\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \\ &\equiv -\frac{1}{\sqrt{3}} |1, 0\rangle_e |+\rangle_e + \sqrt{\frac{2}{3}} |1, 1\rangle_e |-\rangle_e. \end{aligned} \quad (7.33a)$$

$$\begin{aligned} |\frac{1}{2}, 1, -\frac{1}{2}\rangle &= \sum_{m=-1}^1 C_{1m\frac{1}{2}\sigma}^{\frac{1}{2}-\frac{1}{2}} |1, m\rangle |\frac{1}{2}, \sigma\rangle \\ &= C_{1-1\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}-\frac{1}{2}} |1, -1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + C_{10\frac{1}{2}-\frac{1}{2}}^{\frac{1}{2}-\frac{1}{2}} |1, 0\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \\ &= -\sqrt{\frac{2}{3}} |1, -1\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |1, 0\rangle |\frac{1}{2}, -\frac{1}{2}\rangle \\ &\equiv \frac{1}{\sqrt{3}} |1, 0\rangle_e |-\rangle_e - \sqrt{\frac{2}{3}} |1, -1\rangle_e |+\rangle_e. \end{aligned} \quad (7.33b)$$

We add the proton spin to compute the hyperfine basis set of a single atom. As the spin of the proton of the hydrogen atom exerts a torque on the electron revolving

around it producing magnetic dipole field, the set of observables (J, S_p, m_J, m_p) can not be the CSCO anymore. Here, J and S_p are the total electronic angular momentum and the spin angular momentum of the proton whereas m_J and m_p are the magnetic projections of J and S_p . On the other hand, the total angular momentum of the system $\vec{F} = \vec{J} + \vec{S}_p$ and its z-component are conserved. In our case, the allowed values of F are

$$\begin{aligned} F &= \left| \frac{1}{2} - S_p \right|, \dots, \left| \frac{1}{2} + S_p \right| \\ &= 0 \text{ and } 1, \end{aligned} \quad (7.34)$$

whereas F_z varies from $-F$, $-F + 1$, ..., F . Let us denote the state vectors by $|\ell, F, F_z\rangle$. In our system, $\ell = 0$ and $\ell = 1$ refer to the $2S_{1/2}$ and $2P_{1/2}$ states respectively. $F = 0$ and $F = 1$ respectively indicate the hyperfine singlet and hyperfine triplet whereas F_z , the z-component of the total angular momentum of the system, is the magnetic projection of F . Then we have

$$\begin{aligned} |\ell, F, F_z\rangle &= \sum_{\mu=-j}^j \sum_{\beta=-i}^i C_{j\mu i\beta}^{FF_z} |j, \ell, \mu\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\ &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{FF_z} \left| \frac{1}{2}, \ell, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p, \end{aligned} \quad (7.35)$$

provided $\frac{1}{2} + \mu = F$ is satisfied. For S -states $|\ell, F, F_z\rangle = |0, F, F_z\rangle$.

For $\ell = 0$, $F = 0$ and $F_z = 0$,

$$\begin{aligned} |0, 0, 0\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{00} \left| \frac{1}{2}, 0, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\ &= C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{00} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + C_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{00} \left| \frac{1}{2}, 0, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\ &= -\frac{1}{\sqrt{2}} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 0, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \end{aligned}$$

$$\equiv \frac{1}{\sqrt{2}} \left(|+\rangle_e |-\rangle_p - |-\rangle_e |+\rangle_p \right) |0, 0\rangle_e. \quad (7.36)$$

For $\ell = 0$, $F = 1$ and $F_z = 1$,

$$\begin{aligned} |0, 1, 1\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{11} \left| \frac{1}{2}, 0, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p = C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{11} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\ &= \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \equiv |+\rangle_e |+\rangle_p |0, 0\rangle_e. \end{aligned} \quad (7.37)$$

For $\ell = 0$, $F = 1$ and $F_z = 0$,

$$\begin{aligned} |0, 1, 0\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{10} \left| \frac{1}{2}, 0, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\ &= C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{00} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{00} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\ &= \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 0, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\ &\equiv \frac{1}{\sqrt{2}} \left(|-\rangle_e |+\rangle_p + |+\rangle_e |-\rangle_p \right) |0, 0\rangle_e. \end{aligned} \quad (7.38)$$

For $\ell = 0$, $F = 1$ and $F_z = -1$,

$$\begin{aligned} |0, 1, -1\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{1-1} \left| \frac{1}{2}, 0, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p = C_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{1-1} \left| \frac{1}{2}, 0, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\ &= \left| \frac{1}{2}, 0, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \equiv |-\rangle_e |-\rangle_p |0, 0\rangle_e. \end{aligned} \quad (7.39)$$

For $\ell = 1$, $F = 0$ and $F_z = 0$,

$$\begin{aligned} |1, 0, 0\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{00} \left| \frac{1}{2}, 1, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\ &= C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{00} \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + C_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{00} \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\ &= \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p - \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{2}} \left(-\frac{1}{\sqrt{3}} |1, 0\rangle_e |+\rangle_e + \sqrt{\frac{2}{3}} |1, 1\rangle_e |-\rangle_e \right) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\
&\quad - \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{3}} |1, 0\rangle_e |-\rangle_e - \sqrt{\frac{2}{3}} |1, -1\rangle_e |+\rangle_e \right) \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&\equiv \frac{1}{\sqrt{3}} |+\rangle_e |+\rangle_p |1, -1\rangle_e - \frac{1}{\sqrt{6}} |-\rangle_e |+\rangle_p |1, 0\rangle_e \\
&\quad + \frac{1}{\sqrt{3}} |-\rangle_e |-\rangle_p |1, 1\rangle_e - \frac{1}{\sqrt{6}} |+\rangle_e |-\rangle_p |1, 0\rangle_e. \tag{7.40}
\end{aligned}$$

There are four P -states in which $|\ell, F, F_z\rangle = |1, F, F_z\rangle$. For $\ell = 1$, $F = 1$ and $F_z = 1$,

$$\begin{aligned}
|1, 1, 1\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{11} \left| \frac{1}{2}, 1, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\
&= C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{11} \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p = \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&= \left(-\frac{1}{\sqrt{3}} |1, 0\rangle_e |+\rangle_e + \sqrt{\frac{2}{3}} |1, 1\rangle_e |-\rangle_e \right) \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&\equiv -\frac{1}{\sqrt{3}} |+\rangle_e |+\rangle_p |1, 0\rangle_e + \sqrt{\frac{2}{3}} |-\rangle_e |+\rangle_p |1, 1\rangle_e. \tag{7.41}
\end{aligned}$$

For $\ell = 1$, $F = 1$ and $F_z = 0$,

$$\begin{aligned}
|1, 1, 0\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{10} \left| \frac{1}{2}, 1, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\
&= C_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{10} \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + C_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{10} \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&= \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 1, \frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p + \frac{1}{\sqrt{2}} \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&= \frac{1}{\sqrt{2}} \left(-\frac{1}{\sqrt{3}} |1, 0\rangle_e |+\rangle_e + \sqrt{\frac{2}{3}} |1, 1\rangle_e |-\rangle_e \right) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\
&\quad + \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{3}} |1, 0\rangle_e |-\rangle_e - \sqrt{\frac{2}{3}} |1, -1\rangle_e |+\rangle_e \right) \left| \frac{1}{2}, \frac{1}{2} \right\rangle_p \\
&\equiv -\frac{1}{\sqrt{3}} |+\rangle_e |+\rangle_p |1, -1\rangle_e + \frac{1}{\sqrt{6}} |-\rangle_e |+\rangle_p |1, 0\rangle_e \\
&\quad + \frac{1}{\sqrt{3}} |-\rangle_e |-\rangle_p |1, 1\rangle_e - \frac{1}{\sqrt{6}} |+\rangle_e |-\rangle_p |1, 0\rangle_e. \tag{7.42}
\end{aligned}$$

Finally, for $\ell = 1$, $F = 1$ and $F_z = -1$,

$$\begin{aligned}
|1, 1, -1\rangle &= \sum_{\mu=\pm\frac{1}{2}} \sum_{\beta=\pm\frac{1}{2}} C_{\frac{1}{2}\mu\frac{1}{2}\beta}^{1-1} \left| \frac{1}{2}, 1, \mu \right\rangle_e \left| \frac{1}{2}, \beta \right\rangle_p \\
&= C_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}}^{1-1} \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\
&= \left| \frac{1}{2}, 1, -\frac{1}{2} \right\rangle_e \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\
&= \left(\frac{1}{\sqrt{3}} |1, 0\rangle_e |-\rangle_e - \sqrt{\frac{2}{3}} |1, -1\rangle_e |+\rangle_e \right) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_p \\
&\equiv \frac{1}{\sqrt{3}} |-\rangle_e |-\rangle_p |1, 0\rangle_e - \sqrt{\frac{2}{3}} |+\rangle_e |-\rangle_p |1, -1\rangle_e. \tag{7.43}
\end{aligned}$$

These 8 states, namely 4 S -states and 4 P -states given by Eqs. (7.36) - (7.43), serve as the single-atom hyperfine basis states.

7.4. MATRIX ELEMENTS OF ELECTRONIC POSITION OPERATORS

We use the definition of the spherical unit vectors as defined in Ref. [65].

$$\hat{e}_+ = -\frac{1}{\sqrt{2}} (\hat{e}_x + i\hat{e}_y) \tag{7.44a}$$

$$\hat{e}_0 = \hat{e}_z \tag{7.44b}$$

$$\hat{e}_- = \frac{1}{\sqrt{2}} (\hat{e}_x - i\hat{e}_y) \tag{7.44c}$$

Let us evaluate few r -matrix elements.

$$\begin{aligned}
\langle 0, 0, 0 | \vec{r} | 1, 1, 0 \rangle &= \left[\frac{1}{\sqrt{2}} \left(e \langle + |_p \langle - | - e \langle - |_p \langle + | \right) e \langle 00 | \right] \vec{r} \left[-\frac{1}{\sqrt{3}} |+\rangle_e |+\rangle_p |1, -1\rangle_e \right. \\
&\quad \left. + \frac{1}{\sqrt{6}} |-\rangle_e |+\rangle_p |1, 0\rangle_e + \frac{1}{\sqrt{3}} |-\rangle_e |-\rangle_p |1, 1\rangle_e + \frac{1}{\sqrt{6}} |+\rangle_e |-\rangle_p |1, 0\rangle_e \right] \\
&= \frac{1}{\sqrt{2}} \left(-\frac{1}{\sqrt{6}} \right) e \langle 00 | \vec{r} | 1, 0 \rangle_e - \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{6}} \right) e \langle 00 | \vec{r} | 1, 0 \rangle_e \\
&= -\frac{1}{\sqrt{3}} e \langle 00 | \vec{r} | 1, 0 \rangle_e = -\frac{1}{\sqrt{3}} (-3a_0 \hat{e}_z) = \sqrt{3} a_0 \hat{e}_z. \tag{7.45}
\end{aligned}$$

$$\begin{aligned}
\langle 0, 0, 0 | \vec{r} | 1, 1, \pm 1 \rangle &= \left[\frac{1}{\sqrt{2}} \left(e \langle + |_p \langle - | - e \langle - |_p \langle + | \right) e \langle 00 | \right] \vec{r} \left[\mp \frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, 0 \rangle_e \right. \\
&\quad \left. \pm \sqrt{\frac{2}{3}} | - \rangle_e | + \rangle_p | 1 \pm 1 \rangle_e \right] \\
&= -\frac{1}{\sqrt{3}} e \langle 00 | \vec{r} | 1 \pm 1 \rangle_e = -\frac{1}{\sqrt{3}} \left(\frac{3a_0}{\sqrt{2}} \hat{e}_x \pm \frac{3a_0 i}{\sqrt{2}} \hat{e}_y \right) = \sqrt{3} a_0 \hat{e}_\pm. \quad (7.46)
\end{aligned}$$

$$\begin{aligned}
\langle 0, 1, 0 | \vec{r} | 1, 0, 0 \rangle &= \left[\frac{1}{\sqrt{2}} \left(e \langle - |_p \langle + | + e \langle + |_p \langle - | \right) e \langle 00 | \right] \vec{r} \left[\frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, -1 \rangle_e \right. \\
&\quad \left. - \frac{1}{\sqrt{6}} | - \rangle_e | + \rangle_p | 1, 0 \rangle_e + \frac{1}{\sqrt{3}} | - \rangle_e | - \rangle_p | 1, 1 \rangle_e - \frac{1}{\sqrt{6}} | + \rangle_e | - \rangle_p | 1, 0 \rangle_e \right] \\
&= -\frac{1}{\sqrt{12}} e \langle 00 | \vec{r} | 1, 0 \rangle_e - \frac{1}{\sqrt{12}} e \langle 00 | \vec{r} | 1, 0 \rangle_e \\
&= -\frac{1}{\sqrt{3}} e \langle 00 | \vec{r} | 1, 0 \rangle_e = -\frac{1}{\sqrt{3}} (-3 a_0 \hat{e}_z) = \sqrt{3} a_0 \hat{e}_z. \quad (7.47)
\end{aligned}$$

$$\begin{aligned}
\langle 0, 1, \pm 1 | \vec{r} | 1, 0, 0 \rangle &= \left[e \langle \pm |_p \langle \pm |_e \langle 00 | \right] \vec{r} \left[\frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, -1 \rangle_e - \frac{1}{\sqrt{6}} | - \rangle_e | + \rangle_p | 1, 0 \rangle_e \right. \\
&\quad \left. + \frac{1}{\sqrt{3}} | - \rangle_e | - \rangle_p | 1, 1 \rangle_e - \frac{1}{\sqrt{6}} | + \rangle_e | - \rangle_p | 1, 0 \rangle_e \right] \\
&= \frac{1}{\sqrt{3}} e \langle 00 | \vec{r} | 1 \mp 1 \rangle_e = \frac{1}{\sqrt{3}} \frac{3a_0}{\sqrt{2}} (\mp \hat{e}_x + i \hat{e}_y) \\
&= \sqrt{3} a_0 \left[\mp \frac{1}{\sqrt{2}} (\hat{e}_x \mp i \hat{e}_y) \right] = \sqrt{3} a_0 (\hat{e}_\pm)^*. \quad (7.48)
\end{aligned}$$

$$\begin{aligned}
\langle 0, 1, \pm 1 | \vec{r} | 1, 1, \pm 1 \rangle &= \left[e \langle \pm |_p \langle \pm |_e \langle 00 | \right] \vec{r} \left[\mp \frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, 0 \rangle_e \pm \sqrt{\frac{2}{3}} | - \rangle_e | + \rangle_p | 1 \pm 1 \rangle_e \right] \\
&= \mp \frac{1}{\sqrt{3}} e \langle 00 | \vec{r} | 1, 0 \rangle_e = \mp \frac{1}{\sqrt{3}} (-3 a_0 \hat{e}_z) = \pm \sqrt{3} a_0 \hat{e}_z. \quad (7.49)
\end{aligned}$$

$$\begin{aligned}
\langle 0, 1, \pm 1 | \vec{r} | 1, 1, 0 \rangle &= \left[e \langle \pm |_p \langle \pm |_e \langle 00 | \right] \vec{r} \left[-\frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, -1 \rangle_e + \frac{1}{\sqrt{6}} | - \rangle_e | + \rangle_p | 1, 0 \rangle_e \right. \\
&\quad \left. + \frac{1}{\sqrt{3}} | - \rangle_e | - \rangle_p | 1, 1 \rangle_e + \frac{1}{\sqrt{6}} | + \rangle_e | - \rangle_p | 1, 0 \rangle_e \right]
\end{aligned}$$

$$= \mp \frac{1}{\sqrt{3}} {}_e\langle 00 | \vec{r} | 1 \mp 1 \rangle_e = \mp \frac{1}{\sqrt{3}} \frac{3a_0}{\sqrt{2}} (\mp \hat{e}_x + i \hat{e}_y) = \pm \sqrt{3} a_0 \hat{e}_{\mp}. \quad (7.50)$$

$$\begin{aligned} \langle 0, 1, 0 | \vec{r} | 1, 1, \pm 1 \rangle &= \left[\frac{1}{\sqrt{2}} \left({}_e\langle - | {}_p\langle + | + {}_e\langle + | {}_p\langle - | \right) {}_e\langle 00 | \right] \vec{r} \left[\mp \frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, 0 \rangle_e \right. \\ &\quad \left. \pm \sqrt{\frac{2}{3}} | - \rangle_e | + \rangle_p | 1 \pm 1 \rangle_e \right] \\ &= \pm \frac{1}{\sqrt{3}} {}_e\langle 00 | \vec{r} | 1 \pm 1 \rangle_e = \pm \frac{1}{\sqrt{3}} \frac{3a_0}{\sqrt{2}} \left(\pm \hat{e}_x + i \hat{e}_y \right) \\ &= \mp \sqrt{3} a_0 \left(-\frac{1}{2} (\pm \hat{e}_x + i \hat{e}_y) \right) = \mp \sqrt{3} a_0 \hat{e}_{\pm}. \end{aligned} \quad (7.51)$$

All the other r -matrix elements are zero. For example,

$$\begin{aligned} \langle 1, 1, \pm | \vec{r} | 1, 1, \pm 1 \rangle &= \left[\mp \frac{1}{\sqrt{3}} {}_e\langle + | {}_p\langle + | + {}_e\langle 10 | \pm \sqrt{\frac{2}{3}} {}_e\langle - | {}_p\langle + | + {}_e\langle 1 \pm 1 | \right] \\ &\quad \vec{r} \left[\mp \frac{1}{\sqrt{3}} | + \rangle_e | + \rangle_p | 1, 0 \rangle_e \pm \sqrt{\frac{2}{3}} | - \rangle_e | + \rangle_p | 1 \pm 1 \rangle_e \right] \\ &= \frac{1}{3} {}_e\langle 10 | \vec{r} | 1, 0 \rangle_e + \frac{2}{3} {}_e\langle 1 \pm 1 | \vec{r} | 1 \pm 1 \rangle_e = 0, \end{aligned} \quad (7.52a)$$

$$\begin{aligned} \langle 0, 0, 0 | \vec{r} | 0, 0, 0 \rangle &= \left[\frac{1}{\sqrt{2}} \left({}_e\langle + | {}_p\langle - | - {}_e\langle - | {}_p\langle + | \right) {}_e\langle 00 | \right] \\ &\quad \vec{r} \left[\frac{1}{\sqrt{2}} \left(| + \rangle_e | - \rangle_p - | - \rangle_e | + \rangle_p \right) | 0, 0 \rangle_e \right] = {}_e\langle 00 | \vec{r} | 0, 0 \rangle_e = 0, \end{aligned} \quad (7.52b)$$

and so on.

7.5. SCALING PARAMETERS

For the sake of simplicity, we define the following parameters

$$\mathcal{H} \equiv \frac{\alpha^4}{18} g_p \frac{m^2}{M} c^2, \quad (7.53)$$

$$\mathcal{L} \equiv \frac{\alpha^5}{6\pi} \ln \left(\frac{1}{\alpha^2} \right) mc^2, \quad (7.54)$$

$$\mathcal{V} \equiv \alpha \hbar c \frac{a_0^2}{R^3}, \quad (7.55)$$

which we use to scale the expectation values of the hyperfine Hamiltonian, the Lamb shift and the vdW interaction. Substituting the values of the fine-structure constant, g-factor of the proton, masses of the electron and the proton, and the speed of light, the hyperfine splitting constant \mathcal{H} works out to

$$\mathcal{H} = 3.924 \times 10^{-26} J \equiv 5.921 \times 10^7 Hz. \quad (7.56)$$

In terms of \mathcal{H} , the Lamb shift \mathcal{L} and the vdW interaction \mathcal{V} are given as

$$\mathcal{L} = 17.873 \mathcal{H}, \quad (7.57a)$$

$$\mathcal{V} = \frac{4.942 \times 10^{-23}}{R^3} \mathcal{H}. \quad (7.57b)$$

The expectation value of the Lamb shift Hamiltonian amounts to \mathcal{L} and it is nonzero only if both atoms are in the S -states, i.e.,

$$\langle \ell, F, M_F | H_{\text{LS}} | \ell, F, M_F \rangle = \mathcal{L} \delta_{\ell 0}. \quad (7.58)$$

The hyperfine triplets corresponding to the $2P_{1/2}$ are displaced from the corresponding hyperfine singlet by \mathcal{H} , whereas the hyperfine triplet corresponding to the $2S_{1/2}$ is displaced by $3\mathcal{H}$ from the corresponding hyperfine singlet. The triplet is lifted upward and the singlet is pushed downward [66]. Thus, we have

$$\langle 0, 1, M_F | H_{\text{HFS}} | 0, 1, M_F \rangle = \frac{3}{4} \mathcal{H}, \quad (7.59a)$$

$$\langle 1, 1, M_F | H_{\text{HFS}} | 1, 1, M_F \rangle = \frac{1}{4} \mathcal{H}, \quad (7.59b)$$

$$\langle 0, 0, 0 | H_{\text{HFS}} | 0, 0, 0 \rangle = -\frac{9}{4} \mathcal{H}, \quad (7.59c)$$

$$\langle 1, 0, 0 | H_{\text{HFS}} | 1, 0, 0 \rangle = -\frac{3}{4} \mathcal{H}. \quad (7.59d)$$

7.6. GRAPH THEORY (ADJACENCY GRAPH)

In the graph theory, an adjacency graph [67; 68] is a diagrammatic representation of a square matrix whose elements are boolean values. One vertex can be connected to the other vertex by one, or more than one edge. A vertex can be connected to itself as well. If each vertex is connected to every other vertex in some number of steps, then the graph is said to be connected. However, if two vertices are not connected at all, they do not talk with each other. The adjacency matrix corresponding to the undirected graph is symmetric in nature. Note that the eigenvalues of a symmetric matrix are real and it is always possible to get orthonormal eigenvectors [69].

The non-negative power A^k of an adjacency matrix tells us about the number of paths of length k of its elements. For example, $(A^k)_{mn}$ is the count of paths of length k from m to n . The sum $\sum_{i=1}^k A^i$, which depicts the number of paths of length ranging from 1 to k between every pair of vertices, possesses impressive feature. If the final matrix obtained from the sum contains all the nonzero entries, this means the matrix is irreducible. In other words, if the sum contains any zero entries it indicates that the matrix can be reduced into irreducible matrices. The power A^2 is of particular importance. It not only counts the number of paths of length 2 of its entries but also tells us about the connectedness of the corresponding adjacency graph.

The adjacency graph G corresponding to an adjacency matrix A of order n is disconnected if and only if there exists a square matrix $S = A^2$ of order n such that the matrix S can be written as

$$S = \begin{pmatrix} B_{k \times k} & : & 0 \\ \dots & : & \dots \\ 0 & : & C_{(n-k) \times (n-k)} \end{pmatrix}. \quad (7.60)$$

Detailed mathematical proof of the statement of disconnectivity is given in theorem 1.6 of Ref. [70]. The adjacency matrix A containing two disconnected components can be split-up as

$$A = \begin{pmatrix} A(G_1) & : & 0 \\ \cdot & : & \cdot \\ 0 & : & A(G_2) \end{pmatrix}, \quad (7.61)$$

where $A(G_1)$ and $A(G_2)$ stand for the adjacency matrices of the components of the adjacency graphs G_1 and G_2 . The components G_1 and G_2 do not share any edges between their vertices. Thus, there is no coupling between them. In later sections, we will notice that the adjacency graph is very useful to express a hyperfine subspace into two irreducible subspaces.

7.7. HAMILTONIAN MATRICES IN THE HYPERFINE SUBSPACES

As we already mentioned, the 64-dimensional Hilbert space has five manifolds namely, $F_z = +2$, $F_z = +1$, $F_z = 0$, $F_z = -1$, and $F_z = -2$. The $F_z = +2$ and the $F_z = -2$ manifolds are 4-dimensional, the $F_z = +1$ and the $F_z = -1$ manifolds are 16-dimensional, and $F_z = 0$ manifold is 24-dimensional. We analyze all these manifolds separately.

7.7.1. Manifold $F_z = +2$. The four states in the $F_z = +2$ manifold, in the ascending order of quantum numbers, are

$$\begin{aligned} |\phi_1\rangle &= |(0, 1, 1)_A(0, 1, 1)_B\rangle, & |\phi_2\rangle &= |(0, 1, 1)_A(1, 1, 1)_B\rangle, \\ |\phi_3\rangle &= |(1, 1, 1)_A(0, 1, 1)_B\rangle, & |\phi_4\rangle &= |(1, 1, 1)_A(1, 1, 1)_B\rangle. \end{aligned} \quad (7.62)$$

The first element of the matrix $\langle \phi_1 | H | \phi_1 \rangle$ is given by

$$\begin{aligned}
\langle \phi_1 | H | \phi_1 \rangle &= \langle (0, 1, 1)_A (0, 1, 1)_B | H | (0, 1, 1)_A (0, 1, 1)_B \rangle \\
&= {}_{e,A} \langle + | {}_{p,A} \langle + | {}_{e,A} \langle 0, 0 | {}_{e,B} \langle + | {}_{p,B} \langle + | {}_{e,B} \langle 0, 0 | H | + \rangle_{e,A} \\
&\quad \times | + \rangle_{p,A} | 0, 0 \rangle_{e,A} | + \rangle_{e,B} | + \rangle_{p,B} | 0, 0 \rangle_{e,B}, \tag{7.63}
\end{aligned}$$

where $H = H_{\text{LS}, A} + H_{\text{LS}, B} + H_{\text{HFS}, A} + H_{\text{HFS}, B} + H_{\text{vdW}}$. The Lamb shift due to each of the $H_{\text{LS}, A}$ and $H_{\text{LS}, B}$ is \mathcal{L} and the hyperfine splitting due to each of the $H_{\text{HFS}, A}$ and $H_{\text{HFS}, B}$ is $\frac{3}{4}\mathcal{H}$, whereas the vdW interaction does not contribute anything to the diagonal element. Thus, we have

$$\langle \phi_1 | H | \phi_1 \rangle = \frac{3}{2}\mathcal{H} + 2\mathcal{L}. \tag{7.64}$$

The matrix element $\langle \phi_1 | H | \phi_2 \rangle$ is given by

$$\begin{aligned}
\langle \phi_1 | H | \phi_2 \rangle &= \langle (0, 1, 1)_A (0, 1, 1)_B | H | (0, 1, 1)_A (1, 1, 1)_B \rangle \\
&= {}_{e,A} \langle + | {}_{p,A} \langle + | {}_{e,A} \langle 0, 0 | {}_{e,B} \langle + | {}_{p,B} \langle + | {}_{e,B} \langle 0, 0 | H | + \rangle_{e,A} | + \rangle_{p,A} | 0, 0 \rangle_{e,A} \\
&\quad \times \left[-\frac{1}{\sqrt{3}} | + \rangle_{e,B} | + \rangle_{p,B} | 1, 0 \rangle_{e,B} + \sqrt{\frac{2}{3}} | - \rangle_{e,B} | + \rangle_{p,B} | 1, 1 \rangle_{e,B} \right], \tag{7.65}
\end{aligned}$$

The orthogonality relation ${}_{e,B} \langle 0, 0 | 1, 0 \rangle_{e,B} = 0$ requires that the right-hand side of Eq. (7.68) should vanish.

$$\langle \phi_1 | H | \phi_2 \rangle = 0 = (\langle \phi_2 | H | \phi_1 \rangle)^* = \langle \phi_2 | H | \phi_1 \rangle \tag{7.66}$$

Swapping A and B in $\langle \phi_1 | H | \phi_2 \rangle$, we get $\langle \phi_1 | H | \phi_3 \rangle$. Thus, it is straightforward to note that

$$\langle \phi_1 | H | \phi_3 \rangle = 0 = \langle \phi_3 | H | \phi_1 \rangle. \tag{7.67}$$

The matrix element $\langle \phi_1 | H | \phi_4 \rangle$ is given by

$$\begin{aligned}
\langle \phi_1 | H | \phi_4 \rangle &= \langle (0, 1, 1)_A (0, 1, 1)_B | H | (1, 1, 1)_A (1, 1, 1)_B \rangle \\
&= {}_{e,A} \langle + | {}_{p,A} \langle + | {}_{e,A} \langle 0, 0 | {}_{e,B} \langle + | {}_{p,B} \langle + | {}_{e,B} \langle 0, 0 | \\
&\quad H \left[-\frac{1}{\sqrt{3}} |+\rangle_{e,A} |+\rangle_{p,A} |1, 0\rangle_{e,A} + \sqrt{\frac{2}{3}} |-\rangle_{e,A} |+\rangle_{p,A} |1, 1\rangle_{e,A} \right] \\
&\quad \left[-\frac{1}{\sqrt{3}} |+\rangle_{e,B} |+\rangle_{p,B} |1, 0\rangle_{e,B} + \sqrt{\frac{2}{3}} |-\rangle_{e,B} |+\rangle_{p,B} |1, 1\rangle_{e,B} \right] \\
&= \frac{1}{3} {}_{e,A} \langle 0, 0 | {}_{e,B} \langle 0, 0 | H_{\text{vdW}} |1, 0\rangle_{e,A} |1, 0\rangle_{e,B} \\
&= -2\mathcal{V} = \langle \phi_4 | H | \phi_1 \rangle. \tag{7.68}
\end{aligned}$$

In the similar manner, we determine all the element of the matrix $H_{(F_z=+2)}$, which reads

$$H_{(F_z=+2)} = \begin{pmatrix} \frac{3}{2}\mathcal{H} + 2\mathcal{L} & 0 & 0 & -2\mathcal{V} \\ 0 & \mathcal{H} + \mathcal{L} & -2\mathcal{V} & 0 \\ 0 & -2\mathcal{V} & \mathcal{H} + \mathcal{L} & 0 \\ -2\mathcal{V} & 0 & 0 & \frac{1}{2}\mathcal{H} \end{pmatrix}. \tag{7.69}$$

The adjacency matrix associated to the Hamiltonian matrix $H_{(F_z=+2)}$ is

$$A_{(F_z=+2)} = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix}, \tag{7.70}$$

which is obtained by the replacement of the nonzero entries of the matrix $H_{(F_z=+2)}$ by one. The adjacency graphs corresponding to adjacency matrix $A_{(F_z=+2)}$ is shown in Figure 7.2. With the help of the adjacency graph, we see that the $F_z = +2$ manifold



Figure 7.2: An adjacency graph of the matrix $A_{(F_z=+2)}$. The first diagonal entry, i.e., first vertex is adjacent to the fourth diagonal entry, i.e., fourth vertex and vice versa. The second diagonal element, i.e., the second vertex is adjacent to the third diagonal element, i.e., third vertex and vice versa. However, the two pieces of the graph do not share any edges between the vertices.

can be decomposed into two subspaces. The subspace (I) is composed of the states

$$|\phi_1^{(I)}\rangle = |\phi_1\rangle = |(0, 1, 1)_A(0, 1, 1)_B\rangle, \quad (7.71)$$

$$|\phi_2^{(I)}\rangle = |\phi_4\rangle = |(1, 1, 1)_A(1, 1, 1)_B\rangle, \quad (7.72)$$

in which atoms are in S - S or P - P configuration while the subspace (II) is composed of the states

$$|\phi_1^{(II)}\rangle = |\phi_2\rangle = |(0, 1, 1)_A(1, 1, 1)_B\rangle, \quad (7.73)$$

$$|\phi_2^{(II)}\rangle = |\phi_3\rangle = |(1, 1, 1)_A(0, 1, 1)_B\rangle, \quad (7.74)$$

in which atoms are in S - P or P - S configuration. These two subspaces do not couple to each other. The Hamiltonian matrix corresponding to the subspace (I) reads

$$H_{(F_z=+2)}^{(I)} = \begin{pmatrix} \frac{3}{2}\mathcal{H} + 2\mathcal{L} & -2\mathcal{V} \\ -2\mathcal{V} & \frac{1}{2}\mathcal{H} \end{pmatrix}. \quad (7.75)$$

In the subspace (I), the energy levels are non degenerate. The energy eigenvalues corresponding to the subspace (I) are given by

$$E^{(I)} = \mathcal{H} + \mathcal{L} \pm \frac{1}{2}\sqrt{16\mathcal{V}^2 + (\mathcal{H} + 2\mathcal{L})^2}, \quad (7.76)$$

Or,

$$E_+^{(I)} = \frac{3}{2}\mathcal{H} + 2\mathcal{L} + 4\frac{\mathcal{V}^2}{\mathcal{H} + 2\mathcal{L}} + O(\mathcal{V}^4), \quad (7.77a)$$

$$E_-^{(I)} = \frac{1}{2}\mathcal{H} - 4\frac{\mathcal{V}^2}{\mathcal{H} + 2\mathcal{L}} + O(\mathcal{V}^4). \quad (7.77b)$$

This clearly shows that the eigenvalues in the subspace (I) do not experience the first order shift in the vdW interaction \mathcal{V} , i.e., $\Delta E_{\pm}^{(I)} \sim R^{-6}$. From Eqs. (7.77), one can write

$$\Delta E_{\pm}^{(I)} \sim 4\frac{\mathcal{V}^2}{\mathcal{H} + 2\mathcal{L}}. \quad (7.78)$$

We have $\mathcal{H} \equiv 0.055949\mathcal{L}$, and in the atomic units $\mathcal{V} = 3/R^3$ and $\mathcal{L} \rightarrow \frac{\alpha^3}{6\pi} \ln(\alpha^{-2})$. Thus,

$$\Delta E_{\pm}^{(I)} \sim \frac{4 \times 9}{(0.055949\mathcal{L} + 2\mathcal{L}) R^6} \sim \frac{36 \times 6\pi}{2.055949 \alpha^3 \ln(\alpha^{-2}) R^6} \sim \frac{8 \times 10^7}{R^6}. \quad (7.79)$$

Recognizing $E = -C_6/R^6$, we find that the vdW coefficient, C_6 , for $2S(F=0) \rightarrow 2S(F=1)$ or $2P(F=0) \rightarrow 2P(F=1)$ hyperfine transition is in the order of 10^7 . The normalized eigenvectors associated to the eigenvalues $E_+^{(I)}$ and $E_+^{(II)}$ are

$$|\phi_+^{(I)}\rangle = \frac{1}{\sqrt{a_1^2 + a_2^2}} \left(a_1 |\phi_1^{(I)}\rangle + a_2 |\phi_2^{(I)}\rangle \right), \quad (7.80a)$$

$$|\phi_-^{(I)}\rangle = \frac{1}{\sqrt{a_1^2 + a_2^2}} \left(a_2 |\phi_1^{(I)}\rangle - a_1 |\phi_2^{(I)}\rangle \right). \quad (7.80b)$$

where a_1 and a_2 are given by

$$\begin{aligned} a_1 &= -\frac{\mathcal{H} + 2\mathcal{L} + \sqrt{16\mathcal{V}^2 + (\mathcal{H} + 2\mathcal{L})^2}}{4\mathcal{V}} \\ &= -\frac{\mathcal{H} + 2\mathcal{L}}{4\mathcal{V}} \left[1 + \left(1 + \frac{16\mathcal{V}^2}{(\mathcal{H} + 2\mathcal{L})^2} \right)^{1/2} \right] \end{aligned}$$

$$= -\frac{\mathcal{H} + 2\mathcal{L}}{2\mathcal{V}} \left(1 + \frac{4\mathcal{V}^2}{(\mathcal{H} + 2\mathcal{L})^2} \right) + O(\mathcal{V}^3), \quad (7.81a)$$

$$a_2 = 1. \quad (7.81b)$$

Note that for very large interatomic separation, $4\mathcal{V}^2/(\mathcal{H} + 2\mathcal{L})^2 \ll 1$ and hence, $|a_1| \approx (\mathcal{H} + 2\mathcal{L})/(2\mathcal{V}) \gg a_2 = 1$. The Hamiltonian matrix associated to the subspace (II) is

$$H_{(F_z=+2)}^{(\text{II})} = \begin{pmatrix} \mathcal{H} + \mathcal{L} & -2\mathcal{V} \\ -2\mathcal{V} & \mathcal{H} + \mathcal{L} \end{pmatrix}. \quad (7.82)$$

The energy levels are degenerate and coupled by the vdW interaction \mathcal{V} . The eigenenergies and eigenvectors of the Hamiltonian matrix $H_{(F_z=+2)}^{(\text{II})}$ are

$$E_{\pm}^{(\text{II})} = \mathcal{H} + \mathcal{L} \pm 2\mathcal{V}, \quad (7.83)$$

$$|\phi_{\pm}^{(\text{II})}\rangle = \frac{1}{\sqrt{2}} \left(|\phi_1^{(\text{II})}\rangle \pm |\phi_2^{(\text{II})}\rangle \right). \quad (7.84)$$

The shift in the eigenenergies of the subspace (II) are linearly dependent with the vdW interaction energy \mathcal{V} . More explicitly,

$$\Delta E_{\pm}^{(\text{II})} = 4\mathcal{V} \quad (7.85)$$

Thus, the hyperfine transition in the subspace (II) goes to R^{-3} . See Figure 7.3 for an evolution of energy levels as a function of interatomic distance in the $F_z = +2$ hyperfine manifold. For a sufficiently large interatomic distance, $\mathcal{V} \rightarrow 0$, and we have only three energy levels as expected from unperturbed energy values. However, as the interatomic distance decreases the vdW interaction comes into play and energy levels split and deviate from unperturbed values. The energy levels do not cross in the $F_z = +2$ hyperfine manifold.

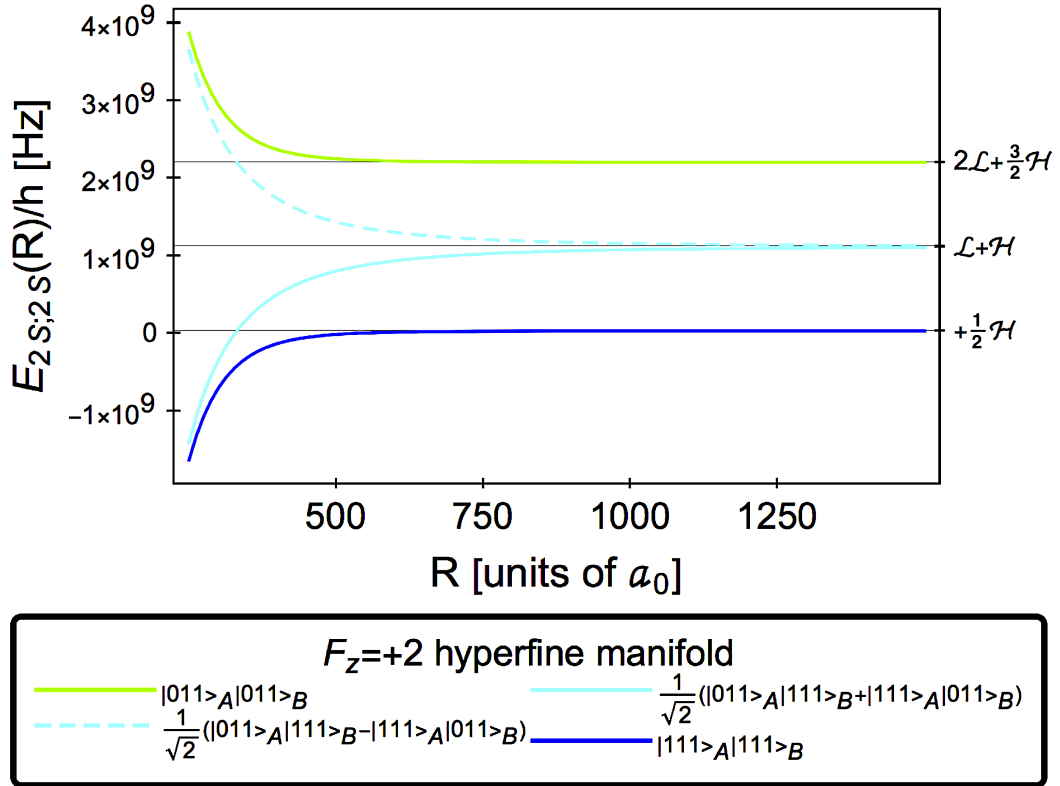


Figure 7.3: Energy levels as a function of interatomic separation R in the $F_z = +2$ hyperfine manifold. The horizontal axis which represents the interatomic distance is expressed in the unit of Bohr's radius, a_0 , and the vertical axis, which is the energy divided by the plank constant, is in hertz. The energy levels in the subspace (I) deviate heavily from their unperturbed values $\frac{1}{2}\mathcal{H}$ and $\frac{3}{2}\mathcal{H} + \mathcal{L}$ for $R < 500a_0$. The doubly degenerate energy level $\mathcal{L} + \mathcal{H}$ splits up into two levels, which repel each other as the interatomic distance decreases.

7.7.2. Manifold $F_z = +1$. The $F_z = +1$ manifold has 16 states as listed

below:

$$|\psi_1\rangle = |(0, 0, 0)_A (0, 1, 1)_B\rangle, \quad |\psi_2\rangle = |(0, 0, 0)_A (1, 1, 1)_B\rangle,$$

$$|\psi_3\rangle = |(0, 1, 0)_A (0, 1, 1)_B\rangle, \quad |\psi_4\rangle = |(0, 1, 0)_A (1, 1, 1)_B\rangle,$$

$$|\psi_5\rangle = |(0, 1, 1)_A (0, 0, 0)_B\rangle, \quad |\psi_6\rangle = |(0, 1, 1)_A (0, 1, 0)_B\rangle,$$

$$|\psi_7\rangle = |(0, 1, 1)_A (1, 0, 0)_B\rangle, \quad |\psi_8\rangle = |(0, 1, 1)_A (1, 1, 0)_B\rangle,$$

See Figure 7.4 for adjacency graph for the matrix $A_{(F_z=+1)}$ which shows the linkage between neighboring vertices in the matrix (7.87). We notice that

$$\sum_{i=1}^{16} A_{(F_z=+1)}^i = \begin{pmatrix} a & 0 & b & 0 & b & b & 0 & 0 & 0 & c & 0 & d & 0 & 0 & d & d \\ 0 & a & 0 & b & 0 & 0 & b & b & c & 0 & d & 0 & d & d & 0 & 0 \\ b & 0 & a & 0 & b & b & 0 & 0 & 0 & d & 0 & c & 0 & 0 & d & d \\ 0 & b & 0 & a & 0 & 0 & b & b & d & 0 & c & 0 & d & d & 0 & 0 \\ b & 0 & b & 0 & a & b & 0 & 0 & 0 & d & 0 & d & 0 & 0 & c & d \\ b & 0 & b & 0 & b & a & 0 & 0 & 0 & d & 0 & d & 0 & 0 & d & c \\ 0 & b & 0 & b & 0 & 0 & a & b & d & 0 & d & 0 & c & d & 0 & 0 \\ 0 & b & 0 & b & 0 & 0 & b & a & d & 0 & d & 0 & d & c & 0 & 0 \\ 0 & c & 0 & d & 0 & 0 & d & d & a & 0 & b & 0 & b & b & 0 & 0 \\ c & 0 & d & 0 & d & d & 0 & 0 & 0 & a & 0 & b & 0 & 0 & b & b \\ 0 & d & 0 & c & 0 & 0 & d & d & b & 0 & a & 0 & b & b & 0 & 0 \\ d & 0 & c & 0 & d & d & 0 & 0 & 0 & b & 0 & a & 0 & 0 & b & b \\ 0 & d & 0 & d & 0 & 0 & c & d & b & 0 & b & 0 & a & b & 0 & 0 \\ 0 & d & 0 & d & 0 & 0 & d & c & b & 0 & b & 0 & b & a & 0 & 0 \\ d & 0 & d & 0 & c & d & 0 & 0 & 0 & b & 0 & b & 0 & 0 & a & b \\ d & 0 & d & 0 & d & c & 0 & 0 & 0 & b & 0 & b & 0 & 0 & b & a \end{pmatrix}, \quad (7.88)$$

where,

$$a = 12106896, \quad b = 12106888, \quad c = 4035624, \quad \text{and} \quad d = 4035632. \quad (7.89)$$

The presence of zeros in $\sum_{i=1}^{16} A_{(F_z=+1)}^i$ indicates that $A_{(F_z=+1)}$ can be reduced into at least two irreducible matrices. It can be clearly seen from the adjacency matrix (7.87) that 1 is adjacent to 12, 15, and 16. 16 is adjacent to 1, 3, and 5. 5 is adjacent to 10, 12, and 16. 12 is adjacent to 1, 5, and 6. 6 is adjacent to 10, 12, and 15. 10

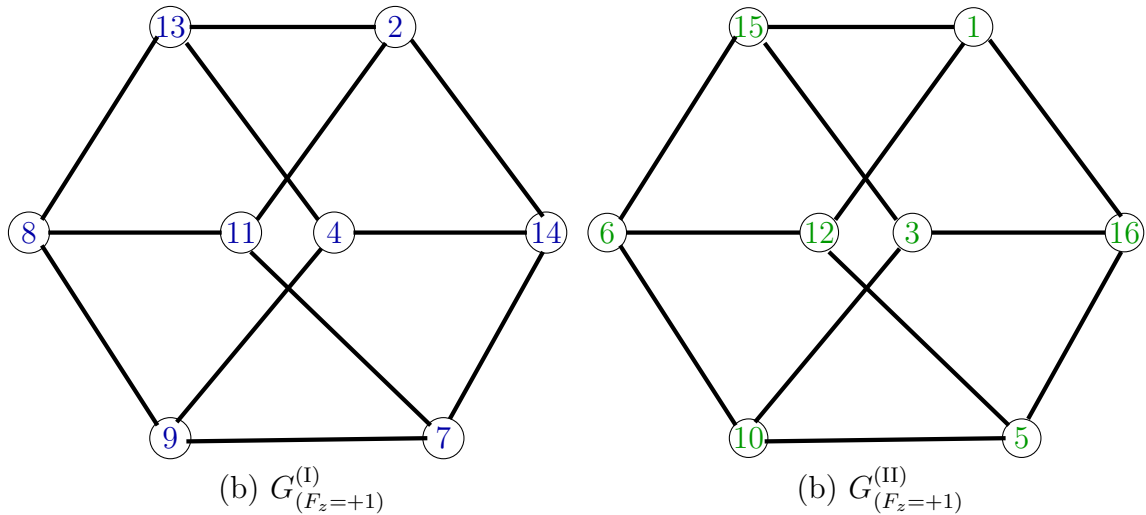


Figure 7.4: An adjacency graph of the matrix $A_{(F_z=+1)}$. The graph for $A_{(F_z=+1)}$ is disconnected having two components $G_{(F_z=+1)}^{(I)}$ and $G_{(F_z=+1)}^{(II)}$ which do not share any edges between the vertices.

is adjacent to 3, 5, and 6. 3 is adjacent to 10, 15, and 16. 15 is adjacent to 1, 3, and 6. However, these vertices are neither adjacent nor linked in any steps to the remaining other vertices. At the same time, 2 is adjacent to 11, 13, and 14. 14 is adjacent to 2, 4, and 7. 7 is adjacent to 9, 11, and 14. 11 is adjacent to 2, 7, and 8. 8 is adjacent to 9, 11, and 13. 13 is adjacent to 2, 4, and 8. 4 is adjacent to 9, 13, and 14. 9 is adjacent to 4, 7, and 8. The power $A_{(F_z=+1)}^2$ of the adjacency matrix $A_{(F_z=+1)}$ contains two diagonal nonzero matrices of order 8 and two same sized off-diagonal zero matrices, which verifies that the adjacency graph corresponding to the matrix $A_{(F_z=+1)}$ has two disconnected components.

The graph 7.4 clearly indicates that the 16-dimensional $F_z = +1$ manifold can be decomposed into two subspaces. These two subspaces do not talk with each other as they are uncoupled. Thus we can analyze each subspace independently. Firstly, we consider the subspace (I) of manifold $F_z = +1$. The subspace (I) is composed of

$|\psi_2\rangle, |\psi_4\rangle, |\psi_7\rangle, |\psi_8\rangle, |\psi_9\rangle, |\psi_{11}\rangle, |\psi_{13}\rangle,$ and $|\psi_{14}\rangle$. We rename these states as below:

$$\begin{aligned}
|\psi_1^{(I)}\rangle &= |\psi_2\rangle = |(0, 0, 0)_A(1, 1, 1)_B\rangle, & |\psi_2^{(I)}\rangle &= |\psi_4\rangle = |(0, 1, 0)_A(1, 1, 1)_B\rangle, \\
|\psi_3^{(I)}\rangle &= |\psi_7\rangle = |(0, 1, 1)_A(1, 0, 0)_B\rangle, & |\psi_4^{(I)}\rangle &= |\psi_8\rangle = |(0, 1, 1)_A(1, 1, 0)_B\rangle, \\
|\psi_5^{(I)}\rangle &= |\psi_9\rangle = |(1, 0, 0)_A(0, 1, 1)_B\rangle, & |\psi_6^{(I)}\rangle &= |\psi_{11}\rangle = |(1, 1, 0)_A(0, 1, 1)_B\rangle, \\
|\psi_7^{(I)}\rangle &= |\psi_{13}\rangle = |(1, 1, 1)_A(0, 0, 0)_B\rangle, & |\psi_8^{(I)}\rangle &= |\psi_{14}\rangle = |(1, 1, 1)_A(0, 1, 0)_B\rangle.
\end{aligned} \tag{7.90}$$

The Hamiltonian matrix of the subspace (I) reads

$$H_{(F_z=+1)}^{(I)} = \begin{pmatrix} \mathcal{L} - 2\mathcal{H} & 0 & 0 & 0 & 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} \\ 0 & \mathcal{H} + \mathcal{L} & 0 & 0 & -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} \\ 0 & 0 & \mathcal{L} & 0 & \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} \\ 0 & 0 & 0 & \mathcal{H} + \mathcal{L} & -\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 \\ 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} & \mathcal{L} & 0 & 0 & 0 \\ -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} & 0 & \mathcal{H} + \mathcal{L} & 0 & 0 \\ \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} & 0 & 0 & \mathcal{L} - 2\mathcal{H} & 0 \\ -\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 & 0 & 0 & 0 & \mathcal{H} + \mathcal{L} \end{pmatrix}. \tag{7.91}$$

If $A_{(F_z=+1)}^{(I)}$ is the adjacency matrix corresponding to $H_{(F_z=+1)}^{(I)}$, we have

$$\sum_i^8 (A_{(F_z=+1)}^{(I)})^i = \begin{pmatrix} 11135 & 10880 & 10880 & 10880 & 10710 & 10965 & 10965 & 10965 \\ 10880 & 11135 & 10880 & 10880 & 10965 & 10710 & 10965 & 10965 \\ 10880 & 10880 & 11135 & 10880 & 10965 & 10965 & 10710 & 10965 \\ 10880 & 10880 & 10880 & 11135 & 10965 & 10965 & 10965 & 10710 \\ 10710 & 10965 & 10965 & 10965 & 11135 & 10880 & 10880 & 10880 \\ 10965 & 10710 & 10965 & 10965 & 10880 & 11135 & 10880 & 10880 \\ 10965 & 10965 & 10710 & 10965 & 10880 & 10880 & 11135 & 10880 \\ 10965 & 10965 & 10965 & 10710 & 10880 & 10880 & 10880 & 11135 \end{pmatrix}. \tag{7.92}$$

As all of the elements of the $\sum_i^8 (A_{(F_z=+1)}^{(I)})^i$ are nonzero, we confirm that all the states are connected with each other.

The energy level $\mathcal{L} - 2\mathcal{H}$ and \mathcal{L} are doubly degenerate and coupled with the nonzero off-diagonal entries \mathcal{V} . However, the energy level $\mathcal{L} + \mathcal{H}$ is four-fold degenerate. Consider the subspace spanned by $|\psi_1^{(I)}\rangle \equiv |\psi_1^{(A)}\rangle$ and $|\psi_7^{(I)}\rangle \equiv |\psi_2^{(A)}\rangle$. The Hamiltonian matrix $H_{(F_z=+1)}^{(A)}$ reads

$$H_{(F_z=+1)}^{(A)} = \begin{pmatrix} \mathcal{L} - 2\mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} - 2\mathcal{H} \end{pmatrix}. \quad (7.93)$$

The eigenvalues and the corresponding eigenvectors of the Hamiltonian matrix (7.93) are

$$E_{\pm}^{(A)} = \mathcal{L} - 2\mathcal{H} \pm \mathcal{V}, \quad (7.94a)$$

$$|\chi_{\pm}^{(A)}\rangle = \frac{1}{2} \left(|\psi_1^{(A)}\rangle \pm |\psi_2^{(A)}\rangle \right). \quad (7.94b)$$

The other doubly degenerate energy level \mathcal{L} is spanned by $|\psi_3^{(I)}\rangle \equiv |\psi_1^{(B)}\rangle$ and $|\psi_5^{(I)}\rangle \equiv |\psi_2^{(B)}\rangle$. The Hamiltonian matrix $H_{(F_z=+1)}^{(B)}$ is

$$H_{(F_z=+1)}^{(B)} = \begin{pmatrix} \mathcal{L} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} \end{pmatrix}. \quad (7.95)$$

The eigenvalues and the corresponding eigenvectors of the Hamiltonian matrix (7.95) are

$$E_{\pm}^{(B)} = \mathcal{L} \pm \mathcal{V}, \quad (7.96a)$$

$$|\chi_{\pm}^{(B)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(B)}\rangle \pm |\psi_2^{(B)}\rangle \right). \quad (7.96b)$$

The four-fold degenerate Hamiltonian matrix

$$H_{(F_z=+1)}^{(C)} = \begin{pmatrix} \mathcal{H} + \mathcal{L} & 0 & 0 & \mathcal{V} \\ 0 & \mathcal{H} + \mathcal{L} & \mathcal{V} & 0 \\ 0 & \mathcal{V} & \mathcal{H} + \mathcal{L} & 0 \\ \mathcal{V} & 0 & 0 & \mathcal{H} + \mathcal{L} \end{pmatrix} \quad (7.97)$$

is spanned by the following vectors

$$|\psi_2^{(I)}\rangle \equiv |\psi_1^{(C)}\rangle, \quad |\psi_4^{(I)}\rangle \equiv |\psi_2^{(C)}\rangle, \quad |\psi_6^{(I)}\rangle \equiv |\psi_3^{(C)}\rangle, \quad |\psi_8^{(I)}\rangle \equiv |\psi_4^{(C)}\rangle. \quad (7.98)$$

The Hamiltonian matrix $H_{(F_z=+1)}^{(C)}$ can again be decomposed into two identical 2×2 matrices.

$$H_{(F_z=+1)}^{(C),1} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} + \mathcal{H} \end{pmatrix}, \quad \text{and} \quad H_{(F_z=+1)}^{(C),2} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} + \mathcal{H} \end{pmatrix}. \quad (7.99)$$

The Hamiltonian matrix $H_{(F_z=+1)}^{(C),1}$ is associated with $|\psi_1^{(C)}\rangle$ and $|\psi_4^{(C)}\rangle$ while $H_{(F_z=+1)}^{(C),2}$ is associated with $|\psi_2^{(C)}\rangle$ and $|\psi_3^{(C)}\rangle$. The eigenvalues of both the matrix are given by

$$E_{\pm}^{(C)} = \mathcal{L} + \mathcal{H} \pm \mathcal{V}, \quad (7.100)$$

whereas the eigenvectors are given as

$$|\chi_{\pm,1}^{(C)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(C)}\rangle \pm |\psi_4^{(B)}\rangle \right), \quad |\chi_{\pm,2}^{(C)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_2^{(C)}\rangle \pm |\psi_3^{(B)}\rangle \right). \quad (7.101)$$

Figure 7.5 is a Born-Oppenheimer potential curve for subspace(I) of $F_z = +1$ hyperfine manifold. For large interatomic distance, $\mathcal{V} \rightarrow 0$, and as the interatomic distance decreases, energy levels split, repel with each other, and experience $\mathcal{V} \rightarrow R^{-3}$ shift.

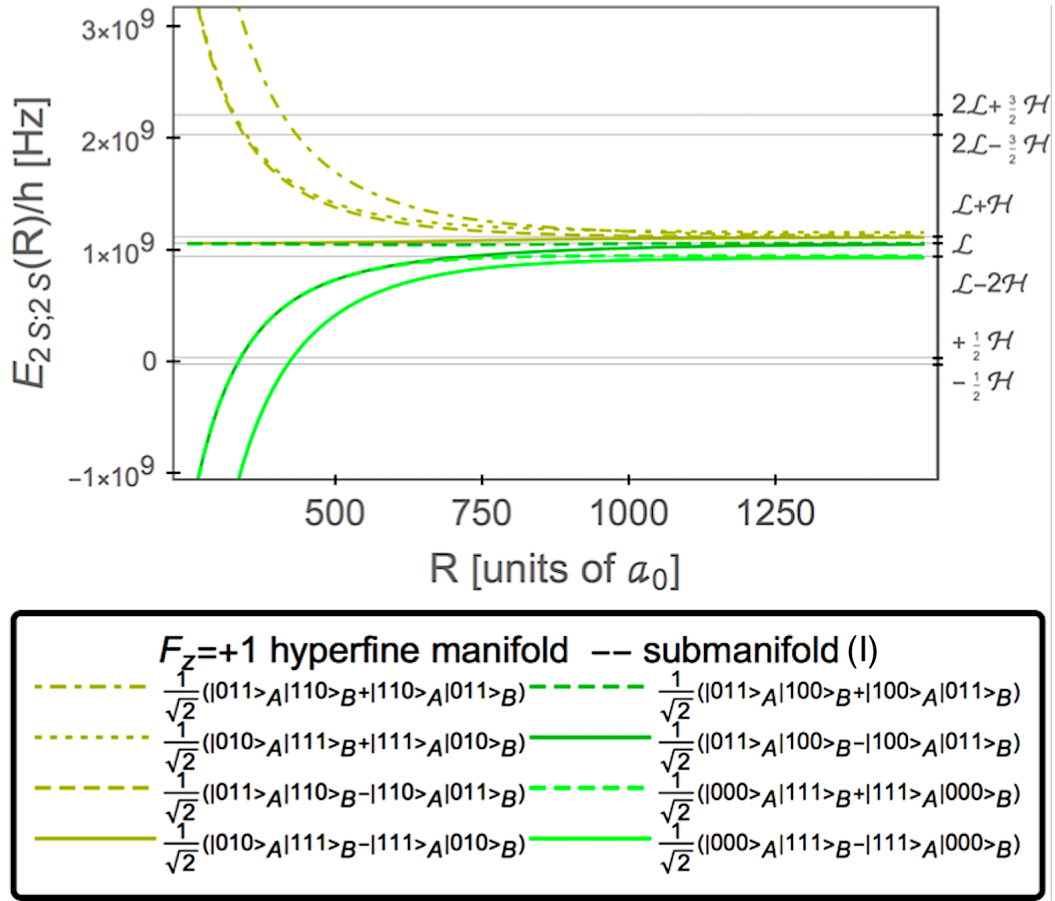


Figure 7.5: Evolution of the energy levels as a function of interatomic separation R in the subspace (I) of the $F_z = +1$ hyperfine manifold. For infinitely long interatomic distance, we observe three distinct energy levels same as in the unperturbed case. However, for small interatomic separation, the energy levels split and deviate from the unperturbed energies and become separate and readable.

Let us now focus on the subspace (II) of manifold $F_z = +1$. The subspace (II) is spanned by $|\psi_1\rangle$, $|\psi_3\rangle$, $|\psi_5\rangle$, $|\psi_6\rangle$, $|\psi_{10}\rangle$, $|\psi_{12}\rangle$, $|\psi_{15}\rangle$, and $|\psi_{16}\rangle$. We rename these states as below:

$$\begin{aligned}
 |\psi_1^{(\text{II})}\rangle &= |\psi_1\rangle = |(0, 0, 0)_A(0, 1, 1)_B\rangle, & |\psi_2^{(\text{II})}\rangle &= |\psi_3\rangle = |(0, 1, 0)_A(0, 1, 1)_B\rangle, \\
 |\psi_3^{(\text{II})}\rangle &= |\psi_5\rangle = |(0, 1, 1)_A(0, 0, 0)_B\rangle, & |\psi_4^{(\text{II})}\rangle &= |\psi_6\rangle = |(0, 1, 1)_A(0, 1, 0)_B\rangle, \\
 |\psi_5^{(\text{II})}\rangle &= |\psi_{10}\rangle = |(1, 0, 0)_A(1, 1, 1)_B\rangle, & |\psi_6^{(\text{II})}\rangle &= |\psi_{12}\rangle = |(1, 1, 0)_A(1, 1, 1)_B\rangle,
 \end{aligned}$$

$$|\psi_7^{(\text{II})}\rangle = |\psi_{15}\rangle = |(1, 1, 1)_A(1, 0, 0)_B\rangle, \quad |\psi_8^{(\text{II})}\rangle = |\psi_{16}\rangle = |(1, 1, 1)_A(1, 1, 0)_B\rangle. \quad (7.102)$$

The atoms in the subspace (II) are in *S-S* or *P-P* configurations. The Hamiltonian matrix of the subspace (II) reads

$$H_{(F_z=+1)}^{(\text{II})} = \begin{pmatrix} 2\mathcal{L} - \frac{3}{2}\mathcal{H} & 0 & 0 & 0 & 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} \\ 0 & 2\mathcal{L} + \frac{3\mathcal{H}}{2} & 0 & 0 & -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} \\ 0 & 0 & 2\mathcal{L} - \frac{3}{2}\mathcal{H} & 0 & \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} \\ 0 & 0 & 0 & 2\mathcal{L} + \frac{3}{2}\mathcal{H} & -\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 \\ 0 & -2\mathcal{V} & \mathcal{V} & -\mathcal{V} & -\frac{1}{2}\mathcal{H} & 0 & 0 & 0 \\ -2\mathcal{V} & 0 & -\mathcal{V} & \mathcal{V} & 0 & \frac{1}{2}\mathcal{H} & 0 & 0 \\ \mathcal{V} & -\mathcal{V} & 0 & -2\mathcal{V} & 0 & 0 & -\frac{1}{2}\mathcal{H} & 0 \\ -\mathcal{V} & \mathcal{V} & -2\mathcal{V} & 0 & 0 & 0 & 0 & \frac{1}{2}\mathcal{H} \end{pmatrix}. \quad (7.103)$$

In this subspace, no two degenerate levels are coupled by \mathcal{V} in first order. Thus, all the energy levels experience R^{-6} vdW shift as shown in Figure 7.6. Thus the states listed in Eq. (7.102) serve as eigenstates of the Hamiltonian matrix, $H_{(F_z=+1)}^{(\text{II})}$, of the system. The hyperfine transition goes second order in \mathcal{V} . If $A_{(F_z=+1)}^{(\text{II})}$ is the adjacency matrix of $H_{(F_z=+1)}^{(\text{II})}$, then the sum $\sum_i^8 (A_{(F_z=+1)}^{(\text{II})})^i$ is identical to Eq. (7.92).

7.7.3. Manifold $F_z = 0$. The $F_z = 0$ hyperfine manifold is composed of

$$\begin{aligned} |\Psi_1\rangle &= |(0, 0, 0)_A(0, 0, 0)_B\rangle, & |\Psi_2\rangle &= |(0, 0, 0)_A(0, 1, 0)_B\rangle, \\ |\Psi_3\rangle &= |(0, 0, 0)_A(1, 0, 0)_B\rangle, & |\Psi_4\rangle &= |(0, 0, 0)_A(1, 1, 0)_B\rangle, \\ |\Psi_5\rangle &= |(0, 1, -1)_A(0, 1, 1)_B\rangle, & |\Psi_6\rangle &= |(0, 1, -1)_A(1, 1, 1)_B\rangle, \\ |\Psi_7\rangle &= |(0, 1, 0)_A(0, 0, 0)_B\rangle, & |\Psi_8\rangle &= |(0, 1, 0)_A(0, 1, 0)_B\rangle, \end{aligned}$$

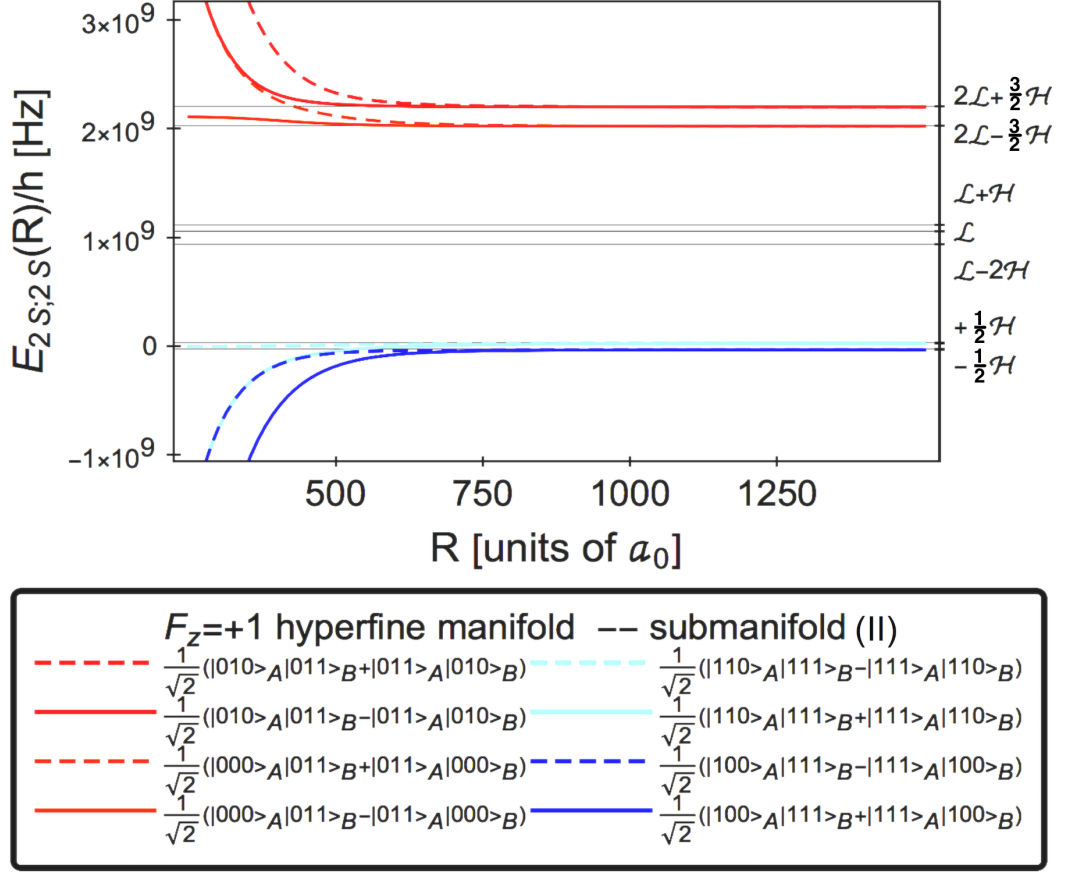


Figure 7.6: Evolution of the energy levels as a function of interatomic separation R in the subspace (II) of the $F_z = +1$ hyperfine manifold. For infinitely long interatomic distance, we observe four distinct energy levels same as in the unperturbed case. However, for small interatomic separation, the energy levels split and deviate from the unperturbed energies and become distinct and readable.

$$|\Psi_9\rangle = |(0, 1, 0)_A(1, 0, 0)_B\rangle,$$

$$|\Psi_{10}\rangle = |(0, 1, 0)_A(1, 1, 0)_B\rangle,$$

$$|\Psi_{11}\rangle = |(0, 1, 1)_A(0, 1, -1)_B\rangle,$$

$$|\Psi_{12}\rangle = |(0, 1, 1)_A(1, 1, -1)_B\rangle,$$

$$|\Psi_{13}\rangle = |(1, 0, 0)_A(0, 0, 0)_B\rangle,$$

$$|\Psi_{14}\rangle = |(1, 0, 0)_A(0, 1, 0)_B\rangle,$$

$$|\Psi_{15}\rangle = |(1, 0, 0)_A(1, 0, 0)_B\rangle,$$

$$|\Psi_{16}\rangle = |(1, 0, 0)_A(1, 1, 0)_B\rangle,$$

$$|\Psi_{17}\rangle = |(1, 1, -1)_A(0, 1, 1)_B\rangle,$$

$$|\Psi_{18}\rangle = |(1, 1, -1)_A(1, 1, 1)_B\rangle,$$

$$|\Psi_{19}\rangle = |(1, 1, 0)_A(0, 0, 0)_B\rangle,$$

$$|\Psi_{20}\rangle = |(1, 1, 0)_A(0, 1, 0)_B\rangle,$$

$$\begin{aligned}
|\Psi_{21}\rangle &= |(1, 1, 0)_A(1, 0, 0)_B\rangle, & |\Psi_{22}\rangle &= |(1, 1, 0)_A(1, 1, 0)_B\rangle, \\
|\Psi_{23}\rangle &= |(1, 1, 1)_A(0, 1, -1)_B\rangle, & |\Psi_{24}\rangle &= |(1, 1, 1)_A(1, 1, -1)_B\rangle.
\end{aligned} \tag{7.104}$$

The Hamiltonian matrix $H_{(F_z=0)}$ is a square matrix of order 24. We first evaluate $H_{(F_z=0)}$, and then replace each of the off-diagonal nonzero entries by 1 and each of the diagonal elements by 0. Thus constructed square matrix, whose entries are of boolean values, is an adjacency matrix $A_{(F_z=0)}$ which reads

$$A_{(F_z=0)} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 1 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}. \tag{7.105}$$

Figure 7.7 is an adjacency graph corresponding to $A_{(F_z=0)}$. The sum $\sum_{i=1}^{24} A_{(F_z=0)}^i$, which counts the number of neighbors of length(d) given by $1 \leq d \leq 24$ that by every

pair of nodes shares, satisfies

$$\sum_{i=1}^{24} A_{(F_z=0)}^i = \left(\begin{array}{cccccccccccccccccccccccc} P & Q & 0 & 0 & S & 0 & Q & Q & 0 & 0 & S & 0 & 0 & 0 & V & V & 0 & W & 0 & 0 & V & X & 0 & W \\ Q & P & 0 & 0 & S & 0 & Q & Q & 0 & 0 & S & 0 & 0 & 0 & V & V & 0 & W & 0 & 0 & X & V & 0 & W \\ 0 & 0 & P & Q & 0 & S & 0 & 0 & Q & Q & 0 & S & V & V & 0 & 0 & W & 0 & V & X & 0 & 0 & W & 0 \\ 0 & 0 & Q & P & 0 & S & 0 & 0 & Q & Q & 0 & S & V & V & 0 & 0 & W & 0 & X & V & 0 & 0 & W & 0 \\ S & S & 0 & 0 & Z & 0 & S & S & 0 & 0 & A & 0 & 0 & 0 & W & W & 0 & B & 0 & 0 & W & W & 0 & C \\ 0 & 0 & S & S & 0 & Z & 0 & 0 & S & S & 0 & A & W & W & 0 & 0 & B & 0 & W & W & 0 & 0 & C & 0 \\ Q & Q & 0 & 0 & S & 0 & P & Q & 0 & 0 & S & 0 & 0 & 0 & V & X & 0 & W & 0 & 0 & V & V & 0 & W \\ Q & Q & 0 & 0 & S & 0 & Q & P & 0 & 0 & S & 0 & 0 & 0 & X & V & 0 & W & 0 & 0 & V & V & 0 & W \\ 0 & 0 & Q & Q & 0 & S & 0 & 0 & P & Q & 0 & S & V & X & 0 & 0 & W & 0 & V & V & 0 & 0 & W & 0 \\ 0 & 0 & Q & Q & 0 & S & 0 & 0 & Q & P & 0 & S & X & V & 0 & 0 & W & 0 & V & V & 0 & 0 & W & 0 \\ S & S & 0 & 0 & A & 0 & S & S & 0 & 0 & Z & 0 & 0 & 0 & W & W & 0 & C & 0 & 0 & W & W & 0 & B \\ 0 & 0 & S & S & 0 & A & 0 & 0 & S & S & 0 & Z & W & W & 0 & 0 & C & 0 & W & W & 0 & 0 & B & 0 \\ 0 & 0 & V & V & 0 & W & 0 & 0 & V & X & 0 & W & P & Q & 0 & 0 & S & 0 & Q & Q & 0 & 0 & S & 0 \\ 0 & 0 & V & V & 0 & W & 0 & 0 & X & V & 0 & W & Q & P & 0 & 0 & S & 0 & Q & Q & 0 & 0 & S & 0 \\ V & V & 0 & 0 & W & 0 & V & X & 0 & 0 & W & 0 & 0 & 0 & P & Q & 0 & S & 0 & 0 & Q & Q & 0 & S \\ V & V & 0 & 0 & W & 0 & X & V & 0 & 0 & W & 0 & 0 & 0 & Q & P & 0 & S & 0 & 0 & Q & Q & 0 & S \\ 0 & 0 & W & W & 0 & B & 0 & 0 & W & W & 0 & C & S & S & 0 & 0 & Z & 0 & S & S & 0 & 0 & A & 0 \\ W & W & 0 & 0 & B & 0 & W & W & 0 & 0 & C & 0 & 0 & 0 & S & S & 0 & Z & 0 & 0 & S & S & 0 & A \\ 0 & 0 & V & X & 0 & W & 0 & 0 & V & V & 0 & W & Q & Q & 0 & 0 & S & 0 & P & Q & 0 & 0 & S & 0 \\ 0 & 0 & X & V & 0 & W & 0 & 0 & V & V & 0 & W & Q & Q & 0 & 0 & S & 0 & Q & P & 0 & 0 & S & 0 \\ V & X & 0 & 0 & W & 0 & V & V & 0 & 0 & W & 0 & 0 & 0 & Q & Q & 0 & S & 0 & 0 & P & Q & 0 & S \\ X & V & 0 & 0 & W & 0 & V & V & 0 & 0 & W & 0 & 0 & 0 & Q & Q & 0 & S & 0 & 0 & Q & P & 0 & S \\ 0 & 0 & W & W & 0 & C & 0 & 0 & W & W & 0 & B & S & S & 0 & 0 & A & 0 & S & S & 0 & 0 & Z & 0 \\ W & W & 0 & 0 & C & 0 & W & W & 0 & 0 & B & 0 & 0 & 0 & S & S & 0 & A & 0 & 0 & S & S & 0 & Z \end{array} \right), \quad (7.106)$$

where

$$\begin{aligned} P &= 13185279766584, & Q &= 13185279766572, & R &= 17374576685400, \\ S &= 18646800486300, & T &= 13185279766572, & U &= 18646800486300, \\ V &= 3444045886572, & W &= 4870616940000, & X &= 3444045886584, \\ Y &= 4870616940000, & Z &= 26370559533156, & A &= 26370559533144, \\ B &= 6888091773156, & \text{and } C &= 6888091773144. \end{aligned} \quad (7.107)$$

Not all the elements of $\sum_{i=1}^{24} A_{(F_z=0)}^i$ are nonzero. Thus, the matrix $H_{(F_z=0)}$ can be reduced into irreducible sub-matrices. The adjacency matrix squared $A_{(F_z=0)}^2$ takes

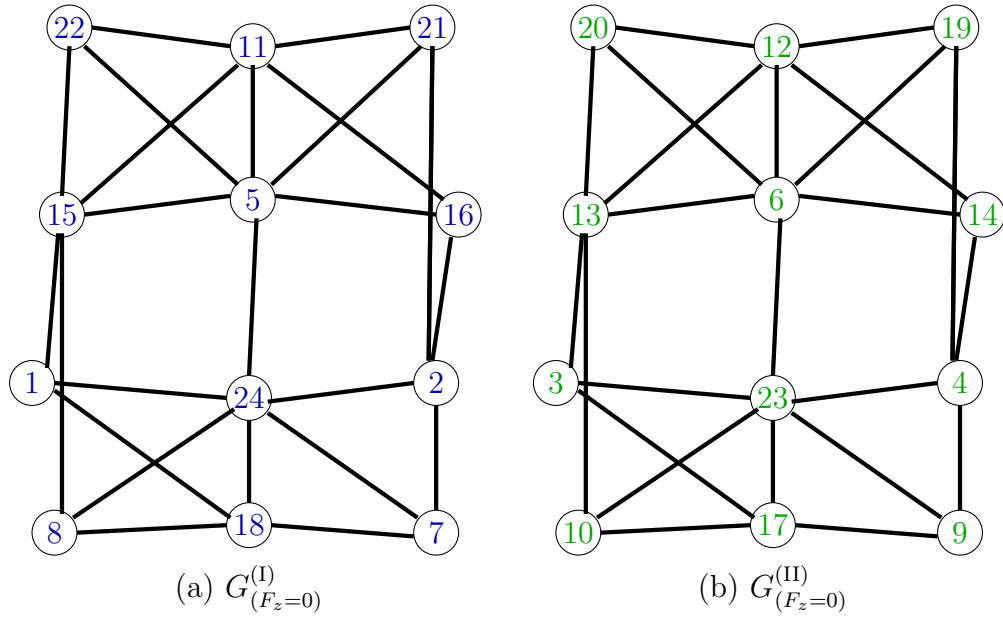


Figure 7.7: An adjacency graph of the matrix $A_{(F_z=0)}$. The graph for $A_{(F_z=0)}$ has two disconnected components $G_{(F_z=0)}^{(I)}$ and $G_{(F_z=0)}^{(II)}$ which do not share any edges between the vertices.

the form

$$A_{(F_z=0)}^2 = \begin{pmatrix} B_{12 \times 12} & : & 0_{12 \times 12} \\ \cdot & : & \cdot \\ 0_{12 \times 12} & : & C_{12 \times 12} \end{pmatrix}, \quad (7.108)$$

where $B_{12 \times 12}$ and $C_{12 \times 12}$ are nonzero matrices of order 12 while $0_{12 \times 12}$ represents a null matrix of order 12. Eq. (7.108) confirms that the adjacency graph corresponding to the adjacency matrix $A_{(F_z=0)}$ has two disconnected components. Each component $G_{(F_z=0)}^{(I)}$ and $G_{(F_z=0)}^{(II)}$ of the adjacency graph has 12 vertices. Eq. (7.108) and Figure 7.7 imply that we can partition the Hamiltonian matrix $H_{(F_z=0)}$ of the $F_z = 0$ hyperfine

manifold as

$$H_{(F_z=0)} = \begin{pmatrix} H_{(F_z=0)}^{(I)} & : & 0 \\ \cdots & : & \cdots \\ 0 & : & H_{(F_z=0)}^{(II)} \end{pmatrix}. \quad (7.109)$$

Thus, our 24-dimensional hyperfine manifold $F_z = 0$ reduces into two irreducible 12-dimensional sub-manifolds. The subspace (I) of the $F_z = 0$ manifold is composed of $|\Psi_1\rangle, |\Psi_2\rangle, |\Psi_5\rangle, |\Psi_7\rangle, |\Psi_8\rangle, |\Psi_{11}\rangle, |\Psi_{15}\rangle, |\Psi_{16}\rangle, |\Psi_{18}\rangle, |\Psi_{21}\rangle, |\Psi_{22}\rangle$, and $|\Psi_{24}\rangle$. Thus,

$$\begin{aligned} |\Psi_1^{(I)}\rangle &= |\Psi_1\rangle = |(0, 0, 0)_A(0, 0, 0)_B\rangle, & |\Psi_2^{(I)}\rangle &= |\Psi_2\rangle = |(0, 0, 0)_A(0, 1, 0)_B\rangle, \\ |\Psi_3^{(I)}\rangle &= |\Psi_5\rangle = |(0, 1, -1)_A(0, 1, 1)_B\rangle, & |\Psi_4^{(I)}\rangle &= |\Psi_7\rangle = |(0, 1, 0)_A(0, 0, 0)_B\rangle, \\ |\Psi_5^{(I)}\rangle &= |\Psi_8\rangle = |(0, 1, 0)_A(0, 1, 0)_B\rangle, & |\Psi_6^{(I)}\rangle &= |\Psi_{11}\rangle = |(0, 1, 1)_A(0, 1, -1)_B\rangle, \\ |\Psi_7^{(I)}\rangle &= |\Psi_{15}\rangle = |(1, 0, 0)_A(1, 0, 0)_B\rangle, & |\Psi_8^{(I)}\rangle &= |\Psi_{16}\rangle = |(1, 0, 0)_A(1, 1, 0)_B\rangle, \\ |\Psi_9^{(I)}\rangle &= |\Psi_{18}\rangle = |(1, 1, -1)_A(1, 1, 1)_B\rangle, & |\Psi_{10}^{(I)}\rangle &= |\Psi_{21}\rangle = |(1, 1, 0)_A(1, 0, 0)_B\rangle, \\ |\Psi_{11}^{(I)}\rangle &= |\Psi_{22}\rangle = |(1, 1, 0)_A(1, 1, 0)_B\rangle, & |\Psi_{12}^{(I)}\rangle &= |\Psi_{24}\rangle = |(1, 1, 1)_A(1, 1, -1)_B\rangle, \end{aligned} \quad (7.110)$$

are the corresponding basis vectors. The Hamiltonian matrix $H_{(F_z=0)}^{(I)}$ reads

$$H_{(F_z=0)}^{(I)} = \begin{pmatrix} 2\mathcal{L} - \frac{9\mathcal{H}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -\mathcal{V} \\ 0 & 2\mathcal{L} - \frac{3\mathcal{H}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} \\ 0 & 0 & 2\mathcal{L} + \frac{3\mathcal{H}}{2} & 0 & 0 & 0 & -\mathcal{V} & \mathcal{V} & 2\mathcal{V} & -\mathcal{V} & \mathcal{V} & 0 \\ 0 & 0 & 0 & 2\mathcal{L} - \frac{3\mathcal{H}}{2} & 0 & 0 & 0 & -2\mathcal{V} & -\mathcal{V} & 0 & 0 & \mathcal{V} \\ 0 & 0 & 0 & 0 & 2\mathcal{L} + \frac{3\mathcal{H}}{2} & 0 & -2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \mathcal{V} \\ 0 & 0 & 0 & 0 & 0 & 2\mathcal{L} + \frac{3\mathcal{H}}{2} & -\mathcal{V} & -\mathcal{V} & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} \\ 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -\mathcal{V} & -\frac{3}{2}\mathcal{H} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} & 0 & -\frac{\mathcal{H}}{2} & 0 & 0 & 0 & 0 \\ -\mathcal{V} & \mathcal{V} & 2\mathcal{V} & -\mathcal{V} & \mathcal{V} & 0 & 0 & 0 & \frac{\mathcal{H}}{2} & 0 & 0 & 0 \\ 0 & -2\mathcal{V} & -\mathcal{V} & 0 & 0 & \mathcal{V} & 0 & 0 & 0 & -\frac{\mathcal{H}}{2} & 0 & 0 \\ -2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \mathcal{V} & 0 & 0 & 0 & 0 & \frac{\mathcal{H}}{2} & 0 \\ -\mathcal{V} & -\mathcal{V} & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} & 0 & 0 & 0 & 0 & 0 & \frac{\mathcal{H}}{2} \end{pmatrix}. \quad (7.111)$$

No two degenerate levels of the matrix (7.111) are coupled. Thus, the states listed in (7.110) serve as the eigenvectors of the matrix (7.111). Figure 7.8 is a Born-Oppenheimer potential curve for $F_z = 0$ in subspace (I). For a very large value of R , $\mathcal{V} \rightarrow 0$, however, the interaction energy experiences a R^{-6} type energy shift as R decreases. Surprisingly, we notice several level crossings and the level crossings are unavoidable. According to the no-crossing rule, this is an unusual outcome.

On the other hand, if $A_{(F_z=0)}^{(I)}$ is the adjacency matrix corresponding to the Hamiltonian matrix $H_{(F_z=0)}^{(I)}$, the sum $\sum_{i=1}^{12} \left(A_{(F_z=0)}^{(I)} \right)^i$ is given by

$$\sum_{i=1}^{12} \left(A_{(F_z=0)}^{(I)} \right)^i = \begin{pmatrix} \alpha & \beta & \gamma & \beta & \beta & \gamma & \delta & \delta & \epsilon & \delta & \zeta & \epsilon \\ \beta & \alpha & \gamma & \beta & \beta & \gamma & \delta & \delta & \epsilon & \zeta & \delta & \epsilon \\ \gamma & \gamma & \eta & \gamma & \gamma & \theta & \epsilon & \epsilon & \iota & \epsilon & \epsilon & \kappa \\ \beta & \beta & \gamma & \alpha & \beta & \gamma & \delta & \zeta & \epsilon & \delta & \delta & \epsilon \\ \beta & \beta & \gamma & \beta & \alpha & \gamma & \zeta & \delta & \epsilon & \delta & \delta & \epsilon \\ \gamma & \gamma & \theta & \gamma & \gamma & \eta & \epsilon & \epsilon & \kappa & \epsilon & \epsilon & \iota \\ \delta & \delta & \epsilon & \delta & \zeta & \epsilon & \alpha & \beta & \gamma & \beta & \beta & \gamma \\ \delta & \delta & \epsilon & \zeta & \delta & \epsilon & \beta & \alpha & \gamma & \beta & \beta & \gamma \\ \epsilon & \epsilon & \iota & \epsilon & \epsilon & \kappa & \gamma & \gamma & \eta & \gamma & \gamma & \theta \\ \delta & \zeta & \epsilon & \delta & \delta & \epsilon & \beta & \beta & \gamma & \alpha & \beta & \gamma \\ \zeta & \delta & \epsilon & \delta & \delta & \epsilon & \beta & \beta & \gamma & \beta & \alpha & \gamma \\ \epsilon & \epsilon & \kappa & \epsilon & \epsilon & \iota & \gamma & \gamma & \theta & \gamma & \gamma & \eta \end{pmatrix}, \quad (7.112)$$

where

$$\begin{aligned} \alpha &= 12697599, \quad \beta = 12693504, \quad \gamma = 17881088, \quad \delta = 12618606, \quad \epsilon = 17918537, \\ \zeta &= 12622701, \quad \eta = 25391103, \quad \theta = 25387008, \quad \iota = 25241307, \quad \kappa = 25237212. \end{aligned} \quad (7.113)$$

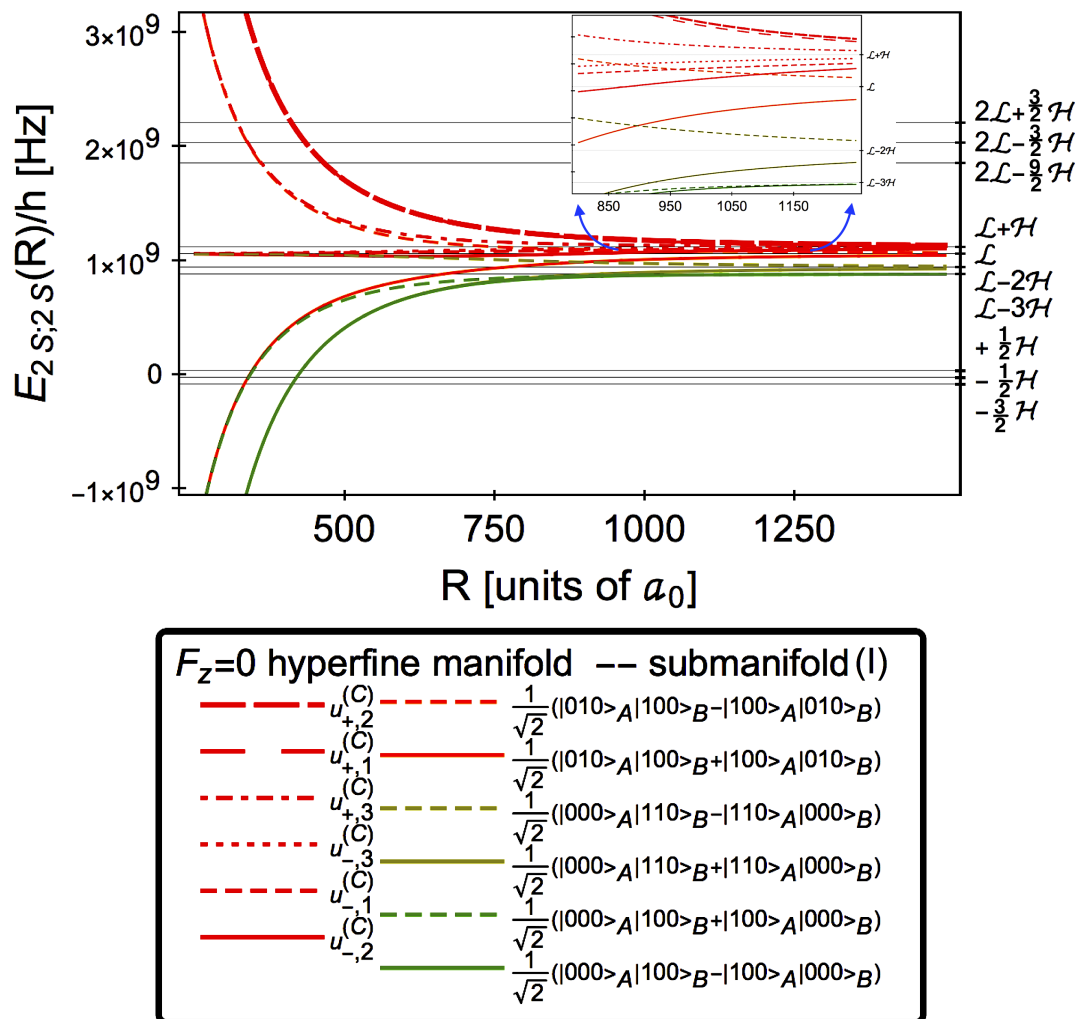


Figure 7.8: Evolution of the energy levels as a function of interatomic separation R in the subspace (I) of $F_z = 0$ hyperfine manifold. The energy levels are asymptotic for large interatomic separation. Although at the large separation, there are six unperturbed energy levels, the degeneracy is removed in small separation and hence, the energy levels spread widely. The small figure inserted on the right top of the main figure is the magnified version of a small portion as indicated in the figure. The figure shows several level crossings.

The absence of the zero in the sum $\sum_{i=1}^{12} \left(A_{(F_z=0)}^{(\text{I})} \right)^i$ indicates that the matrix $H_{(F_z=0)}^{(\text{I})}$ can not be reduced anymore.

Now we focus on the subspace (II) of manifold $F_z = 0$. The subspace (II) of the $F_z = 0$ manifold is composed of $|\Psi_3\rangle, |\Psi_4\rangle, |\Psi_6\rangle, |\Psi_9\rangle, |\Psi_{10}\rangle, |\Psi_{12}\rangle, |\Psi_{13}\rangle, |\Psi_{14}\rangle, |\Psi_{17}\rangle, |\Psi_{19}\rangle, |\Psi_{20}\rangle$, and $|\Psi_{23}\rangle$. Let us rename these states as

$$\begin{aligned}
|\Psi_1^{(\text{II})}\rangle &= |\Psi_3\rangle = |(0, 0, 0)_A(1, 0, 0)_B\rangle, & |\Psi_2^{(\text{II})}\rangle &= |\Psi_4\rangle = |(0, 0, 0)_A(1, 1, 0)_B\rangle, \\
|\Psi_3^{(\text{II})}\rangle &= |\Psi_6\rangle = |(0, 1, -1)_A(1, 1, 1)_B\rangle, & |\Psi_4^{(\text{II})}\rangle &= |\Psi_9\rangle = |(0, 1, 0)_A(1, 0, 0)_B\rangle, \\
|\Psi_5^{(\text{II})}\rangle &= |\Psi_{10}\rangle = |(0, 1, 0)_A(1, 1, 0)_B\rangle, & |\Psi_6^{(\text{II})}\rangle &= |\Psi_{12}\rangle = |(0, 1, 1)_A(1, 1, -1)_B\rangle, \\
|\Psi_7^{(\text{II})}\rangle &= |\Psi_{13}\rangle = |(1, 0, 0)_A(0, 0, 0)_B\rangle, & |\Psi_8^{(\text{II})}\rangle &= |\Psi_{14}\rangle = |(1, 0, 0)_A(0, 1, 0)_B\rangle, \\
|\Psi_9^{(\text{II})}\rangle &= |\Psi_{17}\rangle = |(1, 1, -1)_A(0, 1, 1)_B\rangle, & |\Psi_{10}^{(\text{II})}\rangle &= |\Psi_{19}\rangle = |(1, 1, 0)_A(0, 0, 0)_B\rangle, \\
|\Psi_{11}^{(\text{II})}\rangle &= |\Psi_{20}\rangle = |(1, 1, 0)_A(0, 1, 0)_B\rangle, & |\Psi_{12}^{(\text{II})}\rangle &= |\Psi_{23}\rangle = |(1, 1, 1)_A(0, 1, -1)_B\rangle.
\end{aligned} \tag{7.114}$$

The Hamiltonian matrix $H_{(F_z=0)}^{(\text{II})}$ of the subspace (II) reads

$$H_{(F_z=0)}^{(\text{II})} = \begin{pmatrix} \mathcal{L} - 3\mathcal{H} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -\mathcal{V} \\ 0 & \mathcal{L} - 2\mathcal{H} & 0 & 0 & 0 & 0 & 0 & 0 & \mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} \\ 0 & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 & 0 & -\mathcal{V} & \mathcal{V} & 2\mathcal{V} & -\mathcal{V} & \mathcal{V} & 0 \\ 0 & 0 & 0 & \mathcal{L} & 0 & 0 & 0 & -2\mathcal{V} & -\mathcal{V} & 0 & 0 & \mathcal{V} \\ 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 & -2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \mathcal{V} \\ 0 & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & -\mathcal{V} & -\mathcal{V} & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} \\ 0 & 0 & -\mathcal{V} & 0 & -2\mathcal{V} & -\mathcal{V} & \mathcal{L} - 3\mathcal{H} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mathcal{V} & -2\mathcal{V} & 0 & -\mathcal{V} & 0 & \mathcal{L} & 0 & 0 & 0 & 0 \\ -\mathcal{V} & \mathcal{V} & 2\mathcal{V} & -\mathcal{V} & \mathcal{V} & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 & 0 & 0 \\ 0 & -2\mathcal{V} & -\mathcal{V} & 0 & 0 & \mathcal{V} & 0 & 0 & 0 & \mathcal{L} - 2\mathcal{H} & 0 & 0 \\ -2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \mathcal{V} & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 \\ -\mathcal{V} & -\mathcal{V} & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} & 0 & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} \end{pmatrix}. \tag{7.115}$$

It is interesting to note that if $A_{(F_z=0)}^{(\text{II})}$ is the adjacency matrix corresponding to $H_{(F_z=0)}^{(\text{II})}$, then the sum $\sum_{i=1}^{12} \left(A_{(F_z=0)}^{(\text{II})} \right)^i$ is identical to $\sum_{i=1}^{12} \left(A_{(F_z=0)}^{(\text{I})} \right)^i$. Notice that, there are four degenerate subspaces in the $H_{(F_z=0)}^{(\text{II})}$. The two-fold degenerate level $\mathcal{L} - 3\mathcal{H}$ has vanishing off-diagonal elements. Thus, the degeneracy remains unresolved in the first order correction. The states $|\Psi_1^{(\text{II})}\rangle$ and $|\Psi_7^{(\text{II})}\rangle$ serve as eigenvectors.

The energy level $\mathcal{L} - 2\mathcal{H}$ is two-fold degenerate. The Hamiltonian matrix of this degenerate subspace is

$$H_{(F_z=0)}^{(\text{A})} = \begin{pmatrix} \mathcal{L} - 2\mathcal{H} & -2\mathcal{V} \\ -2\mathcal{V} & \mathcal{L} - 2\mathcal{H} \end{pmatrix}, \quad (7.116)$$

which is spanned by

$$|\Psi_1^{(\text{A})}\rangle = |\Psi_2^{(\text{II})}\rangle \quad \text{and} \quad |\Psi_2^{(\text{A})}\rangle = |\Psi_{10}^{(\text{II})}\rangle. \quad (7.117)$$

The eigenvalues and the eigenvectors are

$$E_{\pm}^{(\text{A})} = \mathcal{L} - 2\mathcal{H} \pm 2\mathcal{V}, \quad (7.118\text{a})$$

$$|\chi_{\pm}^{(\text{A})}\rangle = \frac{1}{\sqrt{2}} \left(|\Psi_1^{(\text{A})}\rangle \pm |\Psi_2^{(\text{A})}\rangle \right). \quad (7.118\text{b})$$

The third degenerate subspace with doubly degenerate energy \mathcal{L} is spanned by

$$|\Psi_1^{(\text{B})}\rangle = |\Psi_4^{(\text{II})}\rangle \quad \text{and} \quad |\Psi_2^{(\text{B})}\rangle = |\Psi_8^{(\text{II})}\rangle. \quad (7.119)$$

The Hamiltonian matrix reads as

$$H_{(F_z=0)}^{(\text{B})} = \begin{pmatrix} \mathcal{L} & -2\mathcal{V} \\ -2\mathcal{V} & \mathcal{L} \end{pmatrix}. \quad (7.120)$$

The eigenvalues and the eigenvectors of the system are

$$E_{\pm}^{(B)} = \mathcal{L} \pm 2\mathcal{V}, \quad (7.121a)$$

$$|\chi_{\pm}^{(B)}\rangle = \frac{1}{\sqrt{2}} \left(|\Psi_1^{(B)}\rangle \pm |\Psi_2^{(B)}\rangle \right). \quad (7.121b)$$

The fourth degenerate subspace is spanned by the states

$$\begin{aligned} |\Psi_1^{(C)}\rangle &= |\Psi_3^{(II)}\rangle, & |\Psi_2^{(C)}\rangle &= |\Psi_5^{(II)}\rangle, \\ |\Psi_3^{(C)}\rangle &= |\Psi_6^{(I)}\rangle, & |\Psi_4^{(C)}\rangle &= |\Psi_9^{(II)}\rangle, \\ |\Psi_5^{(C)}\rangle &= |\Psi_{11}^{(II)}\rangle, & |\Psi_6^{(C)}\rangle &= |\Psi_{12}^{(II)}\rangle, \end{aligned} \quad (7.122)$$

with the 6-fold degenerate Hamiltonian matrix

$$H_{(E_z=0)}^{(C)} = \begin{pmatrix} \mathcal{H} + \mathcal{L} & 0 & 0 & 2\mathcal{V} & \mathcal{V} & 0 \\ 0 & \mathcal{H} + \mathcal{L} & 0 & \mathcal{V} & 0 & \mathcal{V} \\ 0 & 0 & \mathcal{H} + \mathcal{L} & 0 & \mathcal{V} & 2\mathcal{V} \\ 2\mathcal{V} & \mathcal{V} & 0 & \mathcal{H} + \mathcal{L} & 0 & 0 \\ \mathcal{V} & 0 & \mathcal{V} & 0 & \mathcal{H} + \mathcal{L} & 0 \\ 0 & \mathcal{V} & 2\mathcal{V} & 0 & 0 & \mathcal{H} + \mathcal{L} \end{pmatrix}. \quad (7.123)$$

The eigenvalues of the Hamiltonian matrix (7.123) are

$$E_{\pm,1}^{(C)} = \mathcal{L} + \mathcal{H} \pm 2\mathcal{V}, \quad (7.124a)$$

$$E_{\pm,2}^{(C)} = \mathcal{L} + \mathcal{H} \pm \left(\sqrt{3} + 1 \right) \mathcal{V}, \quad (7.124b)$$

$$E_{\pm,3}^{(C)} = \mathcal{L} + \mathcal{H} \pm \left(\sqrt{3} - 1 \right) \mathcal{V}. \quad (7.124c)$$

The degeneracy is completely removed and the energy shifts are first order in \mathcal{V} . The corresponding normalized eigenvectors are

$$|\chi_{\pm,1}^{(C)}\rangle = \frac{1}{2} \left(\mp |\Psi_1^{(C)}\rangle \pm |\Psi_3^{(C)}\rangle - |\Psi_4^{(C)}\rangle + |\Psi_6^{(C)}\rangle \right), \quad (7.125a)$$

$$|\chi_{\pm,2}^{(C)}\rangle = \frac{1}{2\sqrt{3-\sqrt{3}}} \left(\pm |\Psi_1^{(C)}\rangle \pm (\sqrt{3}-1) |\Psi_2^{(C)}\rangle \pm |\Psi_3^{(C)}\rangle + |\Psi_4^{(C)}\rangle \right. \\ \left. + (\sqrt{3}-1) |\Psi_5^{(C)}\rangle + \Psi_6^{(C)} \right), \quad (7.125b)$$

$$|\chi_{\pm,3}^{(C)}\rangle = \frac{1}{2\sqrt{3+\sqrt{3}}} \left(\mp |\Psi_1^{(C)}\rangle \pm (\sqrt{3}+1) |\Psi_2^{(C)}\rangle \mp |\Psi_3^{(C)}\rangle + |\Psi_4^{(C)}\rangle \right. \\ \left. - (\sqrt{3}+1) |\Psi_5^{(C)}\rangle + \Psi_6^{(C)} \right). \quad (7.125c)$$

As interatomic distance decreases, the unperturbed $\mathcal{L} - 3\mathcal{H}$ energy level experience an energy shift which is second order in \mathcal{V} i.e. $\sim R^{-6}$, whereas rest of other unperturbed energy levels experience R^{-3} type energy shift (see Figure 7.9).

7.7.4. Manifold $F_z = -1$. The $F_z = -1$ hyperfine manifold has 16 states. We write the 16 states in this manifolds in the ascending order of quantum numbers as given below:

$$\begin{aligned} |\psi'_1\rangle &= |(0,0,0)_A(0,1,-1)_B\rangle, & |\psi'_2\rangle &= |(0,0,0)_A(1,1,-1)_B\rangle, \\ |\psi'_3\rangle &= |(0,1,-1)_A(0,0,0)_B\rangle, & |\psi'_4\rangle &= |(0,1,-1)_A(0,1,0)_B\rangle, \\ |\psi'_5\rangle &= |(0,1,-1)_A(1,0,0)_B\rangle, & |\psi'_6\rangle &= |(0,1,-1)_A(1,1,0)_B\rangle, \\ |\psi'_7\rangle &= |(0,1,0)_A(0,1,-1)_B\rangle, & |\psi'_8\rangle &= |(0,1,0)_A(1,1,-1)_B\rangle, \\ |\psi'_9\rangle &= |(1,0,0)_A(0,1,-1)_B\rangle, & |\psi'_{10}\rangle &= |(1,0,0)_A(1,1,-1)_B\rangle, \\ |\psi'_{11}\rangle &= |(1,1,-1)_A(0,0,0)_B\rangle, & |\psi'_{12}\rangle &= |(1,1,-1)_A(0,1,0)_B\rangle, \\ |\psi'_{13}\rangle &= |(1,1,-1)_A(1,0,0)_B\rangle, & |\psi'_{14}\rangle &= |(1,1,-1)_A(1,1,0)_B\rangle, \\ |\psi'_{15}\rangle &= |(1,1,0)_A(0,1,-1)_B\rangle, & |\psi'_{16}\rangle &= |(1,1,0)_A(1,1,-1)_B\rangle. \end{aligned} \quad (7.126)$$

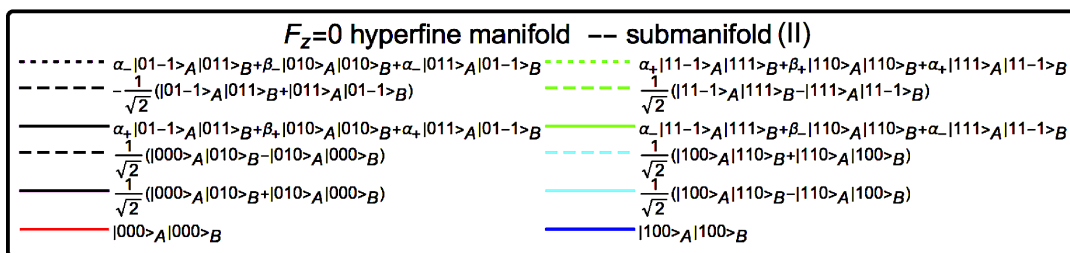
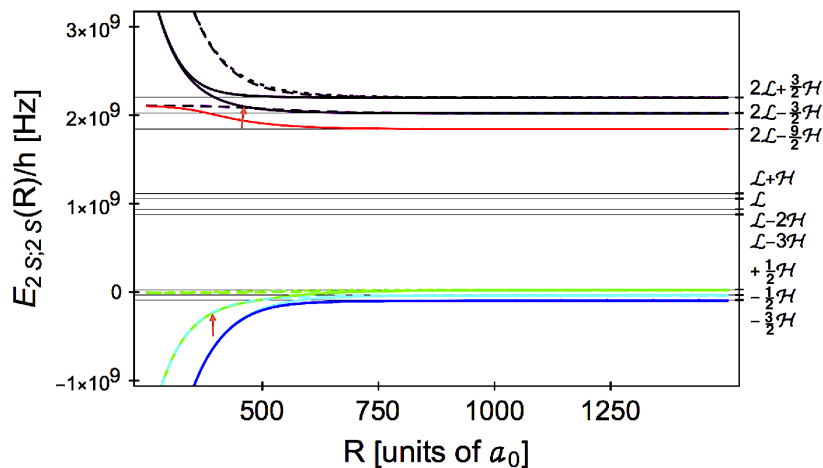


Figure 7.9: Evolution of the energy levels as a function of interatomic separation R in the subspace (II) of $F_z = 0$ hyperfine manifold. The vertical axis is the energy divided by the plank constant, and the horizontal axis is the interatomic distance in the unit of Bohr's radius a_0 . The energy levels are asymptotic for large interatomic separation. Although at the large separation, there are six unperturbed energy levels, the degeneracy is removed in small separation and hence, the energy levels spread widely. We observe two level crossings for small atomic separation. The arrow, ' \uparrow ', shows the location of crossings.

The Hamiltonian matrix for $F_z = -1$ hyperfine manifold is a square symmetric matrix of order 16. We replace all the nonzero off-diagonal element of the Hamiltonian matrix by 1 and all the diagonal elements by zero to construct corresponding undirected

adjacency matrix $A_{(F_z=-1)}$ which reads

$$A_{(F_z=-1)} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (7.127)$$

Figure 7.10 is an adjacency graph corresponding to $A_{(F_z=-1)}$. The sum $\sum_{i=1}^{16} A_{(F_z=-1)}^i$ counts the number of neighbors of length(d) given by $1 \leq d \leq 16$ which is shared by every pair of nodes. Interestingly, we find

$$\sum_{i=1}^{16} A_{(F_z=-1)}^i = \sum_{i=1}^{16} A_{(F_z=+1)}^i. \quad (7.128)$$

Thus, similar to the $H_{(F_z=+1)}$ matrix, the $H_{(F_z=-1)}$ matrix can also be reduced into irreducible sub-matrices. The square of the adjacency matrix $A_{(F_z=-1)}$ can be expressed

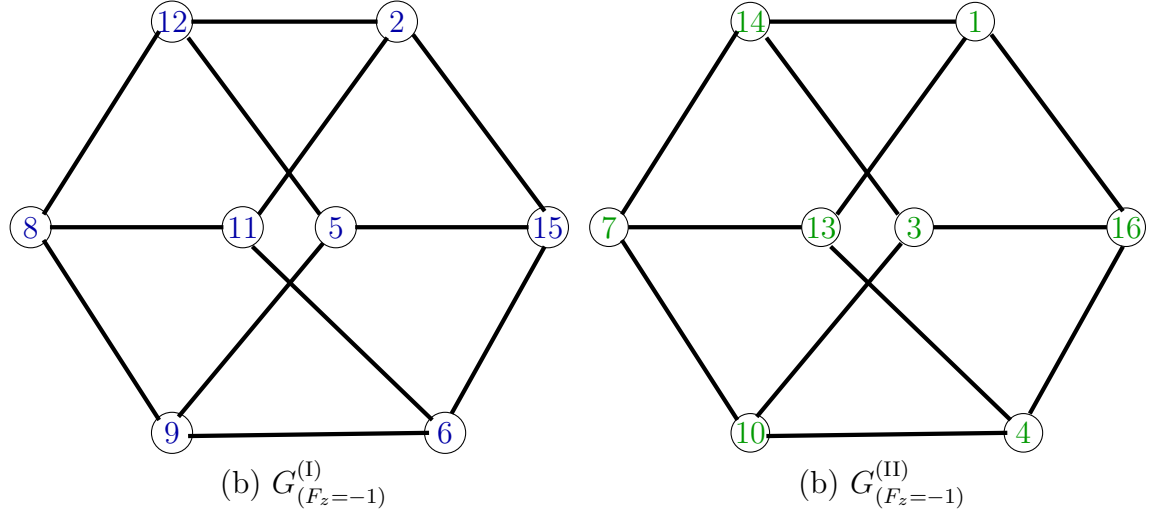


Figure 7.10: An adjacency graph of the matrix $A_{(F_z=-1)}$. The graph for $A_{(F_z=-1)}$ is disconnected having two components $G_{(F_z=-1)}^{(I)}$ and $G_{(F_z=-1)}^{(II)}$ which do not share any edges between the vertices.

as

$$A_{(F_z=-1)}^2 = \begin{pmatrix} B_{8 \times 8} & : & 0_{8 \times 8} \\ \dots & : & \dots \\ 0_{8 \times 8} & : & C_{8 \times 8} \end{pmatrix}, \quad (7.129)$$

where $B_{8 \times 8}$ and $C_{8 \times 8}$ are nonzero matrices of order 8 while $0_{8 \times 8}$ represents a null matrix of order 8. Eq. (7.129) confirms that the adjacency graph corresponding to the adjacency matrix $A_{(F_z=-1)}$ has two disconnected components. Each component $G_{(F_z=-1)}^{(I)}$ and $G_{(F_z=-1)}^{(II)}$ of the adjacency graph has 8 vertices (see Figure 7.10). The graph clearly indicates that the 16-dimensional $F_z = -1$ manifold can be decomposed into two subspaces each of dimension 8. These two subspaces are uncoupled to each other. The first subspace, subspace (I) of the manifold $F_z = -1$, is composed of $|\psi'_2\rangle$,

$|\psi'_5\rangle, |\psi'_6\rangle, |\psi'_8\rangle, |\psi'_9\rangle, |\psi'_{11}\rangle, |\psi'_{12}\rangle$, and $|\psi'_{15}\rangle$. We rename these states as below:

$$\begin{aligned}
|\psi_1^{(I)}\rangle &= |\psi'_2\rangle = |(0, 0, 0)_A(1, 1, -1)_B\rangle, & |\psi_2^{(I)}\rangle &= |\psi'_5\rangle = |(0, 1, -1)_A(1, 0, 0)_B\rangle, \\
|\psi_3^{(I)}\rangle &= |\psi'_6\rangle = |(0, 1, -1)_A(1, 1, 0)_B\rangle, & |\psi_4^{(I)}\rangle &= |\psi'_8\rangle = |(0, 1, 0)_A(1, 1, -1)_B\rangle, \\
|\psi_5^{(I)}\rangle &= |\psi'_9\rangle = |(1, 0, 0)_A(0, 1, -1)_B\rangle, & |\psi_6^{(I)}\rangle &= |\psi'_{11}\rangle = |(1, 1, -1)_A(0, 0, 0)_B\rangle, \\
|\psi_7^{(I)}\rangle &= |\psi'_{12}\rangle = |(1, 1, -1)_A(0, 1, 0)_B\rangle, & |\psi_8^{(I)}\rangle &= |\psi'_{15}\rangle = |(1, 1, 0)_A(0, 1, -1)_B\rangle.
\end{aligned}
\tag{7.130}$$

The Hamiltonian matrix of the subspace (I) reads

$$H_{(F_z=-1)}^{(I)} = \begin{pmatrix} \mathcal{L} - 2\mathcal{H} & 0 & 0 & 0 & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} \\ 0 & \mathcal{L} & 0 & 0 & \mathcal{V} & 0 & 2\mathcal{V} & \mathcal{V} \\ 0 & 0 & \mathcal{L} + \mathcal{H} & 0 & \mathcal{V} & 2\mathcal{V} & 0 & \mathcal{V} \\ 0 & 0 & 0 & \mathcal{L} + \mathcal{H} & 2\mathcal{V} & \mathcal{V} & \mathcal{V} & 0 \\ 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} & \mathcal{L} & 0 & 0 & 0 \\ \mathcal{V} & 0 & 2\mathcal{V} & \mathcal{V} & 0 & \mathcal{L} - 2\mathcal{H} & 0 & 0 \\ \mathcal{V} & 2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \mathcal{L} + \mathcal{H} & 0 \\ 2\mathcal{V} & \mathcal{V} & \mathcal{V} & 0 & 0 & 0 & 0 & \mathcal{L} + \mathcal{H} \end{pmatrix}.
\tag{7.131}$$

Notice that, there are three degenerate subspaces. The energy levels $\mathcal{L} - 2\mathcal{H}$ and \mathcal{L} are doubly degenerate whereas the energy level $\mathcal{L} + \mathcal{H}$ is four-fold degenerate. Consider the subspace spanned by $|\psi_1^{(I)}\rangle \equiv |\psi_1^{(A)}\rangle$ and $|\psi_6^{(I)}\rangle \equiv |\psi_2^{(A)}\rangle$. The Hamiltonian matrix $H_{(F_z=-1)}^{(A)}$ reads

$$H_{(F_z=-1)}^{(A)} = \begin{pmatrix} \mathcal{L} - 2\mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} - 2\mathcal{H} \end{pmatrix}.
\tag{7.132}$$

The eigenvalues and the corresponding eigenvectors of the Hamiltonian matrix (7.132) are

$$E_{\pm}^{(A)} = \mathcal{L} - 2\mathcal{H} \pm \mathcal{V}, \quad (7.133a)$$

$$|\chi_{\pm}^{(A)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(A)}\rangle \pm |\psi_2^{(A)}\rangle \right). \quad (7.133b)$$

The doubly degenerate energy level \mathcal{L} is spanned by $|\psi_2^{(I)}\rangle \equiv |\psi_1^{(B)}\rangle$ and $|\psi_5^{(I)}\rangle \equiv |\psi_2^{(B)}\rangle$. The Hamiltonian matrix $H_{(F_z=-1)}^{(B)}$ is

$$H_{(F_z=-1)}^{(B)} = \begin{pmatrix} \mathcal{L} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} \end{pmatrix}. \quad (7.134)$$

The eigenvalues and the corresponding eigenvectors of the Hamiltonian matrix (7.134) are

$$E_{\pm}^{(B)} = \mathcal{L} \pm \mathcal{V}, \quad (7.135a)$$

$$|\chi_{\pm}^{(B)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(B)}\rangle \pm |\psi_2^{(B)}\rangle \right). \quad (7.135b)$$

The four-fold degenerate Hamiltonian matrix

$$H_{(F_z=-1)}^{(C)} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & 0 & 0 & \mathcal{V} \\ 0 & \mathcal{L} + \mathcal{H} & \mathcal{V} & 0 \\ 0 & \mathcal{V} & \mathcal{L} + \mathcal{H} & 0 \\ \mathcal{V} & 0 & 0 & \mathcal{L} + \mathcal{H} \end{pmatrix} \quad (7.136)$$

is spanned by the following vectors

$$|\psi_3^{(I)}\rangle \equiv |\psi_1^{(C)}\rangle, \quad |\psi_4^{(I)}\rangle \equiv |\psi_2^{(C)}\rangle, \quad |\psi_7^{(I)}\rangle \equiv |\psi_3^{(C)}\rangle, \quad |\psi_8^{(I)}\rangle \equiv |\psi_4^{(C)}\rangle. \quad (7.137)$$

The Hamiltonian matrix $H_{(F_z=-1)}^{(C)}$ can again be decomposed into two identical 2×2 sub-matrices.

$$H_{(F_z=-1)}^{(C),1} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} + \mathcal{H} \end{pmatrix}, \quad \text{and} \quad H_{(F_z=-1)}^{(C),2} = \begin{pmatrix} \mathcal{L} + \mathcal{H} & \mathcal{V} \\ \mathcal{V} & \mathcal{L} + \mathcal{H} \end{pmatrix}. \quad (7.138)$$

The Hamiltonian matrix $H_{(F_z=-1)}^{(C),1}$ is associated with $|\psi_1^{(C)}\rangle$ and $|\psi_4^{(C)}\rangle$ while $H_{(F_z=-1)}^{(C),2}$ is associated with $|\psi_2^{(C)}\rangle$ and $|\psi_3^{(C)}\rangle$. The eigenvalues for both the matrix are given by

$$E_{\pm}^{(C)} = \mathcal{L} + \mathcal{H} \pm \mathcal{V}, \quad (7.139)$$

whereas the eigenvectors are given as

$$|\chi_{\pm,1}^{(C)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(C)}\rangle \pm |\psi_4^{(B)}\rangle \right), \quad (7.140a)$$

$$|\chi_{\pm,2}^{(C)}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_2^{(C)}\rangle \pm |\psi_3^{(B)}\rangle \right). \quad (7.140b)$$

See Figure 7.11 for an evolution of energy levels as a function of interatomic separation, R , in the subspace (I) of the $F_z = -1$ hyperfine manifold. As the interatomic distance increases, each of the unperturbed energy levels experience a R^{-3} type energy shift. In contrast to the $F_z = 0$ hyperfine manifold, there is no level-crossing in the subspace (I) of the $F_z = -1$ hyperfine manifold. Notice that, energy curves for subspace (I) of $F_z = \pm 1$ are alike.

The subspace (II) of the $F_z = -1$ manifold is spanned by $|\psi'_1\rangle$, $|\psi'_3\rangle$, $|\psi'_4\rangle$, $|\psi'_7\rangle$, $|\psi'_{10}\rangle$, $|\psi'_{13}\rangle$, $|\psi'_{14}\rangle$, and $|\psi'_{16}\rangle$. Let us rename these state vectors as below:

$$|\psi_1^{(\text{II})}\rangle = |\psi'_1\rangle = |(0, 0, 0)_A(0, 1, -1)_B\rangle, \quad |\psi_2^{(\text{II})}\rangle = |\psi'_3\rangle = |(0, 1, -1)_A(0, 0, 0)_B\rangle,$$

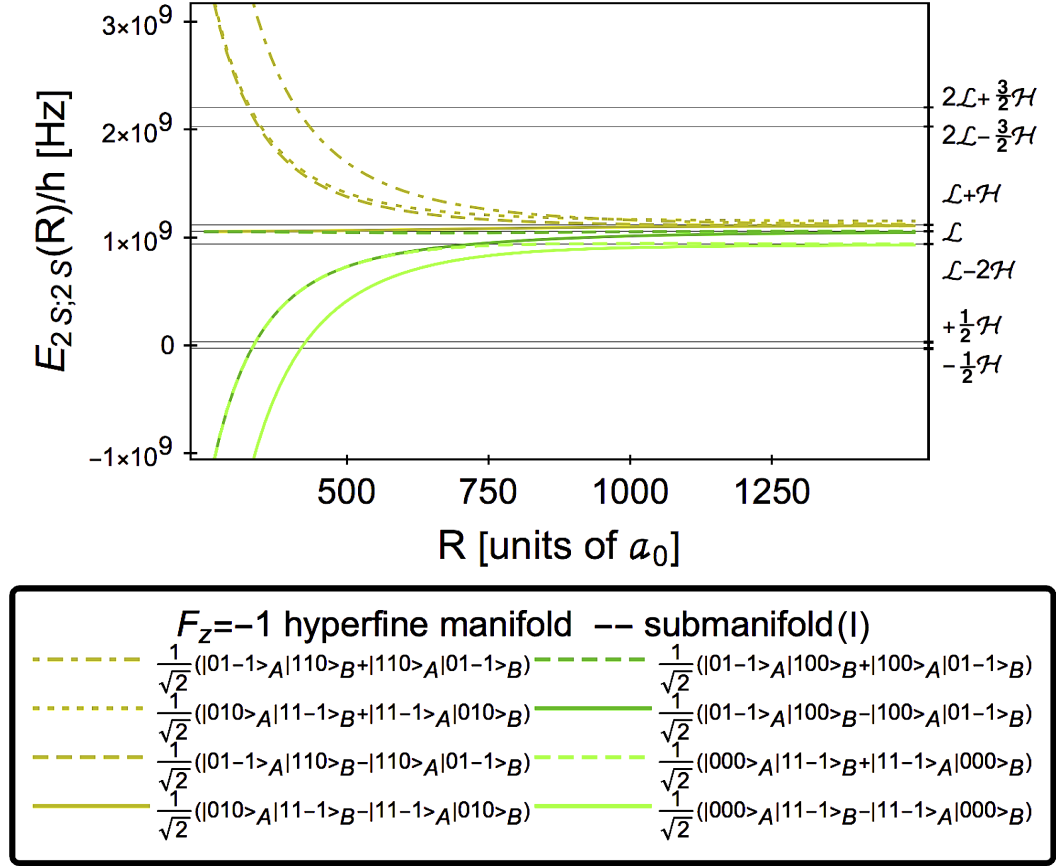


Figure 7.11: Energy levels as a function of interatomic separation R in the subspace (I) of the $F_z = -1$ hyperfine manifold. For infinitely long interatomic separation, there are three distinct energy levels, as expected from the unperturbed energy values of the Hamiltonian matrix, $H_{(F_z=-1)}^{(I)}$, given by Eq. (7.131). However, for small interatomic separation, the energy levels split.

$$\begin{aligned}
 |\psi_3^{(\text{II})}\rangle &= |\psi_4'\rangle = |(0, 1, -1)_A(0, 1, 0)_B\rangle, & |\psi_4'^{(\text{II})}\rangle &= |\psi_7'\rangle = |(0, 1, 0)_A(0, 1, -1)_B\rangle, \\
 |\psi_5^{(\text{II})}\rangle &= |\psi_{10}'\rangle = |(1, 0, 0)_A(1, 1, -1)_B\rangle, & |\psi_6'^{(\text{II})}\rangle &= |\psi_{13}'\rangle = |(1, 1, -1)_A(1, 0, 0)_B\rangle, \\
 |\psi_7^{(\text{II})}\rangle &= |\psi_{14}'\rangle = |(1, 1, -1)_A(1, 1, 0)_B\rangle, & |\psi_8'^{(\text{II})}\rangle &= |\psi_{16}'\rangle = |(1, 1, 0)_A(1, 1, -1)_B\rangle.
 \end{aligned}$$

(7.141)

The Hamiltonian matrix of the subspace (II) reads

$$H_{(F_z=-1)}^{(\text{II})} = \begin{pmatrix} 2\mathcal{L} - \frac{3}{2}\mathcal{H} & 0 & 0 & 0 & 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} \\ 0 & 2\mathcal{L} - \frac{3}{2}\mathcal{H} & 0 & 0 & \mathcal{V} & 0 & 2\mathcal{V} & \mathcal{V} \\ 0 & 0 & \frac{3}{2}\mathcal{H} + 2\mathcal{L} & 0 & \mathcal{V} & 2\mathcal{V} & 0 & \mathcal{V} \\ 0 & 0 & 0 & \frac{3}{2}\mathcal{H} + 2\mathcal{L} & 2\mathcal{V} & \mathcal{V} & \mathcal{V} & 0 \\ 0 & \mathcal{V} & \mathcal{V} & 2\mathcal{V} & -\frac{1}{2}\mathcal{H} & 0 & 0 & 0 \\ \mathcal{V} & 0 & 2\mathcal{V} & \mathcal{V} & 0 & -\frac{1}{2}\mathcal{H} & 0 & 0 \\ \mathcal{V} & 2\mathcal{V} & 0 & \mathcal{V} & 0 & 0 & \frac{1}{2}\mathcal{H} & 0 \\ 2\mathcal{V} & \mathcal{V} & \mathcal{V} & 0 & 0 & 0 & 0 & \frac{1}{2}\mathcal{H} \end{pmatrix}. \quad (7.142)$$

In this subspace, no two degenerate levels are coupled to each other. Thus, the diagonal elements serve as the eigenvalues, and the state vectors serve as the eigenvectors. An evolution of energy levels as a function of interatomic distance is presented in Figure 7.12. As interatomic distance decreases, energy levels experience the second order shift in \mathcal{V} and evolve as R^{-6} type shift.

Analysis shows very interesting feature in the comparison of the $F_z = +1$ and $F_z = -1$ manifolds. The components of the adjacency graph corresponding to the matrix $A_{(F_z=+1)}$ and $A_{(F_z=-1)}$ look identical though ordering of the vertices is not identical. Furthermore, the Hamiltonian matrix $H_{(F_z=+1)}$ is not exactly same to that of $H_{(F_z=-1)}$. However, they do have the same eigenvalues.

7.7.5. Manifold $F_z = -2$. Similar to the $F_z = +2$ hyperfine manifold, the $F_z = -2$ manifold is also a 4-dimensional subspace. It is composed of

$$\begin{aligned} |\phi'_1\rangle &= |(0, 1, -1)_A(0, 1, -1)_B\rangle, & |\phi'_2\rangle &= |(0, 1, -1)_A(1, 1, -1)_B\rangle, \\ |\phi'_3\rangle &= |(1, 1, -1)_A(0, 1, -1)_B\rangle, & |\phi'_4\rangle &= |(1, 1, -1)_A(1, 1, -1)_B\rangle. \end{aligned} \quad (7.143)$$

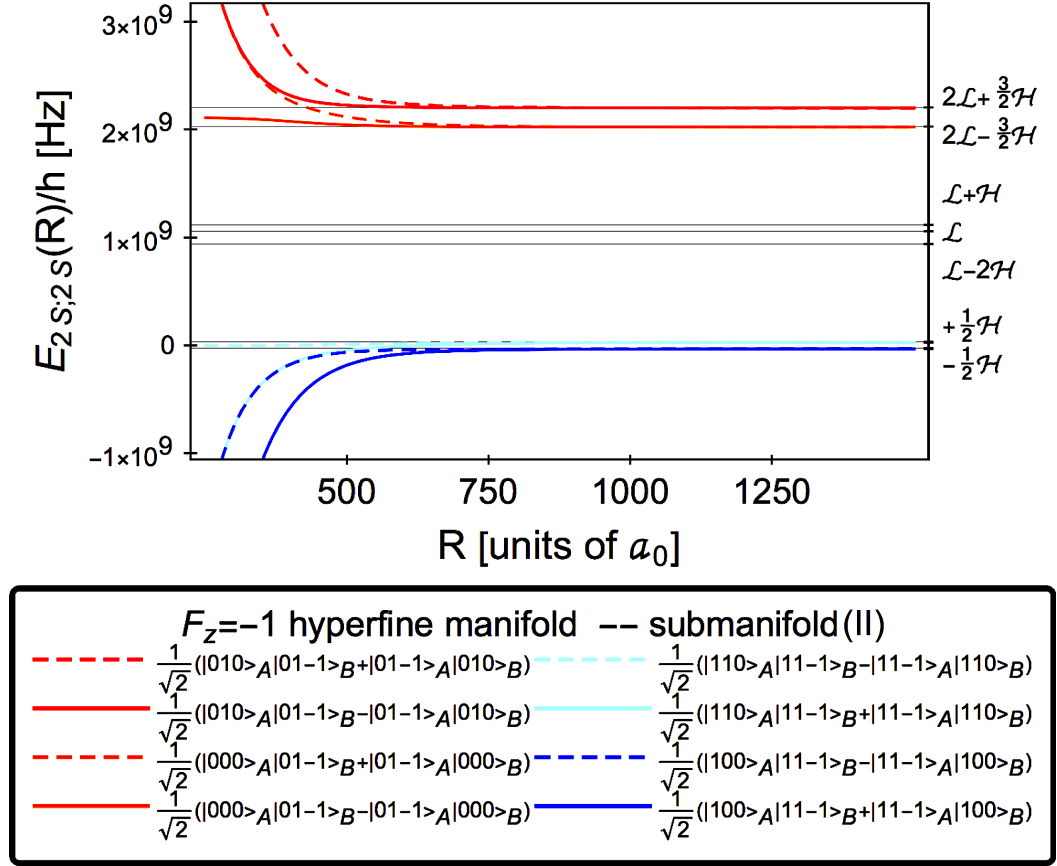


Figure 7.12: Energy levels as a function of interatomic separation R in the subspace (II) of the $F_z = -1$ hyperfine manifold. For infinitely long interatomic separation, there are four distinct energy levels, as expected from the unperturbed energy values of the Hamiltonian matrix, $H_{(F_z=-1)}^{(\text{II})}$, given by Eq. (7.142). However, for small interatomic separation, the energy levels split and deviate from the unperturbed values.

The Hamiltonian matrix of the $F_z = -2$ reads

$$H_{(F_z=-2)} = \begin{pmatrix} \frac{3}{2}\mathcal{H} + 2\mathcal{L} & 0 & 0 & -2\mathcal{V} \\ 0 & \mathcal{H} + \mathcal{L} & -2\mathcal{V} & 0 \\ 0 & -2\mathcal{V} & \mathcal{H} + \mathcal{L} & 0 \\ -2\mathcal{V} & 0 & 0 & \frac{1}{2}\mathcal{H} \end{pmatrix}. \quad (7.144)$$

This is same to that of the $F_z = +2$ manifold. The Hamiltonian matrix $H_{(F_z=-2)}$ can be decoupled into two 2×2 matrices $H_{(F_z=-2)}^{(I)}$ and $H_{(F_z=-2)}^{(II)}$ which read

$$H_{(F_z=-2)}^{(I)} = \begin{pmatrix} \frac{3\mathcal{H}}{2} + 2\mathcal{L} & -2\mathcal{V} \\ -2\mathcal{V} & \frac{\mathcal{H}}{2} \end{pmatrix} \quad \text{and} \quad H_{(F_z=-2)}^{(II)} = \begin{pmatrix} \mathcal{H} + \mathcal{L} & -2\mathcal{V} \\ -2\mathcal{V} & \mathcal{H} + \mathcal{L} \end{pmatrix}. \quad (7.145)$$

The subspace (I) with the Hamiltonian matrix $H_{(F_z=-2)}^{(I)}$ is spanned by

$$|\phi_1^{(I)}\rangle = |\phi'_1\rangle = |(0, 1, -1)_A(0, 1, -1)_B\rangle, \quad \text{and} \quad |\phi_2^{(I)}\rangle = |\phi'_4\rangle = |(1, 1, -1)_A(1, 1, -1)_B\rangle. \quad (7.146)$$

The eigenvalues of the Hamiltonian matrix $H_{(F_z=-2)}^{(I)}$ are

$$E_{\pm}^{(I)} = \mathcal{H} + \mathcal{L} \pm \frac{1}{2}\sqrt{16\mathcal{V}^2 + (\mathcal{H} + 2\mathcal{L})^2}, \quad (7.147)$$

Or,

$$E_+^{(II)} = \frac{3}{2}\mathcal{H} + 2\mathcal{L} + 4\frac{\mathcal{V}^2}{\mathcal{H} + 2\mathcal{L}} + O(\mathcal{V}^4), \quad (7.148a)$$

$$E_-^{(I)} = \frac{1}{2}\mathcal{H} - 4\frac{\mathcal{V}^2}{\mathcal{H} + 2\mathcal{L}} + O(\mathcal{V}^4), \quad (7.148b)$$

with the corresponding eigenvectors

$$|\phi_+^{(I)}\rangle = \frac{1}{\sqrt{\alpha_1^2 + \alpha_2^2}} \left(\alpha_1 |\phi_1^{(I)}\rangle + \alpha_2 |\phi_2^{(I)}\rangle \right), \quad (7.149a)$$

$$|\phi_-^{(I)}\rangle = \frac{1}{\sqrt{\alpha_1^2 + \alpha_2^2}} \left(\alpha_2 |\phi_1^{(I)}\rangle - \alpha_1 |\phi_2^{(I)}\rangle \right), \quad (7.149b)$$

where α_1 and α_2 are given by

$$\alpha_1 = -\frac{\sqrt{16\mathcal{V}^2 + (\mathcal{H} + 2\mathcal{L})^2} + \mathcal{H} + 2\mathcal{L}}{4\mathcal{V}} \equiv a_1, \quad (7.150a)$$

$$\alpha_2 = 1 \equiv a_2. \quad (7.150b)$$

The subspace(II) is composed of

$$|\phi_1^{(\text{II})}\rangle = |\phi_2'\rangle = |(0, 1, -1)_A(1, 1, -1)_B\rangle, \text{ and } |\phi_2^{(\text{II})}\rangle = |\phi_3'\rangle = |(1, 1, -1)_A(0, 1, -1)_B\rangle. \quad (7.151)$$

with the hamiltonian matrix $H_{(F_z=-2)}^{(\text{II})}$ given in Eq. (7.145). The eigenenergies and eigenvectors of the Hamiltonian matrix $H_{(F_z=-2)}^{(\text{II})}$ are given by

$$E_+^{(\text{I})} = \mathcal{H} + \mathcal{L} \pm 2\mathcal{V}, \quad (7.152)$$

$$|\phi_{\pm}^{(\text{II})}\rangle = \frac{1}{2} \left(|\phi_1^{(\text{II})}\rangle \pm |\phi_2^{(\text{II})}\rangle \right). \quad (7.153)$$

See Figure 7.13 for evolution of energy levels as a function of interatomic separation R in the $F_z = -2$ hyperfine manifold. Note that, the eigenvalues of the $F_z = -2$ manifold are identical to that of $F_z = +2$ and eigenvectors of one manifold can be acquired from the other one just by swapping $|\phi_j\rangle \leftrightarrow |\phi_j'\rangle$.

7.8. REPUDIATION OF NON-CROSSING RULE

The non-crossing theorem for a polyatomic system [71] says that for a system with N atoms, there will be $3N - 6$ coupling parameters, as a result, level-crossing would occur, however, the number of level-crossing does not exceed $3N - 6$, where $N \geq 2$. For example, for a system containing three atoms, there are three coupling parameters. Thus the potential curves can have maximum three level-crossings. Similarly, a four-atom system can have maximum six level-crossings. On the other hand, a system containing two atoms has just one coupling parameter. In the long-range interaction, this coupling parameter is the interatomic distance R . Thus, the two

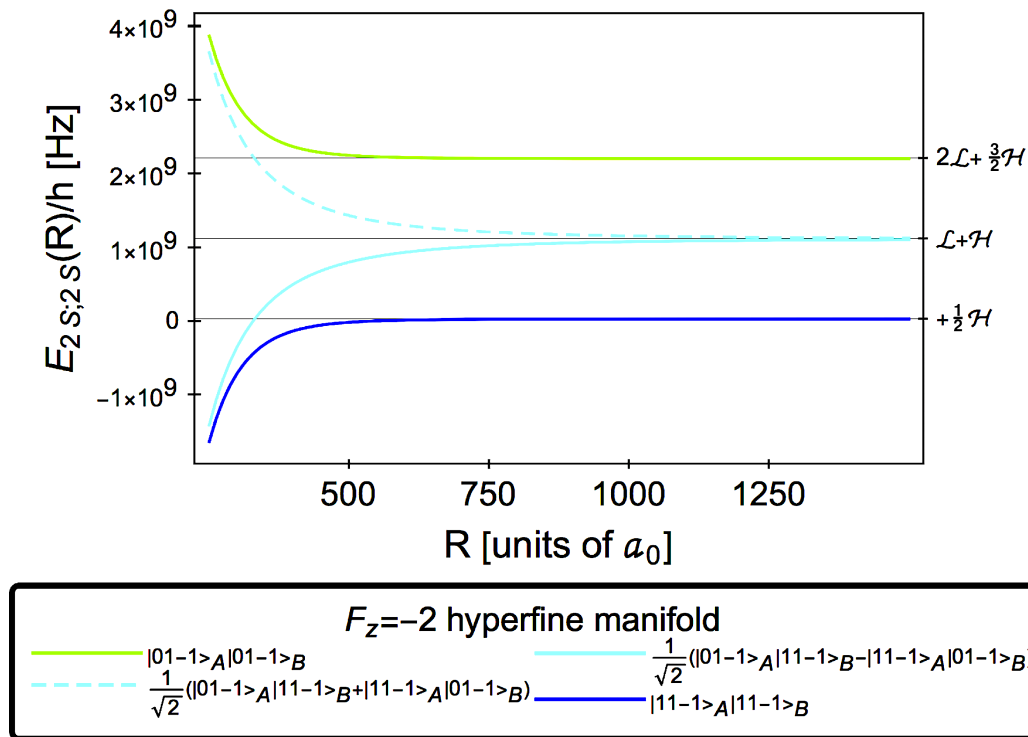


Figure 7.13: Energy levels as a function of interatomic separation R in the $F_z = -2$ hyperfine manifold. For large interatomic separation, there are three distinct energy levels. However, for small interatomic separation, the degenerate energy level $\mathcal{L} + \mathcal{H}$ splits into two, and the level repulsion occurs.

atom system is supposed not to have any level-crossing, which requires no level crossings also in our system of two neutral hydrogen atoms both of them being in the first excited states.

For $F_z = \pm 2$ hyperfine manifolds of the $2S-2S$ system, each of the irreducible subspaces is of dimension two. As expected from the non-crossing rule, we also do not see the level crossings in either of the four subspaces. In the $F_z = \pm 1$ hyperfine manifolds, each of irreducible subspaces is of dimension 8. There is no level crossing within the irreducible subspaces although some of the energy curves from different irreducible subspaces cross. Peculiar things happen in the $F_z = 0$ hyperfine subspace. In the subspace in which the atoms are in $S-P$ or $P-S$ configurations, we

witness two level crossings. On the other subspace in which the atoms are either in S - S or P - P configurations, several level crossings occur. In our work, we have employed an extended-precision arithmetic near the crossing point and confirmed that the crossing points are not due to the numerical insufficiency [72]. This finding confirms that the level crossings do present and are unavoidable, which indicates that the non-crossing theorem discussed in the literature so far does not hold true in higher dimensional quantum mechanical systems. Taking the example of water dimer, authors in Ref. [73] also have shown possibility of the curve crossings between two Born-Oppenheimer potential energy surfaces. Interestingly, they also found several curve crossings of potential energy surfaces. Their results also favor our findings. The following rewording seems appropriate: “A system with two energy levels follows non-crossing theorem. However, the higher-dimensional irreducible matrices do not always follow the non-crossing theorem”.

7.9. HYPERFINE SHIFT IN SPECIFIC SPECTATOR STATES

In this section, we investigate the energy differences of $2S$ singlet and triplet hyperfine sub levels. The spectator can be in any arbitrary atomic state. We present detailed calculation of the Hamiltonian matrices, the normalized eigenvectors and the corresponding eigenvalues in all three possible hyperfine manifolds, viz. $F_z = +1$, $F_z = 0$ and $F_z = -1$.

7.9.1. Manifold $F_z = +1$. The atom A , in the following states

$$|\psi_1^{(\text{II})}\rangle = |(0, 0, 0)_A(0, 1, 1)_B\rangle \quad \text{and} \quad |\psi_1^{(\text{I})}\rangle = |(0, 0, 0)_A(1, 1, 1)_B\rangle \quad (7.154)$$

is in the hyperfine singlet whereas the atom B is in the hyperfine triplet in the states

$$|\psi_2^{(\text{II})}\rangle = |(0, 1, 0)_A(0, 1, 1)_B\rangle \quad \text{and} \quad |\psi_2^{(\text{I})}\rangle = |(0, 1, 0)_A(1, 1, 1)_B\rangle. \quad (7.155)$$

The spectator atom, i.e., the atom B is in $2S_{1/2}$ state in the transition $|\psi_1^{(\text{II})}\rangle \rightarrow |\psi_2^{(\text{II})}\rangle$ while the spectator atom B is in the $2P_{1/2}$ state in the transition $|\psi_1^{(\text{I})}\rangle \rightarrow |\psi_2^{(\text{I})}\rangle$. Note that the state $|\psi_1^{(\text{I})}\rangle$ is same to that of $|\psi_7^{(\text{I})}\rangle = |(1, 1, 1)_A(0, 0, 0)_B\rangle$ and the state $|\psi_2^{(\text{I})}\rangle$ is also same to that of $|\psi_8^{(\text{I})}\rangle = |(1, 1, 1)_A(0, 1, 0)_B\rangle$ under the interchange of the subscripts A and B . Thus, the state $|\psi_1^{(\text{I})}\rangle$ is energetically degenerate to $|\psi_7^{(\text{I})}\rangle$ and the state $|\psi_2^{(\text{I})}\rangle$ is energetically degenerate to $|\psi_8^{(\text{I})}\rangle$ which are coupled with each other through the off-diagonal elements \mathcal{V} . We have

$$\langle \psi_1^{(\text{I})} | H_{\text{vdW}} | \psi_7^{(\text{I})} \rangle = \mathcal{V}, \quad (7.156a)$$

$$\langle \psi_2^{(\text{I})} | H_{\text{vdW}} | \psi_8^{(\text{I})} \rangle = \mathcal{V}. \quad (7.156b)$$

Eqs. (7.156a) and (7.156b) tell us that, in the $F_z = +1$ manifold, if the spectator atom is at $2P_{1/2}$ -state, the hyperfine transition is linear to \mathcal{V} . On the other hand, $|\psi_1^{(\text{II})}\rangle$ and $|\psi_2^{(\text{II})}\rangle$ are not coupled to any other energetically degenerate level. This implies that there is no first order vdW shift proportional to \mathcal{V} . The absence of the first order shift does not guarantee that $|\psi_1^{(\text{II})}\rangle$ and $|\psi_2^{(\text{II})}\rangle$ are completely decoupled. Let us define the effective Hamiltonian H_{eff} as

$$H_{\text{eff}} = \lim_{\epsilon \rightarrow 0} H_{\text{eff}}^{(\epsilon)} = \lim_{\epsilon \rightarrow 0} H_1 \cdot \left(\frac{1}{E_{0,\psi} - H_0 + \epsilon} \right) \cdot H_1, \quad (7.157)$$

where H_1 is the off-diagonal part of the Hamiltonian matrix of respective hyperfine manifold and $E_{0,\psi}$ is the energy corresponding to the reference state $|\psi\rangle$. We take the limit $\epsilon \rightarrow 0$ at the end of the calculation.

Interchanging the subscripts A and B in the state $|\psi_1^{(\text{II})}\rangle$, we get the state $|\psi_3^{(\text{II})}\rangle = |(0, 1, 1)_A(0, 0, 0)_B\rangle$. This implies that the state $|\psi_1^{(\text{II})}\rangle$ with energy $\mathcal{L} - \frac{3}{2}\mathcal{H}$ is

energetically degenerate with respect to $|\psi_3^{(\text{II})}\rangle$. The Hamiltonian matrix $H_{1,3}$ reads

$$H_{1,3} = \lim_{\epsilon \rightarrow 0} \begin{pmatrix} \langle \psi_1^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_1^{(\text{II})} \rangle & \langle \psi_1^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_3^{(\text{II})} \rangle \\ \langle \psi_3^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_1^{(\text{II})} \rangle & \langle \psi_3^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_3^{(\text{II})} \rangle \end{pmatrix}. \quad (7.158)$$

Let us now evaluate the elements of the matrix $H_{1,3}$.

$$(H_{1,3})_{11} = \lim_{\epsilon \rightarrow 0} \langle \psi_1^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_1^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_1^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_1^{(\text{II})} \rangle. \quad (7.159)$$

Let us introduce a completeness relation:

$$\sum_{\beta} |\beta\rangle \langle \beta| = 1. \quad (7.160)$$

This is the so-called spectral decomposition of unity [74]. Using relation (7.160) in Eq. (7.159), we get

$$\begin{aligned} (H_{1,3})_{11} &= \lim_{\epsilon \rightarrow 0} \sum_m \sum_n \langle \psi_1^{(\text{II})} | H_1 | m \rangle \langle m | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | n \rangle \langle n | H_1 | \psi_1^{(\text{II})} \rangle \\ &= \lim_{\epsilon \rightarrow 0} \left[\langle \psi_6^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_6^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_6^{(\text{II})} \rangle \langle \psi_6^{(\text{II})} | H_1 | \psi_1^{(\text{II})} \rangle \right. \\ &\quad + \langle \psi_7^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_7^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_7^{(\text{II})} \rangle \langle \psi_7^{(\text{II})} | H_1 | \psi_1^{(\text{II})} \rangle \\ &\quad \left. + \langle \psi_8^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_8^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_8^{(\text{II})} \rangle \langle \psi_8^{(\text{II})} | H_1 | \psi_1^{(\text{II})} \rangle \right] \\ &= \frac{4\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} + \frac{\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} + \frac{1}{2}\mathcal{H}} + \frac{\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} \\ &= \frac{5\mathcal{V}^2}{2(\mathcal{L} - \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}}. \end{aligned} \quad (7.161)$$

$$\begin{aligned}
(H_{1,3})_{12} &= \lim_{\epsilon \rightarrow 0} \langle \psi_1^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_3^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_1^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_3^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_m \sum_n \langle \psi_1^{(\text{II})} | H_1 | m \rangle \langle m | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | n \rangle \langle n | H_1 | \psi_3^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \left[\langle \psi_1^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_1^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_1^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \right. \\
&\quad + \langle \psi_6^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_6^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_6^{(\text{II})} \rangle \langle \psi_6^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \\
&\quad + \langle \psi_7^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_7^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_7^{(\text{II})} \rangle \langle \psi_7^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \\
&\quad \left. + \langle \psi_8^{(\text{II})} | \frac{1}{E_{0,\psi_1^{(\text{II})}} - H_0 + \epsilon} | \psi_8^{(\text{II})} \rangle \langle \psi_1^{(\text{II})} | H_1 | \psi_8^{(\text{II})} \rangle \langle \psi_8^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \right] \\
&= 0 + \frac{(-2\mathcal{V})(-\mathcal{V})}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} + 0 + \frac{(-\mathcal{V})(-2\mathcal{V})}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} \\
&= \frac{2\mathcal{V}^2}{\mathcal{L} - \mathcal{H}}. \tag{7.162}
\end{aligned}$$

To obtain the second last line of Eq. (7.162), we substituted the values $\langle \psi_1^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle = 0$, $\langle \psi_7^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle = 0$ and then we took $\epsilon = 0$. The Hamiltonian matrix $H_{(F_2=+1)}^{(\text{II})}$ is symmetric. Thus, we have

$$(H_{1,3})_{12} = (H_{1,3})_{21}. \tag{7.163}$$

Similarly,

$$\begin{aligned}
(H_{1,3})_{22} &= \lim_{\epsilon \rightarrow 0} \langle \psi_3^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_3^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_3^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_3^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_m \sum_n \langle \psi_3^{(\text{II})} | H_1 | m \rangle \langle m | \frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} | n \rangle \langle n | H_1 | \psi_3^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \left[\langle \psi_3^{(\text{II})} | \frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} | \psi_3^{(\text{II})} \rangle \langle \psi_3^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \langle \psi_3^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \right. \\
&\quad \left. + \langle \psi_5^{(\text{II})} | \frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} | \psi_5^{(\text{II})} \rangle \langle \psi_3^{(\text{II})} | H_1 | \psi_5^{(\text{II})} \rangle \langle \psi_5^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \right]
\end{aligned}$$

$$\begin{aligned}
& + \langle \psi_6^{(\text{II})} | \frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} | \psi_6^{(\text{II})} \rangle \langle \psi_3^{(\text{II})} | H_1 | \psi_6^{(\text{II})} \rangle \langle \psi_6^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \\
& + \langle \psi_8^{(\text{II})} | \frac{1}{E_{0,\psi_3^{(\text{II})}} - H_0 + \epsilon} | \psi_8^{(\text{II})} \rangle \langle \psi_3^{(\text{II})} | H_1 | \psi_8^{(\text{II})} \rangle \langle \psi_8^{(\text{II})} | H_1 | \psi_3^{(\text{II})} \rangle \Big] \\
& = \frac{\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} + \frac{1}{2}\mathcal{H}} + \frac{\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} + \frac{4\mathcal{V}^2}{2\mathcal{L} - \frac{3}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} \\
& = \frac{5\mathcal{V}^2}{2(\mathcal{L} - \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}}. \tag{7.164}
\end{aligned}$$

The matrix $H_{1,3}$ given in Eq. (7.158) reads

$$H_{1,3} = \begin{pmatrix} \frac{5\mathcal{V}^2}{2(\mathcal{L}-\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}-\mathcal{H}} & \frac{2\mathcal{V}^2}{\mathcal{L}-\mathcal{H}} \\ \frac{2\mathcal{V}^2}{\mathcal{L}-\mathcal{H}} & \frac{5\mathcal{V}^2}{2(\mathcal{L}-\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}-\mathcal{H}} \end{pmatrix}. \tag{7.165}$$

The matrix (7.165) has the following eigenvalues and eigenvectors:

$$E_{1,3}^{\pm} = \frac{5\mathcal{V}^2}{2(\mathcal{L} - \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \pm \frac{2\mathcal{V}^2}{\mathcal{L} - \mathcal{H}}, \tag{7.166a}$$

$$|\psi_{1,3}^{(\text{II})\pm}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle \pm |\psi_3^{(\text{II})}\rangle \right). \tag{7.166b}$$

Let us now discuss the reference state $|\psi_2^{(\text{II})}\rangle$. The state $|\psi_2^{(\text{II})}\rangle$ is degenerate with the state $|\psi_4^{(\text{II})}\rangle$. The unperturbed energy corresponding to these states is $2\mathcal{L} + \frac{3}{2}\mathcal{H}$. The Hamiltonian matrix $H_{2,4}$ is given by

$$H_{2,4} = \lim_{\epsilon \rightarrow 0} \begin{pmatrix} \langle \psi_2^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_2^{(\text{II})} \rangle & \langle \psi_2^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_4^{(\text{II})} \rangle \\ \langle \psi_4^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_2^{(\text{II})} \rangle & \langle \psi_4^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_4^{(\text{II})} \rangle \end{pmatrix}. \tag{7.167}$$

The first diagonal element $(H_{2,4})_{11}$ is given by

$$\begin{aligned}
(H_{2,4})_{11} & = \lim_{\epsilon \rightarrow 0} \langle \psi_2^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_2^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_2^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_2^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_2^{(\text{II})} \rangle \\
& = \lim_{\epsilon \rightarrow 0} \sum_m \sum_n \langle \psi_2^{(\text{II})} | H_1 | m \rangle \langle m | \frac{1}{E_{0,\psi_2^{(\text{II})}} - H_0 + \epsilon} | n \rangle \langle n | H_1 | \psi_2^{(\text{II})} \rangle
\end{aligned}$$

$$\begin{aligned}
&= \lim_{\epsilon \rightarrow 0} \sum_{k=5,7,8} \langle \psi_k^{(\text{II})} | \frac{1}{E_{0,\psi_2^{(\text{II})}} - H_0 + \epsilon} | \psi_k^{(\text{II})} \rangle \langle \psi_2^{(\text{II})} | H_1 | \psi_k^{(\text{II})} \rangle \langle \psi_k^{(\text{II})} | H_1 | \psi_2^{(\text{II})} \rangle \\
&= \frac{5\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}}.
\end{aligned} \tag{7.168}$$

The next diagonal element $(H_{2,4})_{22}$ is given by

$$\begin{aligned}
(H_{2,4})_{22} &= \lim_{\epsilon \rightarrow 0} \langle \psi_4^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_4^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_4^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_4^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_4^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=5,6,7} \langle \psi_k^{(\text{II})} | \frac{1}{E_{0,\psi_4^{(\text{II})}} - H_0 + \epsilon} | \psi_k^{(\text{II})} \rangle \langle \psi_4^{(\text{II})} | H_1 | \psi_k^{(\text{II})} \rangle \langle \psi_k^{(\text{II})} | H_1 | \psi_4^{(\text{II})} \rangle \\
&= \frac{5\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}}.
\end{aligned} \tag{7.169}$$

The off-diagonal elements are given by

$$\begin{aligned}
(H_{2,4})_{12} &= \lim_{\epsilon \rightarrow 0} \langle \psi_2^{(\text{II})} | H_{\text{eff}}^{(\epsilon)} | \psi_4^{(\text{II})} \rangle = \lim_{\epsilon \rightarrow 0} \langle \psi_2^{(\text{II})} | H_1 \cdot \left(\frac{1}{E_{0,\psi_2^{(\text{II})}} - H_0 + \epsilon} \right) \cdot H_1 | \psi_4^{(\text{II})} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=5,7} \langle \psi_k^{(\text{II})} | \frac{1}{E_{0,\psi_2^{(\text{II})}} - H_0 + \epsilon} | \psi_k^{(\text{II})} \rangle \langle \psi_2^{(\text{II})} | H_1 | \psi_k^{(\text{II})} \rangle \langle \psi_k^{(\text{II})} | H_1 | \psi_4^{(\text{II})} \rangle \\
&= \frac{2\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} = (H_{2,4})_{21}.
\end{aligned} \tag{7.170}$$

The Hamiltonian matrix $H_{2,4}$ thus reads

$$H_{2,4} = \begin{pmatrix} \frac{5\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} & \frac{2\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} \\ \frac{2\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} & \frac{5\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} \end{pmatrix} \tag{7.171}$$

which has the eigenvalues

$$E_{2,4}^{\pm} = \frac{5\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} \pm \frac{2\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} \tag{7.172}$$

with eigenvectors

$$|\psi_{2,4}^{(\text{II})\pm}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_2^{(\text{II})}\rangle \pm |\psi_4^{(\text{II})}\rangle \right). \quad (7.173)$$

The first order vdW shift \mathcal{V} is proportional to R^{-3} , where R is the interatomic distance. This clearly indicates that the transition energies are R -dependent. In the $|\psi_1^{(\text{II})}\rangle \rightarrow |\psi_2^{(\text{II})}\rangle$ transition, the energy difference between the symmetric superpositions $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle + |\psi_3^{(\text{II})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_2^{(\text{II})}\rangle + |\psi_4^{(\text{II})}\rangle \right)$ and the energy difference between the antisymmetric superposition $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle - |\psi_3^{(\text{II})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_2^{(\text{II})}\rangle - |\psi_4^{(\text{II})}\rangle \right)$ are given in the Table 7.1. In the $|\psi_1^{(\text{I})}\rangle \rightarrow |\psi_2^{(\text{I})}\rangle$ transition, the energy difference be-

Table 7.1: The energy differences between the symmetric superposition $\Delta E_{\text{II}}^{(+)}$ and the antisymmetric superposition $\Delta E_{\text{II}}^{(-)}$ in the unit of the hyperfine splitting constant \mathcal{H} . In this transition, the spectator atom is in the $2S_{1/2}$ state.

R	$\Delta E_{\text{II}}^{(+)}$	$\Delta E_{\text{II}}^{(-)}$
∞	0	0
750 a_0	-0.007 01	-0.00133
500 a_0	0.383 31	0.043 94
250 a_0	37.042 26	22.835 56

tween the symmetric superpositions $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{I})}\rangle + |\psi_7^{(\text{I})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_2^{(\text{I})}\rangle + |\psi_8^{(\text{I})}\rangle \right)$ and the energy difference between the antisymmetric superposition $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{I})}\rangle - |\psi_7^{(\text{I})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_2^{(\text{I})}\rangle - |\psi_8^{(\text{I})}\rangle \right)$ are given in the Table 7.2.

7.9.2. Manifold $F_z = 0$. The 24-dimensional $F_z = 0$ hyperfine manifold has 4 states having atom A in the $2S$ singlet level as given below:

$$\begin{aligned} |\Psi_1^{(\text{I})}\rangle &= |(0, 0, 0)_A(0, 0, 0)_B\rangle, & |\Psi_2^{(\text{I})}\rangle &= |(0, 0, 0)_A(0, 1, 0)_B\rangle, \\ |\Psi_1^{(\text{II})}\rangle &= |(0, 0, 0)_A(1, 0, 0)_B\rangle, & |\Psi_2^{(\text{II})}\rangle &= |(0, 0, 0)_A(1, 1, 0)_B\rangle. \end{aligned} \quad (7.174)$$

Table 7.2: The energy differences between the symmetric superposition $\Delta E_{\text{I}}^{(+)}$ and the antisymmetric superposition $\Delta E_{\text{I}}^{(-)}$ in the unit of the hyperfine splitting constant \mathcal{H} . In this transition, the spectator atom is in the $2P_{1/2}$ state.

R	$\Delta E_{\text{I}}^{(+)}$	$\Delta E_{\text{I}}^{(-)}$
∞	0	0
750 a_0	2.637 62	2.817 36
500 a_0	13.267 84	13.322 29
250 a_0	125.041 24	125.042 34

The atom A is in the hyperfine triplet in the following 4 states:

$$\begin{aligned}
 |\Psi_4^{(\text{I})}\rangle &= |(0, 1, 0)_A(0, 0, 0)_B\rangle, & |\Psi_5^{(\text{I})}\rangle &= |(0, 1, 0)_A(0, 1, 0)_B\rangle, \\
 |\Psi_4^{(\text{II})}\rangle &= |(0, 1, 0)_A(1, 0, 0)_B\rangle, & |\Psi_5^{(\text{II})}\rangle &= |(0, 1, 0)_A(1, 1, 0)_B\rangle.
 \end{aligned} \tag{7.175}$$

The spectator atom B is in the state $|2S_{1/2}\rangle$, which is preserved in the transitions $|\Psi_1^{(\text{I})}\rangle \rightarrow |\Psi_4^{(\text{I})}\rangle$ and $|\Psi_2^{(\text{I})}\rangle \rightarrow |\Psi_5^{(\text{I})}\rangle$ whereas the state $|2P_{1/2}\rangle$ of the spectator atom B is preserved in the transitions $|\Psi_1^{(\text{II})}\rangle \rightarrow |\Psi_4^{(\text{II})}\rangle$ and $|\Psi_2^{(\text{II})}\rangle \rightarrow |\Psi_5^{(\text{II})}\rangle$. The state $|\Psi_4^{(\text{II})}\rangle$ is energetically degenerate with $|\Psi_8^{(\text{II})}\rangle$ and coupled each other by the first order vdW interaction $-2\mathcal{V}$, i.e.,

$$\langle \Psi_4^{(\text{II})} | H_{\text{vdW}} | \Psi_8^{(\text{II})} \rangle = -2\mathcal{V}. \tag{7.176}$$

Same thing happens for $|\Psi_2^{(\text{II})}\rangle$ which is degenerate to $|\Psi_{10}^{(\text{II})}\rangle$ and $|\Psi_5^{(\text{II})}\rangle$ which is degenerate to $|\Psi_9^{(\text{II})}\rangle$ and $|\Psi_{12}^{(\text{II})}\rangle$, i.e.,

$$\langle \Psi_2^{(\text{II})} | H_{\text{vdW}} | \Psi_{10}^{(\text{II})} \rangle = -2\mathcal{V}, \tag{7.177}$$

$$\langle \Psi_5^{(\text{II})} | H_{\text{vdW}} | \Psi_9^{(\text{II})} \rangle = \langle \Psi_5^{(\text{II})} | H_{\text{vdW}} | \Psi_{12}^{(\text{II})} \rangle = -2\mathcal{V}. \tag{7.178}$$

Interesting thing happens in the transition $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(I)}\rangle$ as the state $|\Psi_1^{(I)}\rangle$ is non-degenerate. Here is the detailed calculation of the energy $\Delta E_{\Psi_1^{(I)}}$.

$$\begin{aligned}
\Delta E_{\Psi_1^{(I)}} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_1^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_1^{(I)} \rangle = \lim_{\epsilon \rightarrow 0} \langle \Psi_1^{(I)} | H_1 \cdot \left(\frac{1}{E_{0, \Psi_1^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_1^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_m \sum_n \langle \Psi_1^{(I)} | H_1 | m \rangle \langle m | \frac{1}{E_{0, \Psi_1^{(I)}} - H_0 + \epsilon} | n \rangle \langle n | H_1 | \Psi_1^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=9,11,12} \langle \Psi_k^{(I)} | \frac{1}{E_{0, \Psi_1^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_1^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_1^{(I)} \rangle \\
&= \frac{(-\mathcal{V})^2}{2\mathcal{L} - \frac{9}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} + \frac{(-2\mathcal{V})^2}{2\mathcal{L} - \frac{9}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} + \frac{(-\mathcal{V})^2}{2\mathcal{L} - \frac{9}{2}\mathcal{H} - \frac{1}{2}\mathcal{H}} \\
&= \frac{6\mathcal{V}^2}{2\mathcal{L} - 5\mathcal{H}}. \tag{7.179}
\end{aligned}$$

The state $|\Psi_4^{(I)}\rangle$ is energetically degenerate to the $|\Psi_2^{(I)}\rangle$. However, the degenerate states are not coupled directly. So, the first order vdW shift is absent. We want to determine the matrix $\mathbb{H}_{2,4}$ given by

$$\mathbb{H}_{2,4} = \lim_{\epsilon \rightarrow 0} \begin{pmatrix} \langle \Psi_2^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_2^{(I)} \rangle & \langle \Psi_2^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_4^{(I)} \rangle \\ \langle \Psi_4^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_2^{(I)} \rangle & \langle \Psi_4^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_4^{(I)} \rangle \end{pmatrix}. \tag{7.180}$$

Here, we have used a new symbol \mathbb{H} to denote the Hamiltonian matrix $\mathbb{H}_{2,4}$ instead of $H_{2,4}$ just to distinguish the matrix (7.180) from (7.167). The new symbol does not carry new physical meaning. Following the same procedure which we applied to calculate $H_{2,4}$ in the subspace (II) of the $F_z = +1$ manifold, we can easily calculate the Hamiltonian matrix $\mathbb{H}_{2,4}$ in the subspace (I) of the $F_z = 0$ manifold which yields

$$\mathbb{H}_{2,4} = \begin{pmatrix} \frac{\mathcal{V}^2}{\mathcal{L} - \mathcal{H}} + \frac{4\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} & \frac{\mathcal{V}^2}{-\mathcal{L} + \mathcal{H}} \\ \frac{\mathcal{V}^2}{-\mathcal{L} + \mathcal{H}} & \frac{\mathcal{V}^2}{\mathcal{L} - \mathcal{H}} + \frac{4\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \end{pmatrix}. \tag{7.181}$$

The eigenvalues and the eigenvectors corresponding to the Hamiltonian matrix $\mathbb{H}_{2,4}$ are

$$\mathbb{E}_{2,4}^{\pm} = \frac{\mathcal{V}^2}{\mathcal{L} - \mathcal{H}} + \frac{4\mathcal{V}^2}{2\mathcal{L} - \mathcal{H}} \pm \frac{\mathcal{V}^2}{-\mathcal{L} + \mathcal{H}}, \quad (7.182a)$$

$$|\Psi_{2,4}^{\pm}\rangle = \frac{1}{\sqrt{2}} \left(|\Psi_2^{(I)}\rangle \pm |\Psi_4^{(I)}\rangle \right). \quad (7.182b)$$

Let us now analyze the state $|\Psi_5^{(I)}\rangle$ corresponding to the unperturbed energy $2\mathcal{L} + \frac{3}{2}\mathcal{H}$, which is degenerate to the states $|\Psi_3^{(I)}\rangle$ and $|\Psi_6^{(I)}\rangle$. The Hamiltonian matrix $H_{3,5,6}$ is given by

$$H_{3,5,6} = \lim_{\epsilon \rightarrow 0} \begin{pmatrix} \langle \Psi_3^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_3^{(I)} \rangle & \langle \Psi_3^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_5^{(I)} \rangle & \langle \Psi_3^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_6^{(I)} \rangle \\ \langle \Psi_5^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_3^{(I)} \rangle & \langle \Psi_5^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_5^{(I)} \rangle & \langle \Psi_5^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_6^{(I)} \rangle \\ \langle \Psi_6^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_3^{(I)} \rangle & \langle \Psi_6^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_5^{(I)} \rangle & \langle \Psi_6^{(I)} | H_{\text{eff}}^{(\epsilon)} | \Psi_6^{(I)} \rangle \end{pmatrix}. \quad (7.183)$$

The elements of the matrix $H_{3,5,6}$ can be calculated in a similar way to $H_{1,3}$ in the subspace (II) of the $F_z = +1$ manifold. We have,

$$\begin{aligned} (H_{3,5,6})_{11} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_3^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_3^{(I)} \rangle \\ &= \lim_{\epsilon \rightarrow 0} \sum_{k=7,8,9,10,11} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_3^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_3^{(I)} \rangle \\ &= \frac{\mathcal{V}^2}{2\mathcal{L} + 3\mathcal{H}} + \frac{\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} + \frac{5\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}}. \end{aligned} \quad (7.184)$$

$$\begin{aligned} (H_{3,5,6})_{12} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_3^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_5^{(I)} \rangle \\ &= \lim_{\epsilon \rightarrow 0} \sum_{k=7,9} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_3^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_5^{(I)} \rangle \\ &= \frac{2\mathcal{V}^2}{2\mathcal{L} + 3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} = (H_{3,5,6})_{21}. \end{aligned} \quad (7.185)$$

$$\begin{aligned}
(H_{3,5,6})_{13} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_3^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_6^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=7,8,10,11} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_3^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_3^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_6^{(I)} \rangle \\
&= \frac{\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} - \frac{\mathcal{V}^2}{2(\mathcal{L} + \mathcal{H})} - \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} + \frac{\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} \\
&= 0 = (H_{3,5,6})_{31}.
\end{aligned} \tag{7.186}$$

$$\begin{aligned}
(H_{3,5,6})_{22} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_5^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_5^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_5^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=7,9,12} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_5^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_5^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_5^{(I)} \rangle \\
&= \frac{4\mathcal{V}^2}{2\mathcal{L} + 3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}}.
\end{aligned} \tag{7.187}$$

$$\begin{aligned}
(H_{3,5,6})_{23} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_5^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_5^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_6^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=7,9,12} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_5^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_5^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_6^{(I)} \rangle \\
&= \frac{2\mathcal{V}^2}{2\mathcal{L} + 3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}} = (H_{3,5,6})_{32}.
\end{aligned} \tag{7.188}$$

$$\begin{aligned}
(H_{3,5,6})_{33} &= \lim_{\epsilon \rightarrow 0} \langle \Psi_6^{(I)} | H_1 \cdot \left(\frac{1}{E_{0,\Psi_6^{(I)}} - H_0 + \epsilon} \right) \cdot H_1 | \Psi_6^{(I)} \rangle \\
&= \lim_{\epsilon \rightarrow 0} \sum_{k=7,8,10,11,12} \langle \Psi_k^{(I)} | \frac{1}{E_{0,\Psi_6^{(I)}} - H_0 + \epsilon} | \Psi_k^{(I)} \rangle \langle \Psi_6^{(I)} | H_1 | \Psi_k^{(I)} \rangle \langle \Psi_k^{(I)} | H_1 | \Psi_6^{(I)} \rangle \\
&= \frac{\mathcal{V}^2}{2\mathcal{L} + 3\mathcal{H}} + \frac{\mathcal{V}^2}{\mathcal{L} + \mathcal{H}} + \frac{5\mathcal{V}^2}{2\mathcal{L} + \mathcal{H}}.
\end{aligned} \tag{7.189}$$

The matrix $H_{3,5,6}$ takes the following form

$$H_{3,5,6} = \begin{pmatrix} \frac{\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{\mathcal{V}^2}{\mathcal{L}+\mathcal{H}} + \frac{5\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & \frac{2\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & 0 \\ \frac{2\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & \frac{4\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & \frac{2\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} \\ 0 & \frac{2\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{2\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & \frac{\mathcal{V}^2}{2\mathcal{L}+3\mathcal{H}} + \frac{\mathcal{V}^2}{\mathcal{L}+\mathcal{H}} + \frac{5\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} \end{pmatrix}. \quad (7.190)$$

If we apply the additional approximation $\mathcal{H} \ll \mathcal{L}$ in Eq. (7.190), the matrix $H_{3,5,6}$ reduces to the following simpler form:

$$H_{3,5,6} \approx \begin{pmatrix} \frac{4\mathcal{V}^2}{\mathcal{L}} & \frac{2\mathcal{V}^2}{\mathcal{L}} & 0 \\ \frac{2\mathcal{V}^2}{\mathcal{L}} & \frac{3\mathcal{V}^2}{\mathcal{L}} & \frac{4\mathcal{V}^2}{\mathcal{L}} \\ 0 & \frac{2\mathcal{V}^2}{\mathcal{L}} & \frac{4\mathcal{V}^2}{\mathcal{L}} \end{pmatrix}. \quad (7.191)$$

The eigenvalues of the the matrix (7.191) are

$$E_{3,5,6}^{(1)} = \frac{(7 + \sqrt{33}) \mathcal{V}^2}{2\mathcal{L}}, \quad (7.192a)$$

$$E_{3,5,6}^{(2)} = \frac{4\mathcal{V}^2}{\mathcal{L}}, \quad (7.192b)$$

$$E_{3,5,6}^{(3)} = \frac{(7 - \sqrt{33}) \mathcal{V}^2}{2\mathcal{L}}, \quad (7.192c)$$

with the corresponding eigenvectors

$$|\Psi_{3,5,6}^{(1)}\rangle = \frac{1}{\sqrt{2(33 - \sqrt{33})}} \left(4|\Psi_3^{(I)}\rangle + (\sqrt{33} - 1)|\Psi_5^{(I)}\rangle + 4|\Psi_6^{(I)}\rangle \right), \quad (7.193a)$$

$$|\Psi_{3,5,6}^{(2)}\rangle = -\frac{1}{\sqrt{2}} \left(|\Psi_3^{(I)}\rangle - |\Psi_6^{(I)}\rangle \right), \quad (7.193b)$$

$$|\Psi_{3,5,6}^{(3)}\rangle = \frac{1}{\sqrt{2(33 + \sqrt{33})}} \left(4|\Psi_3^{(I)}\rangle - (\sqrt{33} + 1)|\Psi_5^{(I)}\rangle + 4|\Psi_6^{(I)}\rangle \right). \quad (7.193c)$$

In the $|\Psi_1^{(I)}\rangle \rightarrow |\Psi_4^{(I)}\rangle$ transition, the energy difference between the symmetric superpositions $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(I)}\rangle + |\Psi_2^{(I)}\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(I)}\rangle + |\Psi_4^{(I)}\rangle\right)$ and the energy difference between the antisymmetric superpositions $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(I)}\rangle - |\Psi_2^{(I)}\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(I)}\rangle - |\Psi_4^{(I)}\rangle\right)$ are given in the Table 7.3). In the $|\Psi_1^{(II)}\rangle \rightarrow |\Psi_4^{(II)}\rangle$ transition, the energy difference

Table 7.3: The energy differences between the symmetric superposition $\Delta\mathcal{E}_I^{(+)}$ and the antisymmetric superposition $\Delta\mathcal{E}_I^{(-)}$ in the unit of the hyperfine splitting constant \mathcal{H} . In this transition, the spectator atom is in the $2S_{1/2}$ state.

R	$\Delta\mathcal{E}_I^{(+)}$	$\Delta\mathcal{E}_I^{(-)}$
∞	0	0
750 a_0	0.054 21	0.018 16
500 a_0	-0.249 93	-0.077 32
250 a_0	21.732 18	-2.882 35

between the symmetric superpositions $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(II)}\rangle + |\Psi_7^{(II)}\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|\Psi_4^{(II)}\rangle + |\Psi_8^{(II)}\rangle\right)$ and the energy difference between the antisymmetric superposition $\frac{1}{\sqrt{2}}\left(|\Psi_1^{(I)}\rangle - |\Psi_7^{(I)}\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|\Psi_4^{(I)}\rangle - |\Psi_8^{(I)}\rangle\right)$ are given in the Table 7.4.

Table 7.4: The energy differences between the symmetric superposition $\Delta\mathcal{E}_{II}^{(+)}$ and the antisymmetric superposition $\Delta\mathcal{E}_{II}^{(-)}$ in the unit of the hyperfine splitting constant \mathcal{H} . In this transition, the spectator atom is in the $2P_{1/2}$ state.

R	$\Delta\mathcal{E}_{II}^{(+)}$	$\Delta\mathcal{E}_{II}^{(-)}$
∞	0	0
750 a_0	-1.586 70	2.186 39
500 a_0	-2.571 28	12.317 98
250 a_0	-2.938 37	38.704 42

7.9.3. Manifold $F_z = -1$. The difference in the Hamiltonian matrix between the $F_z = +1$ and $F_z = -1$ manifolds tells us that we need a detailed analysis of the $F_z = -1$ manifold as well. We have the following two states, in which the atom A is in the hyperfine singlet

$$|\psi_1^{(I)}\rangle = |(0, 0, 0)_A(1, 1, -1)_B\rangle \quad \text{and} \quad |\psi_1^{(II)}\rangle = |(0, 0, 0)_A(0, 1, -1)_B\rangle \quad (7.194)$$

whereas the atom A is in the hyperfine triplet in the states

$$|\psi_4^{(I)}\rangle = |(0, 1, 0)_A(1, 1, -1)_B\rangle \quad \text{and} \quad |\psi_4^{(II)}\rangle = |(0, 1, 0)_A(0, 1, -1)_B\rangle. \quad (7.195)$$

The spectator atom, i.e., the atom B is in $2S_{1/2}$ state in the transition $|\psi_1^{(II)}\rangle \rightarrow |\psi_4^{(II)}\rangle$ while the spectator atom B is in the $2P_{1/2}$ state in the transition $|\psi_1^{(I)}\rangle \rightarrow |\psi_4^{(I)}\rangle$. Interchanging the subscripts A and B of the states $|\psi_1^{(I)}\rangle$ and $|\psi_4^{(I)}\rangle$ we get $|\psi_6^{(I)}\rangle = |(1, 1, -1)_A(0, 1, 0)_B\rangle$ and $|\psi_7^{(I)}\rangle = |(1, 1, -1)_A(0, 1, 0)_B\rangle$. Thus, the state $|\psi_1^{(I)}\rangle$ is energetically degenerate to $|\psi_6^{(I)}\rangle$ and the state $|\psi_4^{(I)}\rangle$ is energetically degenerate to $|\psi_7^{(I)}\rangle$. These states are coupled with each other through the off-diagonal elements \mathcal{V} indicating that the interaction energy is proportional to R^{-3} . We have

$$\langle \psi_1^{(I)} | H_{\text{vdW}} | \psi_6^{(I)} \rangle = \mathcal{V}, \quad (7.196a)$$

$$\langle \psi_4^{(I)} | H_{\text{vdW}} | \psi_7^{(I)} \rangle = \mathcal{V}. \quad (7.196b)$$

The state $|\psi_1^{(II)}\rangle$ and $|\psi_4^{(II)}\rangle$ are not coupled to any other energetically degenerate levels which implies that the first order vdW shift is absent. Hence we expect the leading order shift to be of second order in \mathcal{V} . Exchanging the subscripts A and B , in the state $|\psi_1^{(II)}\rangle$, we get, $|\psi_2^{(II)}\rangle$. We now calculate the Hamiltonian $H'_{1,2}$ as we did for $H_{1,3}$ in $F_z = +1$ manifold.

$$H'_{1,2} = \lim_{\epsilon \rightarrow 0} \begin{pmatrix} \langle \psi_1^{(II)} | H_{\text{eff}}^{(\epsilon)} | \psi_1^{(II)} \rangle & \langle \psi_1^{(II)} | H_{\text{eff}}^{(\epsilon)} | \psi_2^{(II)} \rangle \\ \langle \psi_2^{(II)} | H_{\text{eff}}^{(\epsilon)} | \psi_1^{(II)} \rangle & \langle \psi_2^{(II)} | H_{\text{eff}}^{(\epsilon)} | \psi_2^{(II)} \rangle \end{pmatrix}. \quad (7.197)$$

where

$$H_{\text{eff}}^{(\epsilon)} = H_1 \cdot \left(\frac{1}{E_{0,\psi_1^{(II)}} - H_0 + \epsilon} \right) \cdot H_1. \quad (7.198)$$

The elements of the matrix $H'_{1,2}$ can be calculated as we did for $H_{1,3}$, which yields

$$H'_{1,2} = \begin{pmatrix} \frac{5\mathcal{V}^2}{2(\mathcal{L}-\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}-\mathcal{H}} & \frac{2\mathcal{V}^2}{\mathcal{L}-\mathcal{H}} \\ \frac{2\mathcal{V}^2}{\mathcal{L}-\mathcal{H}} & \frac{5\mathcal{V}^2}{2(\mathcal{L}-\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}-\mathcal{H}} \end{pmatrix}. \quad (7.199)$$

This is same to that of matrix $H_{1,3}$. The unperturbed energy corresponding to the states $|\psi_1^{(\text{II})}\rangle$ and $|\psi_2^{(\text{II})}\rangle$ is $2\mathcal{L} - \frac{3}{2}\mathcal{H}$. The matrix (7.199) has the following eigenvalues and eigenvectors:

$$E'_{1,2}{}^{\pm} = \frac{5\mathcal{V}^2}{2(\mathcal{L}-\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}-\mathcal{H}} \pm \frac{2\mathcal{V}^2}{\mathcal{L}-\mathcal{H}}, \quad (7.200a)$$

$$|\psi_{1,2}^{(\text{II})\pm}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle \pm |\psi_2^{(\text{II})}\rangle \right). \quad (7.200b)$$

Let us now turn to the reference state $|\psi_4^{(\text{II})}\rangle$. The state $|\psi_4^{(\text{II})}\rangle$ is degenerate with the state $|\psi_3^{(\text{II})}\rangle$. The Hamiltonian matrix $H'_{4,3}$ is found to be identical to $H_{2,4}$ which reads

$$H'_{4,3} = \begin{pmatrix} \frac{5\mathcal{V}^2}{2(\mathcal{L}+\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} & \frac{2\mathcal{V}^2}{\mathcal{L}+\mathcal{H}} \\ \frac{2\mathcal{V}^2}{\mathcal{L}+\mathcal{H}} & \frac{5\mathcal{V}^2}{2(\mathcal{L}+\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} \end{pmatrix} \quad (7.201)$$

with eigenvalues

$$E'_{4,3}{}^{\pm} = \frac{5\mathcal{V}^2}{2(\mathcal{L}+\mathcal{H})} + \frac{\mathcal{V}^2}{2\mathcal{L}+\mathcal{H}} \pm \frac{2\mathcal{V}^2}{\mathcal{L}+\mathcal{H}} \quad (7.202)$$

and eigenvectors

$$|\psi_{4,3}^{(\text{II})\pm}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_4^{(\text{II})}\rangle \pm |\psi_3^{(\text{II})}\rangle \right). \quad (7.203)$$

In the $|\psi_1^{(\text{II})}\rangle \rightarrow |\psi_4^{(\text{II})}\rangle$ transition, the symmetric superpositions are $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle + |\psi_2^{(\text{II})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_4^{(\text{II})}\rangle + |\psi_3^{(\text{II})}\rangle \right)$ whereas $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{II})}\rangle - |\psi_2^{(\text{II})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_4^{(\text{II})}\rangle - |\psi_3^{(\text{II})}\rangle \right)$ are

the antisymmetric superpositions. The energy differences between the symmetric levels $\Delta E_{II}^{(+)}$ and the antisymmetric levels $\Delta E_{II}^{(-)}$ can be read from the Table 7.2 with the substitutions

$$|\psi_1^{(\text{II})}\rangle \rightarrow |\psi_1'^{(\text{II})}\rangle, \quad |\psi_3^{(\text{II})}\rangle \rightarrow |\psi_2'^{(\text{II})}\rangle, \quad |\psi_2^{(\text{II})}\rangle \rightarrow |\psi_4'^{(\text{II})}\rangle, \quad |\psi_4^{(\text{II})}\rangle \rightarrow |\psi_3'^{(\text{II})}\rangle. \quad (7.204)$$

Similarly, in the case of $|\psi_1^{(\text{I})}\rangle \rightarrow |\psi_4^{(\text{I})}\rangle$ transition, the energy differences between the symmetric superposition $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{I})}\rangle + |\psi_6^{(\text{I})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_4^{(\text{I})}\rangle + |\psi_7^{(\text{I})}\rangle \right)$ as well as the antisymmetric superposition $\frac{1}{\sqrt{2}} \left(|\psi_1^{(\text{I})}\rangle - |\psi_6^{(\text{I})}\rangle \right)$ and $\frac{1}{\sqrt{2}} \left(|\psi_4^{(\text{I})}\rangle - |\psi_7^{(\text{I})}\rangle \right)$ can be read from Table 7.1 with the substitutions

$$|\psi_1^{(\text{I})}\rangle \rightarrow |\psi_1'^{(\text{I})}\rangle, \quad |\psi_7^{(\text{I})}\rangle \rightarrow |\psi_6'^{(\text{I})}\rangle, \quad |\psi_2^{(\text{I})}\rangle \rightarrow |\psi_4'^{(\text{I})}\rangle, \quad |\psi_8^{(\text{I})}\rangle \rightarrow |\psi_7'^{(\text{I})}\rangle. \quad (7.205)$$

8. LONG-RANGE INTERACTION IN nS - $1S$ SYSTEMS

8.1. DIRECT INTERACTION ENERGY IN THE vdW RANGE

In this Section , we concentrate on the interaction between two hydrogen atom in which one of them is in the ground state, and the other one is in the higher excited state of the atom. In such a system, an extra contribution to the interaction energy naturally arises as the Wick-rotated contour enclosed poles. The source of the poles is the low-lying virtual states of the reference atom available by a dipole transition. We here focus on the nS - $1S$ system with $n = 3, 4, 5$. We refer to Ref. [75] for a detailed analysis of nS - $1S$ systems for $3 \leq n \leq 12$.

The $1S$ -state is a nondegenerate state while the nS -state has nP -states as its quasi-degenerate neighbors. The state corresponding to the $|nP_{1/2}\rangle$ is shifted from the nS -state by the Lamb shift \mathcal{L}_n and the state corresponding to the $|nP_{3/2}\rangle$ is shifted from the nS -state by the fine structure \mathcal{F}_n i.e.

$$E(nS_{1/2}) - E(nP_{1/2}) \equiv \mathcal{L}_n, \quad (8.1a)$$

$$E(nP_{3/2}) - E(nS_{1/2}) \equiv \mathcal{F}_n. \quad (8.1b)$$

The Lamb shift and the fine structure of hydrogen for $n = 3, 4$, and 5 can be found in Refs. [76; 77; 78]. In the units of Hartree energy, E_h , \mathcal{L}_n and \mathcal{F}_n , for $3 \leq n \leq 5$, are given as

$$\mathcal{L}_3 = 4.78 \times 10^{-8} E_h, \quad \mathcal{F}_3 = 4.46 \times 10^{-7} E_h, \quad (8.2a)$$

$$\mathcal{L}_4 = 2.02 \times 10^{-8} E_h, \quad \mathcal{F}_4 = 1.88 \times 10^{-7} E_h, \quad (8.2b)$$

$$\mathcal{L}_5 = 9.82 \times 10^{-9} E_h, \quad \mathcal{F}_5 = 9.45 \times 10^{-8} E_h. \quad (8.2c)$$

A few more values of \mathcal{L}_n and \mathcal{F}_n can be found in Refs. [6; 51]. Notice that, $\mathcal{F}_n \approx 10 \mathcal{L}_n$. Furthermore, both the Lamb shift, \mathcal{L}_n and the fine structure splittings, \mathcal{F}_n decreases approximately as $1/n^3$ as the principal quantum number n increases.

As oscillator strength of $|nP_{1/2}\rangle$ and $|nP_{3/2}\rangle$ states with respect to the nS state are distributed in a ratio $\frac{1}{3} \div \frac{2}{3}$, the matrix element $\bar{P}_{nS}(\omega)$ is given by

$$\begin{aligned} \bar{P}_{nS}(\omega) &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle n, 0, 0 | x^i | n, \ell, m \rangle|^2}{-\mathcal{L}_n + \hbar\omega - i\epsilon} + \frac{2e^2}{9} \sum_{i=1}^3 \sum_{\mu} \frac{|\langle n, 0, 0 | x^i | n, \ell, m \rangle|^2}{\mathcal{F}_n + \hbar\omega - i\epsilon} \\ &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} |\langle n, 0, 0 | x^i | n, \ell, m \rangle|^2 \left(\frac{1}{-\mathcal{L}_n + \hbar\omega - i\epsilon} + \frac{2}{\mathcal{F}_n + \hbar\omega - i\epsilon} \right). \end{aligned} \quad (8.3)$$

The polarizability to the nS state $\alpha_{nS}(\omega)$ is the sum of the matrix elements $P_{nS}(\omega)$ and $P_{nS}(-\omega)$, thus the Wick-rotated form of the degenerate polarizability $\bar{\alpha}_{nS}(i\omega)$ can be written as

$$\begin{aligned} \bar{\alpha}_{nS}(i\omega) &= \bar{P}_{nS}(i\omega) + \bar{P}_{nS}(-i\omega) \\ &= \frac{e^2}{9} \sum_{i=1}^3 \sum_{\mu} |\langle nS | x^i | nP(m = \mu) \rangle|^2 \left(\frac{-2\mathcal{L}_n}{(-\mathcal{L}_n - i\epsilon)^2 + (\hbar\omega)^2} + \frac{4\mathcal{F}_n}{(\mathcal{F}_n - i\epsilon)^2 + (\hbar\omega)^2} \right). \end{aligned} \quad (8.4)$$

We substitute Eq. (8.4) in the following expression

$$\bar{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \left(\int_0^{\infty} d\omega \bar{\alpha}_{nS}(i\omega) \alpha_{1S}(i\omega) \right), \quad (8.5)$$

to determine the degenerate contribution to the interaction energy in vdW range, $\bar{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$. Namely,

$$\bar{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{e^2}{3} \frac{\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \sum_{i=1}^3 \sum_{\mu} |\langle nS | x^i | nP(m = \mu) \rangle|^2$$

$$\begin{aligned}
& \times \int_0^\infty d\omega \left(\frac{-2\mathcal{L}_n}{(-\mathcal{L}_n - i\epsilon)^2 + (\hbar\omega)^2} + \frac{4\mathcal{F}_n}{(\mathcal{F}_n - i\epsilon)^2 + (\hbar\omega)^2} \right) \alpha_{1S}(i\omega) \\
& = -\frac{e^2}{3} \sum_{i=1}^3 \sum_{\mu} |\langle nS|x^i|nP(m=\mu)\rangle|^2 \frac{\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \alpha_{1S}(0) \left(\frac{\pi}{\hbar} + \frac{2\pi}{\hbar} \right) \\
& = -\sum_{i=1}^3 \sum_{\mu} |\langle nS|x^i|nP(m=\mu)\rangle|^2 \frac{e^2}{(4\pi\epsilon_0)^2 R^6} \frac{9}{2} \left(\frac{\hbar}{\alpha mc} \right)^2 \frac{e^2}{\alpha^2 mc^2} \\
& = -\frac{9}{2} \sum_{i=1}^3 \sum_{\mu} |\langle nS|x^i|nP(m=\mu)\rangle|^2 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 mc^2 \frac{1}{R^6} \left(\frac{\hbar}{\alpha mc} \right)^4 \\
& = -\frac{9}{2} \sum_{i=1}^3 \sum_{\mu} |\langle nS|x^i|nP(m=\mu)\rangle|^2 E_h \frac{a_0^4}{R^6}. \tag{8.6}
\end{aligned}$$

Here, we have used $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ and $a_0 = \hbar/(\alpha mc)$. The nondegenerate contribution to vdW interaction $\widetilde{\mathcal{W}}_{nS;1S}(R)$ arising due to the virtual kP states, where $k \geq n$, can be calculated numerically using

$$\widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \tilde{\alpha}_{nS}(i\omega) \alpha_{1S}(i\omega). \tag{8.7}$$

Then, we get the Wick-rotated contribution as the sum

$$\mathcal{W}_{nS;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) + \widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R). \tag{8.8}$$

In the short range limit, the direct pole term, $\mathcal{P}_{nS;1S}^{\text{direct}}(R)$, is given by

$$\mathcal{P}_{nS;1S}^{\text{direct}}(R) = -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_m \alpha_{1S} \left(\omega = \frac{E_{mP} - E_{nS}}{\hbar} \right) \sum_i |\langle nS|x^i|mP\rangle|^2. \tag{8.9}$$

The pole term also follows the R^{-6} power law in the vdW range.

8.1.1. 3S-1S System. For the 3S-1S system, we have

$$\sum_{i=1}^3 \sum_{\mu} |\langle 3S|x^i|3P(m=\mu)\rangle|^2 = 162a_0^2. \tag{8.10}$$

Thus, the degenerate contribution $\overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R)$ reads

$$\overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -\frac{9}{2} \times 162 a_0^2 E_h \frac{a_0^4}{R^6} = -729 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.11)$$

The nondegenerate contribution $\widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R)$ is calculated numerically using

$$\widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \tilde{\alpha}_{3S}(i\omega) \alpha_{1S}(i\omega). \quad (8.12)$$

As usual, $\tilde{\alpha}_{3S}(i\omega)$ is the sum $\tilde{\alpha}_{3S}(i\omega) = \tilde{P}_{3S}(i\omega) + \tilde{P}_{3S}(-i\omega)$, where the matrix element $Q_{3S}(\pm i\omega)$ in terms of frequency, can be acquired replacing $t = (1 \pm i18\hbar\omega/(\alpha^2 mc^2))^{-1/2}$ in the matrix element derived in section (3.4.3). The numerical calculation yields

$$\widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -180.320\,073\,947 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.13)$$

The sum of the $\overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R)$ and $\widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R)$ is the total contribution due to the Wick-rotated term, $\mathcal{W}_{3S;1S}^{\text{direct}}(R)$, which reads

$$\begin{aligned} \mathcal{W}_{3S;1S}^{\text{direct}}(R) &= \overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) + \widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -729 E_h \left(\frac{a_0}{R}\right)^6 - 180.320\,073\,947 E_h \left(\frac{a_0}{R}\right)^6 \\ &= -909.320\,073\,947 E_h \left(\frac{a_0}{R}\right)^6. \end{aligned} \quad (8.14)$$

The pole term, $\mathcal{P}_{3S;1S}^{\text{direct}}(R)$, arises due to the presence of the virtual $2P$ state, which reads

$$\begin{aligned} \mathcal{P}_{3S;1S}^{\text{direct}}(R) &= -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\pm, k} \frac{e^2 \langle 3S|x^i|2P\rangle \langle 2P|x^i|3S\rangle \langle 1S|x^j|k\rangle \langle k|x^j|1S\rangle}{E_{1S} \pm (E_{2P} - E_{3S})} \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{2P} - E_{3S}}{\hbar} \right) \sum_i \langle 3S|x^i|2P\rangle \langle 2P|x^i|3S\rangle \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = -\frac{5\alpha^2 mc^2}{72\hbar} \right) \sum_i |\langle 3S|x^i|2P\rangle|^2 \end{aligned}$$

$$\begin{aligned}
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \left(Q_{1S}(t = \frac{6}{\sqrt{41}}) + Q_{1S}(t = \frac{6}{\sqrt{31}}) \right) \frac{2^{15} \times 3^8 \hbar^2}{5^{12} \alpha^2 m^2 c^2} \\
&= -\frac{2}{R^6} \hbar^2 c^2 \alpha^2 \times \frac{4.632338310 \hbar^2}{\alpha^4 m^3 c^4} \times \frac{2^{15} \times 3^8 a_0^2}{5^{12}} \\
&= -8.158497517 E_h \left(\frac{a_0}{R} \right)^6. \tag{8.15}
\end{aligned}$$

In the second line of Eq. (8.15), we have used $\omega = -\alpha^2 mc^2/(8\hbar) + \alpha^2 mc^2/(18\hbar) = -5\alpha^2 mc^2/(72\hbar)$ for ω in the expression $t = 1/\sqrt{1 \pm E_{(n=1)}/(\hbar\omega)}$ to calculate the corresponding values of the P-matrix element. On the fifth line of Eq. (8.15), we have used $E_h = \alpha^2 mc^2$ and $a_0 = \hbar/(\alpha mc)$ to express our result in terms of the Hartree energy and the Bohr radius.

The total vdW interaction to direct term, $E_{3S;1S}^{\text{direct}}(R)$, is the sum

$$\begin{aligned}
E_{3S;1S}^{\text{direct}}(R) &= \mathcal{W}_{3S;1S}^{\text{direct}}(R) + \mathcal{P}_{3S;1S}^{\text{direct}}(R) \\
&= -909.320\,073\,947 E_h \left(\frac{a_0}{R} \right)^6 - 8.158497517 E_h \left(\frac{a_0}{R} \right)^6 \\
&= -917.478\,571\,464 E_h \left(\frac{a_0}{R} \right)^6. \tag{8.16}
\end{aligned}$$

8.1.2. 4S-1S System. For the 4S-1S system, we have

$$\sum_{i=1}^3 \sum_{\mu} |\langle 4S|x^i|4P(m = \mu)\rangle|^2 = 540a_0^2. \tag{8.17}$$

Thus, the degenerate contribution $\overline{\mathcal{W}}_{4S;1S}^{\text{direct}}(R)$ reads

$$\begin{aligned}
\overline{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) &= -\frac{9}{2} \sum_{i=1}^3 \sum_{\mu} |\langle 4S|x^i|4P(m = \mu)\rangle|^2 E_h \frac{a_0^4}{R^6} \\
&= -\frac{9}{2} \times 540 a_0^2 E_h \frac{a_0^4}{R^6} = -2430 E_h \left(\frac{a_0}{R} \right)^6. \tag{8.18}
\end{aligned}$$

The nondegenerate contribution $\widetilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R)$ is calculated numerically using

$$\widetilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \widetilde{\alpha}_{4S}(i\omega) \alpha_{1S}(i\omega), \quad (8.19)$$

which yields

$$\widetilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -415.860\,208\,974 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.20)$$

On the other hand, the pole term, $\mathcal{P}_{4S;1S}^{\text{direct}}(R)$, is given by

$$\begin{aligned} \mathcal{P}_{4S;1S}^{\text{direct}}(R) &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_{2 \leq k < 4} \alpha_{1S} \left(\omega = \frac{E_{kP} - E_{4S}}{\hbar} \right) \times \sum_i |\langle 4S | x^i | kP \rangle|^2 \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{2P} - E_{4S}}{\hbar} \right) \frac{2^{21} a_0^2}{3^{15}} \\ &\quad - \frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{3P} - E_{4S}}{\hbar} \right) \frac{2^{29} \times 3^7 \times 13^2 a_0^2}{7^{16}} \\ &= -55.313\,793\,349 E_h \left(\frac{a_0}{R}\right)^6. \end{aligned} \quad (8.21)$$

Finally, the total contribution, $E_{4S;1S}^{\text{direct}}(R)$, reads

$$\begin{aligned} E_{4S;1S}^{\text{direct}}(R) &= \mathcal{W}_{4S;1S}^{\text{direct}}(R) + \mathcal{P}_{4S;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) + \widetilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) + \mathcal{P}_{4S;1S}^{\text{direct}}(R) \\ &= -2901.174\,002\,323 E_h \left(\frac{a_0}{R}\right)^6. \end{aligned} \quad (8.22)$$

8.1.3. 5S-1S System.

$$\begin{aligned} \overline{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) &= -\frac{9}{2} \sum_{i=1}^3 \sum_{\mu} |\langle 5S | x^i | 5P(m = \mu) \rangle|^2 E_h \frac{a_0^4}{R^6} \\ &= -\frac{9}{2} \times 1350 a_0^2 E_h \frac{a_0^4}{R^6} = -6075 E_h \left(\frac{a_0}{R}\right)^6. \end{aligned} \quad (8.23)$$

The nondegenerate contribution $\widetilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R)$ is calculated numerically using

$$\widetilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \widetilde{\alpha}_{5S}(i\omega) \alpha_{1S}(i\omega), \quad (8.24)$$

which yields

$$\widetilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -797.620\,619\,336 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.25)$$

On the other hand, the pole term, $\mathcal{P}_{5S;1S}^{\text{direct}}(R)$, is given by

$$\begin{aligned} \mathcal{P}_{5S;1S}^{\text{direct}}(R) &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_{2 \leq k < 5} \alpha_{1S} \left(\omega = \frac{E_{kP} - E_{5S}}{\hbar} \right) \times \sum_i |\langle 5S | x^i | kP \rangle|^2 \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{2P} - E_{5S}}{\hbar} \right) \frac{2^{15} \times 3^3 \times 5^9 a_0^2}{7^{16}} \\ &\quad - \frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{3P} - E_{5S}}{\hbar} \right) \frac{3^7 \times 5^9 \times 11^2 a_0^2}{2^{39}} \\ &\quad - \frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{1S} \left(\omega = \frac{E_{4P} - E_{5S}}{\hbar} \right) \frac{2^{22} \times 5^{10} \times 1447^2 a_0^2}{3^{39}} \\ &= -199.631\,309\,749 E_h \left(\frac{a_0}{R}\right)^6. \end{aligned} \quad (8.26)$$

The total contribution, $E_{5S;1S}^{\text{direct}}(R)$, is the sum

$$E_{5S;1S}^{\text{direct}}(R) = \mathcal{W}_{5S;1S}^{\text{direct}}(R) + \mathcal{P}_{5S;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) + \widetilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) + \mathcal{P}_{5S;1S}^{\text{direct}}(R), \quad (8.27)$$

which yields

$$E_{5S;1S}^{\text{direct}}(R) = -7072.251\,929\,086 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.28)$$

In this range, both the Wick-rotated and the pole term are of the R^{-6} type. However, the Wick-rotated term dominates over the pole term. Notice that higher the principal

quantum number of the atom interacting with the ground state atom, larger the direct term contribution to the interaction energy.

8.2. MIXING INTERACTION ENERGY IN THE vdW RANGE

Similar to the direct term, the mixing term contribution can be written as

$$\overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) = -\alpha_{nS\underline{1S}}(0) \sum_{i=1}^3 |\langle nS|x^i|nP\rangle \langle nP|x^i|1S\rangle| E_h \frac{a_0^4}{R^6}, \quad (8.29)$$

$$\widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha_{nS\underline{1S}}(i\omega) \widetilde{\alpha}_{\underline{nS}1S}(i\omega), \quad (8.30)$$

$$\begin{aligned} \mathcal{P}_{nS;1S}^{\text{mixing}}(R) = & -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_m \alpha_{nS\underline{1S}} \left(\omega = \frac{E_{mP} - E_{nS}}{\hbar} \right) \\ & \times \sum_i \langle nS|x^i|mP\rangle \langle mP|x^i|1S\rangle, \end{aligned} \quad (8.31)$$

such that,

$$E_{nS;1S}^{\text{mixing}} = \mathcal{W}_{nS;1S}^{\text{mixing}}(R) + \mathcal{P}_{nS;1S}^{\text{mixing}}(R) = \overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) + \widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) + \mathcal{P}_{nS;1S}^{\text{mixing}}(R). \quad (8.32)$$

8.2.1. 3S-1S System. Proceeding as in the case of 2S-1S system, the mixing P-matrix element between 1S and 3S states for the generalized energy variable ν can be formulated as

$$\begin{aligned} P_{3S1S}(\nu) = & \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \left[\frac{9\sqrt{3}\nu^2}{64(\nu-3)^4(\nu+3)^3(\nu^2-1)^2} \left[16975\nu^9 + 6419\nu^8 - 66744\nu^7 \right. \right. \\ & \left. \left. - 20952\nu^6 + 270\nu^5 - 810\nu^4 - 3888\nu^3 + 11664\nu^2 + 2187\nu - 6561 \right] \right. \\ & \left. - \frac{2304\sqrt{3}\nu^9(7\nu^2-27)}{(\nu^2-9)^4(\nu^2-1)^2} {}_2F_1 \left(1, -\nu; 1-\nu; \frac{\nu^2-4\nu+3}{\nu^2+4\nu+3} \right) \right], \end{aligned} \quad (8.33)$$

where $\nu = n_{\text{ref}} t$. The quantum number n_{ref} is 1 for the E_{1S} and 3 for the E_{3S} . There are three sources which contribute to the vdW interaction, namely, the nondegenerate

contribution arising from the nP states with principal quantum number $n \geq 4$, the input from the $3P$ states which are degenerate with the $3S$ state, and the pole term arises due to the presence of the $2P$ states which are accessible from $3S$ states by a dipole transition. The first two of them are of Wick-rotated type contribution, and the third one is the pole type contribution. The Wick-rotated mixing polarizability $\alpha_{3S1S}(i\omega)$ is the sum $\sum_{\pm} P_{3S1S}(\pm i\omega)$. The contribution of the degenerate $3P$ levels to the mixing interaction energy is given by

$$\begin{aligned}
\overline{W}_{3S;1S}^{\text{mixing}}(R) &= -\frac{3\hbar}{2\pi(4\pi\epsilon_0)^2 R^6} \frac{2e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|3P(m=\mu)\rangle \cdot \langle 3P(m=\mu)|x^j|3S\rangle \\
&\lim_{\epsilon \rightarrow 0} \lim_{\mathcal{L}_3 \rightarrow 0} \lim_{\mathcal{F}_3 \rightarrow 0} \int_{-\infty}^{\infty} d\omega \alpha_{3S1S}(i\omega) \left[\frac{-\mathcal{L}_3}{(-\mathcal{L}_3 - i\epsilon)^2 + (\hbar\omega)^2} + \frac{2\mathcal{F}_3}{(\mathcal{F}_3 - i\epsilon)^2 + (\hbar\omega)^2} \right] \\
&= -\frac{\hbar e^2}{3\pi(4\pi\epsilon_0)^2 R^6} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|3P(m=\mu)\rangle \cdot \langle 3P(m=\mu)|x^j|3S\rangle \\
&\quad \times \alpha_{3S1S}(0) \left(\frac{\pi}{\hbar} + \frac{2\pi}{\hbar} \right) \\
&= -\frac{e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{3S1S}(0) \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|3P(m=\mu)\rangle \cdot \langle 3P(m=\mu)|x^j|3S\rangle \\
&= -\frac{e^2}{(4\pi\epsilon_0)^2 R^6} \left(-\frac{621\sqrt{3}\hbar^2 e^2}{512\alpha^4 m^3 c^4} \right) \left(-\frac{243\sqrt{3}\hbar^2}{64\alpha^2 m^2 c^2} \right) \\
&= -\frac{3^9 \times 23}{2^{15}} E_h \left(\frac{a_0}{R} \right)^6 = -13.815\,582\,275 E_h \left(\frac{a_0}{R} \right)^6. \tag{8.34}
\end{aligned}$$

The contribution due to nondegenerate nP states for $n \geq 4$

$$\widetilde{W}_{3S;1S}^{\text{mixing}}(R) = -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^{\infty} d\omega \alpha_{3S1S}(i\omega) \alpha_{3S1S}(i\omega), \tag{8.35}$$

is evaluated numerically which gives

$$\widetilde{W}_{3S;1S}^{\text{mixing}}(R) = 5.588\,159\,518 E_h \left(\frac{a_0}{R} \right)^6. \tag{8.36}$$

Thus, the Wick-rotated type contribution is given by

$$\begin{aligned}\mathcal{W}_{3S;1S}^{\text{mixing}}(R) &= \overline{\mathcal{W}}_{3S;1S}^{\text{mixing}}(R) + \widetilde{\mathcal{W}}_{3S;1S}^{\text{mixing}}(R) \\ &= -8.227\,422\,757 E_h \left(\frac{a_0}{R}\right)^6.\end{aligned}\quad (8.37)$$

The Wick-rotated contour enclosed a pole at $\hbar\omega = \pm[(E_{2P} - E_{3S}) - i\epsilon]$ in the complex plane. The pole term contribution reads

$$\begin{aligned}\mathcal{P}_{3S;1S}^{\text{mixing}}(R) &= -\frac{2e^4}{3(4\pi\epsilon_0)^2 R^6} \sum_{\pm, k} \frac{\langle 3S|x^i|2P\rangle \cdot \langle 2P|x^i|1S\rangle \langle 1S|x^j|k\rangle \cdot \langle k|x^j|3S\rangle}{E_{1S} \pm (E_{2P} - E_{3S})} \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{3S1S} \left(\frac{E_{2P} - E_{3S}}{\hbar}\right) \sum_{j=1}^3 \langle 1S|x^j|2P\rangle \cdot \langle 2P|x^j|3S\rangle \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \left(-\frac{2.159\,394\,992\,5916 \hbar^2 e^2}{\alpha^4 m^3 c^4}\right) \left(\frac{2^{15} \hbar^2}{5^6 \sqrt{3} \alpha^2 m^2}\right) \\ &= 5.229\,153\,219 E_h \left(\frac{a_0}{R}\right)^6.\end{aligned}\quad (8.38)$$

The total contribution of the mixing vdW interaction is the sum

$$\begin{aligned}E_{3S;1S}^{\text{mixing}}(R) &= \mathcal{W}_{3S;1S}^{\text{mixing}}(R) + \mathcal{P}_{3S;1S}^{\text{mixing}}(R) \\ &= -2.998\,269\,538 E_h \left(\frac{a_0}{R}\right)^6.\end{aligned}\quad (8.39)$$

We do get the same result taking the average energy

$$E_{\text{avg}} = \frac{E_{1S} + E_{3S}}{2}, \quad (8.40)$$

as the reference energy as we did for the $2S$ - $1S$ system and calculating the mixing vdW coefficient using the Chibisov approach.

8.2.2. $4S$ - $1S$ System. We can now move on to the higher energy states.

For the $4S$ - $1S$ system, the nondegenerate and the degenerate vdW interactions are

given by

$$\begin{aligned}\widetilde{\mathcal{W}}_{4S;1S}^{\text{mixing}}(R) &= -\frac{3\hbar}{\pi(4\pi\epsilon_0)^2 R^6} \int_0^\infty d\omega \alpha_{4S1S}(\mathrm{i}\omega) \alpha_{4S1S}(\mathrm{i}\omega) \\ &= 3.063\,629\,331\,906 E_h \left(\frac{a_0}{R}\right)^6,\end{aligned}\quad (8.41)$$

and

$$\begin{aligned}\overline{\mathcal{W}}_{4S;1S}^{\text{mixing}}(R) &= -\frac{3\hbar}{2\pi(4\pi\epsilon_0)^2 R^6} \frac{2e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|4P(m=\mu)\rangle \\ &\quad \times \langle 4P(m=\mu)|x^j|4S\rangle \alpha_{4S1S}(0)(3\pi) \\ &= -\frac{2^{26} \times 3^6}{5^{14}} E_h \left(\frac{a_0}{R}\right)^6 = -8.015\,439\,766\,487 E_h \left(\frac{a_0}{R}\right)^6.\end{aligned}\quad (8.42)$$

Thus, the Wick-rotated term of the interaction energy, $\mathcal{W}_{4S;1S}^{\text{mixing}}(R)$, in the vdW range is given by

$$\mathcal{W}_{4S;1S}^{\text{mixing}}(R) = \widetilde{\mathcal{W}}_{4S;1S}^{\text{mixing}}(R) + \overline{\mathcal{W}}_{4S;1S}^{\text{mixing}}(R) = -4.951\,810\,434\,581 E_h \left(\frac{a_0}{R}\right)^6. \quad (8.43)$$

The Wick-rotated contour picks up the poles at $\hbar\omega = -(E_{2P} - E_{4S}) + \mathrm{i}\epsilon$ and $\hbar\omega = -(E_{3P} - E_{4S}) + \mathrm{i}\epsilon$, which give rise the pole term contributions, $\mathcal{P}_{4S;1S}^{\text{mixing}}(R)$. In the short range limit, the $\mathcal{P}_{4S;1S}^{\text{mixing}}(R)$ also follows the R^{-6} power law. We have,

$$\begin{aligned}\mathcal{P}_{4S;1S}^{\text{mixing}}(R) &= -\frac{2e^4}{3(4\pi\epsilon_0)^2 R^6} \sum_{\pm,k} \frac{\langle 4S|x^i|2P\rangle \cdot \langle 2P|x^i|1S\rangle \langle 1S|x^j|k\rangle \cdot \langle k|x^j|4S\rangle}{E_{1S} \pm (E_{2P} - E_{4S})} \\ &\quad - \frac{2e^4}{3(4\pi\epsilon_0)^2 R^6} \sum_{\pm,k} \frac{\langle 4S|x^i|3P\rangle \cdot \langle 3P|x^i|1S\rangle \langle 1S|x^j|k\rangle \cdot \langle k|x^j|4S\rangle}{E_{1S} \pm (E_{3P} - E_{4S})} \\ &= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{4S1S} \left(\frac{E_{2P} - E_{4S}}{\hbar}\right) \sum_{j=1}^3 \langle 1S|x^j|2P\rangle \cdot \langle 2P|x^j|4S\rangle \\ &\quad - \frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \alpha_{4S1S} \left(\frac{E_{3P} - E_{4S}}{\hbar}\right) \sum_{j=1}^3 \langle 1S|x^j|3P\rangle \cdot \langle 3P|x^j|4S\rangle\end{aligned}$$

$$\begin{aligned}
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \left(-\frac{1.181\,398\,063\,825\,\hbar^2 e^2}{\alpha^4 m^3 c^4} \right) \left(\frac{2^{18} \hbar^2}{3^{12} \alpha^2 m^2} \right) \\
&\quad - \frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \left(-\frac{1.135\,676\,172\,453\,\hbar^2 e^2}{\alpha^4 m^3 c^4} \right) \left(\frac{2^8 \times 3^7 \times 13 \hbar^2}{7^8 \alpha^2 m^2} \right) \\
&= 4.033\,187\,464\,293\,E_h \left(\frac{a_0}{R} \right)^6. \tag{8.44}
\end{aligned}$$

This yields

$$E_{4S;1S}^{\text{mixing}}(R) = \mathcal{W}_{4S;1S}^{\text{mixing}}(R) + \mathcal{P}_{4S;1S}^{\text{mixing}}(R) = -0.918\,622\,970\,288\,E_h \left(\frac{a_0}{R} \right)^6. \tag{8.45}$$

8.2.3. 5S-1S System. Similarly, for the 5S-1S system, we obtain

$$\begin{aligned}
\overline{\mathcal{W}}_{5S;1S}^{\text{mixing}}(R) &= -\frac{3\hbar}{2\pi(4\pi\epsilon_0)^2 R^6} \frac{2e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 \langle 1S|x^j|5P(m=\mu) \rangle \\
&\quad \times \langle 5P(m=\mu)|x^j|5S \rangle \alpha_{5S1S}(0)(3\pi) \\
&= -\frac{2 \times 5^9 \times 7}{3^{14}} E_h \left(\frac{a_0}{R} \right)^6 = -5.716\,898\,855\,084\,E_h \left(\frac{a_0}{R} \right)^6, \tag{8.46}
\end{aligned}$$

$$\widetilde{\mathcal{W}}_{5S;1S}^{\text{mixing}}(R) = 2.006\,704\,605\,106\,E_h \left(\frac{a_0}{R} \right)^6. \tag{8.47}$$

The contribution of the poles at $\hbar\omega = -(E_{2P} - E_{5S}) + i\epsilon$, $\hbar\omega = -(E_{3P} - E_{5S}) + i\epsilon$ and $\hbar\omega = -(E_{4P} - E_{5S}) + i\epsilon$ to the interaction energy is given by

$$\begin{aligned}
\mathcal{P}_{5S;1S}^{\text{mixing}}(R) &= -\frac{2e^4}{3(4\pi\epsilon_0)^2 R^6} \sum_{m=2,3,4} \sum_{\pm,k} \frac{\langle 5S|x^i|mP \rangle \langle mP|x^i|1S \rangle \langle 1S|x^j|k \rangle \langle k|x^j|5S \rangle}{E_{1S} \pm (E_{mP} - E_{5S})} \\
&= -\frac{2e^2}{(4\pi\epsilon_0)^2 R^6} \sum_{m=2,3,4} \alpha_{5S1S} \left(\frac{E_{mP} - E_{5S}}{\hbar} \right) \sum_{j=1}^3 \langle 1S|x^j|mP \rangle \cdot \langle mP|x^j|5S \rangle \\
&= 3.302\,240\,658\,867\,E_h \left(\frac{a_0}{R} \right)^6. \tag{8.48}
\end{aligned}$$

The total mixing vdW coefficient for the 5S-1S system is the sum

$$E_{5S;1S}^{\text{mixing}}(R) = \mathcal{W}_{5S;1S}^{\text{mixing}}(R) + \mathcal{P}_{5S;1S}^{\text{mixing}}(R) = -0.407\,953\,591\,110\,E_h \left(\frac{a_0}{R} \right)^6. \tag{8.49}$$

Calculation shows that higher the principal quantum number of the atom interacting with the ground state atom the smaller the mixing type contribution to the interaction energy.

8.3. DIRECT INTERACTION ENERGY IN THE CP RANGE

The degenerate contribution, $\overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$, calculated in the vdW range is still valid in the CP range as well. However, the non-degenerate contribution, $\widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$, and the pole term, $\mathcal{P}_{nS;1S}^{\text{direct}}(R)$, change appreciably. The integrand in

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \tilde{\alpha}_{nS}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ & \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right]. \end{aligned} \quad (8.50)$$

is damped by oscillations in ω . The contribution of the non vanishing frequencies in the polarizabilities is exponentially suppressed which yields

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = & -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \tilde{\alpha}_{nS}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ & \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ = & -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \tilde{\alpha}_{nS}(0). \end{aligned} \quad (8.51)$$

Here, we have substituted the value of the integral

$$\int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] = \frac{23c^5}{4R^7}. \quad (8.52)$$

Let us now substitute

$$\alpha_{1S}(0) = \frac{9e^2\hbar^2}{2\alpha^4 m^3 c^4}, \quad \tilde{\alpha}_{nS}(0) = \frac{e^2\hbar^2}{\alpha^4 m^3 c^4} \times \langle \tilde{\alpha}_{nS}(0) \rangle_{a.u.}, \quad (8.53)$$

where $\langle \tilde{\alpha}_{nS}(0) \rangle_{a.u.}$ is the value of the static polarizability $\tilde{\alpha}_{nS}(0)$ in atomic units. Thus, Eq. (8.54) yields

$$\tilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{207}{8\pi\alpha} \langle \tilde{\alpha}_{nS}(0) \rangle_{a.u.} E_h \left(\frac{a_0}{R} \right)^7. \quad (8.54)$$

Note that, the nondegenerate contribution to the interaction energy in the CP range has the R^{-7} dependence. The prefactor of the polarizabilities $\langle \tilde{\alpha}_{nS}(0) \rangle_{a.u.}$ are given as

$$\langle \tilde{\alpha}_{3S}(0) \rangle_{a.u.} = \frac{2025}{2}, \quad \langle \tilde{\alpha}_{4S}(0) \rangle_{a.u.} = 4992, \quad \langle \tilde{\alpha}_{5S}(0) \rangle_{a.u.} = \frac{35625}{2}. \quad (8.55)$$

Thus, the nondegenerate contribution to the direct interaction energy, $\tilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$, for $n = 3, 4, 5$ reads

$$\tilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -\frac{419175}{16\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7, \quad (8.56a)$$

$$\tilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -\frac{129168}{\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7, \quad (8.56b)$$

$$\tilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -\frac{7374375}{16\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7. \quad (8.56c)$$

Introducing a new dimensionless variable $\rho = R/a_0$, the Wick-rotated term for the interaction energy are given as

$$\mathcal{W}_{3S;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) + \tilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -729 \frac{E_h}{\rho^6} - \frac{419175}{16\pi\alpha} \frac{E_h}{\rho^7}, \quad (8.57a)$$

$$\mathcal{W}_{4S;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) + \tilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -2430 \frac{E_h}{\rho^6} - \frac{129168}{\pi\alpha} \frac{E_h}{\rho^7}, \quad (8.57b)$$

$$\mathcal{W}_{5S;1S}^{\text{direct}}(R) = \overline{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) + \tilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -6075 \frac{E_h}{\rho^6} - \frac{7374375}{16\pi\alpha} \frac{E_h}{\rho^7}. \quad (8.57c)$$

Let us now look into the pole term contribution, $\mathcal{P}_{nS;1S}^{\text{direct}}(R)$, in the CP range. Below the $3S$ energy level, we have a quasi-degenerate $3P$ and a low lying $2P$ levels. The

Wick-rotation of the integration contour along the positive real axis to the imaginary axis picks up two poles at $\omega = -E_{3P,3S}/\hbar + i\epsilon$ and $\omega = -E_{2P,3S}/\hbar + i\epsilon$. The contribution of the quasi degenerate level to the pole term is negligible in comparison to the contribution coming from the low lying $2P$ level. Thus the direct term for $3S$ - $1S$ system reads

$$\begin{aligned}
\mathcal{P}_{3S;1S}^{\text{direct}}(R) &= -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} |\langle 3S | e \vec{r} | 2P(m = \mu) \rangle|^2 \alpha_{1S} \left(\frac{E_{2P,3S}}{\hbar} \right) \\
&\times \left\{ \cos \left(\frac{2E_{2P,3S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,3S}R}{\hbar c} \right)^2 + \left(\frac{E_{2P,2S}R}{\hbar c} \right)^4 \right] \right. \\
&+ \left. \frac{2E_{2P,3S}R}{\hbar c} \sin \left(\frac{2E_{2P,3S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{2P,3S}R}{\hbar c} \right)^2 \right] \right\} \\
&= -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^6} \frac{2^{15} \times 3^8 a_0^2}{5^{12}} \alpha_{1S} \left(\frac{5E_h}{72\hbar} \right) \left\{ \cos \left(\frac{5E_h R}{36\hbar c} \right) \left[3 - 5 \left(\frac{5E_h R}{72\hbar c} \right)^2 \right. \right. \\
&+ \left. \left. \left(\frac{5E_h R}{72\hbar c} \right)^4 \right] + \frac{5E_h R}{36\hbar c} \sin \left(\frac{5E_h R}{36\hbar c} \right) \left[3 - \left(\frac{5E_h R}{72\hbar c} \right)^2 \right] \right\} \\
&= -\frac{2^{15} \times 3^8}{5^{12}} \frac{e^2 a_0^2}{(4\pi\epsilon_0)^2 R^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{5E_h}{72\hbar} \right) \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \left\{ \cos \left(\frac{5E_h R}{36\hbar c} \right) \left[3 - 5 \right. \right. \\
&\times \left. \left. \left(\frac{5E_h R}{72\hbar c} \right)^2 + \left(\frac{5E_h R}{72\hbar c} \right)^4 \right] + \frac{5E_h R}{36\hbar c} \sin \left(\frac{5E_h R}{36\hbar c} \right) \left[3 - \left(\frac{5E_h R}{72\hbar c} \right)^2 \right] \right\},
\end{aligned} \tag{8.58}$$

where $\langle \alpha_{1S} \rangle_{a.u.}$ represents value of the ground state polarizability in atomic units. Recognizing that $e^2/(4\pi\epsilon_0\hbar c) = \alpha$, $\hbar/(\alpha mc) = a_0$, $\alpha^2 mc^2 = E_h$, and $E_h/(\hbar c) = \alpha/a_0$, we have

$$\begin{aligned}
\mathcal{P}_{3S;1S}^{\text{direct}}(R) &= -\frac{2^{15} \times 3^8}{5^{12}} \frac{E_h a_0^6}{R^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{5E_h}{72\hbar} \right) \left\{ \cos \left(\frac{5\alpha R}{36a_0} \right) \left[3 - 5 \left(\frac{5\alpha R}{72a_0} \right)^2 \right. \right. \\
&+ \left. \left. \left(\frac{5\alpha R}{72a_0} \right)^4 \right] + \frac{5\alpha R}{36a_0} \sin \left(\frac{5\alpha R}{36a_0} \right) \left[3 - \left(\frac{5\alpha R}{72a_0} \right)^2 \right] \right\},
\end{aligned} \tag{8.59}$$

In terms of the new variable $\rho = R/a_0$, Eq. (8.59) gives

$$\begin{aligned} \mathcal{P}_{3S;1S}^{\text{direct}}(R) = & -\frac{2^{15} \times 3^8 E_h}{5^{12} \rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{5 E_h}{72 \hbar} \right) \left\{ \cos \left(\frac{5\alpha\rho}{36} \right) \left[3 - 5 \left(\frac{5\alpha\rho}{72} \right)^2 \right. \right. \\ & \left. \left. + \left(\frac{5\alpha\rho}{72} \right)^4 \right] + \frac{5\alpha\rho}{36} \sin \left(\frac{5\alpha\rho}{36} \right) \left[3 - \left(\frac{5\alpha\rho}{72} \right)^2 \right] \right\}. \end{aligned} \quad (8.60)$$

Figure 8.1 shows a comparison between an absolute value of the Wick-Rotated and the pole term for direct type contribution of the 3S-1S system. Initially, the Wick-rotated term dominates the pole term, however, as interatomic distance increases the pole type contribution dominates the Wick-rotated type contribution.

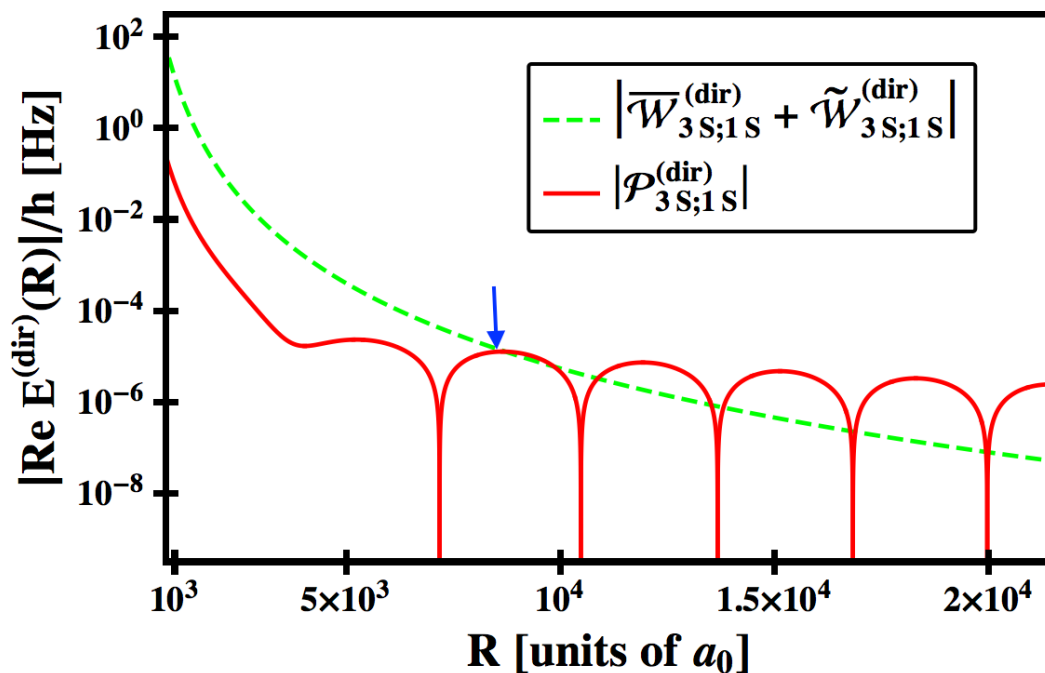


Figure 8.1: Distance dependent direct-type interaction energy in the 3S-1S system in the CP range. The vertical axis is an absolute value of the interaction energy divided by the Plank constant. We have used the logarithmic scale on the vertical axis. The horizontal axis is the interatomic separation in units of Bohr's radius. The arrow indicates the minimum distance where the pole term and the Wick-rotated term are equal.

In the 4S-1S system, the Wick-rotated integration contour encloses three poles, namely, $\omega = -E_{4P,4S}/\hbar + i\epsilon$, $\omega = -E_{3P,4S}/\hbar + i\epsilon$ and $\omega = -E_{2P,4S}/\hbar + i\epsilon$.

The $4P$ -level shifts only by the Lamb shift from the reference state, i.e., $4S$ -level. Thus, the contribution of the quasi degenerate $4P$ -level to the pole term is negligible in comparison to the contribution coming from the low lying $3P$ and $2P$ levels. Thus, the direct pole term for $4S$ - $1S$ system reads

$$\begin{aligned}
\mathcal{P}_{4S;1S}^{\text{direct}}(R) &= -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} |\langle 4S | e \vec{r} | 3P(m = \mu) \rangle|^2 \alpha_{1S} \left(\frac{E_{3P,4S}}{\hbar} \right) \\
&\times \left\{ \cos \left(\frac{2E_{3P,4S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{3P,4S}R}{\hbar c} \right)^2 + \left(\frac{E_{3P,4S}R}{\hbar c} \right)^4 \right] \right. \\
&+ \left. \frac{2E_{3P,4S}R}{\hbar c} \sin \left(\frac{2E_{3P,4S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{3P,4S}R}{\hbar c} \right)^2 \right] \right\} \\
&- \frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} |\langle 4S | e \vec{r} | 2P(m = \mu) \rangle|^2 \alpha_{1S} \left(\frac{E_{2P,4S}}{\hbar} \right) \\
&\times \left\{ \cos \left(\frac{2E_{2P,4S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,4S}R}{\hbar c} \right)^2 + \left(\frac{E_{2P,4S}R}{\hbar c} \right)^4 \right] \right. \\
&+ \left. \frac{2E_{2P,4S}R}{\hbar c} \sin \left(\frac{2E_{2P,4S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{2P,4S}R}{\hbar c} \right)^2 \right] \right\} \\
&= -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^6} \frac{2^{29} \times 3^7 \times 13^2 a_0^2}{7^{16}} \alpha_{1S} \left(\frac{7E_h}{288\hbar} \right) \left\{ \cos \left(\frac{7E_h R}{144\hbar c} \right) \left[3 - \right. \right. \\
&5 \left. \left(\frac{7E_h R}{288\hbar c} \right)^2 + \left(\frac{7E_h R}{288\hbar c} \right)^4 \right] + \frac{7E_h R}{144\hbar c} \sin \left(\frac{7E_h R}{144\hbar c} \right) \left[3 - \left(\frac{7E_h R}{288\hbar c} \right)^2 \right] \right\} \\
&- \frac{2e^2}{3(4\pi\epsilon_0)^2 R^6} \frac{2^{21} a_0^2}{3^{15}} \alpha_{1S} \left(\frac{3E_h}{32\hbar} \right) \left\{ \cos \left(\frac{3E_h R}{16\hbar c} \right) \left[3 - 5 \left(\frac{3E_h R}{32\hbar c} \right)^2 \right. \right. \\
&+ \left. \left. \left(\frac{3E_h R}{32\hbar c} \right)^4 \right] + \frac{3E_h R}{16\hbar c} \sin \left(\frac{3E_h R}{16\hbar c} \right) \left[3 - \left(\frac{3E_h R}{32\hbar c} \right)^2 \right] \right\}. \tag{8.61}
\end{aligned}$$

Using $\alpha_{1S}(\omega) = e^2 \hbar^2 / (\alpha^4 m^3 c^4) \times \langle \alpha_{1S} \rangle_{a.u.}$, replacing R/a_0 by ρ , and recognizing that $e^2 / (4\pi\epsilon_0 \hbar c) = \alpha$, $\hbar / (\alpha m c) = a_0$, $\alpha^2 m c^2 = E_h$, and $E_h / (\hbar c) = \alpha / a_0$, we have

$$\mathcal{P}_{4S;1S}^{\text{direct}}(\rho) = -\frac{2^{30} \times 3^6 \times 13^2 E_h}{7^{16} \rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{7E_h}{288\hbar} \right) \left\{ \cos \left(\frac{7\alpha\rho}{144} \right) \left[3 - \right. \right.$$

$$\begin{aligned}
& \left. 5 \left(\frac{7\alpha\rho}{288} \right)^2 + \left(\frac{7\alpha\rho}{288} \right)^4 \right] + \frac{7\alpha\rho}{144} \sin \left(\frac{7\alpha\rho}{144} \right) \left[3 - \left(\frac{7\alpha\rho}{288} \right)^2 \right] \Bigg\} \\
& - \frac{2^{22} E_h}{3^{16} \rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{3 E_h}{32 \hbar} \right) \left\{ \cos \left(\frac{3\alpha\rho}{16} \right) \left[3 - 5 \left(\frac{3\alpha\rho}{32} \right)^2 \right. \right. \\
& \left. \left. + \left(\frac{3\alpha\rho}{32} \right)^4 \right] + \frac{3\alpha\rho}{16} \sin \left(\frac{3\alpha\rho}{16} \right) \left[3 - \left(\frac{3\alpha\rho}{32} \right)^2 \right] \right\}. \tag{8.62}
\end{aligned}$$

See Figure 8.2 for a comparison between the Wick-Rotated and the pole term for direct type contribution of the 4S-1S system.

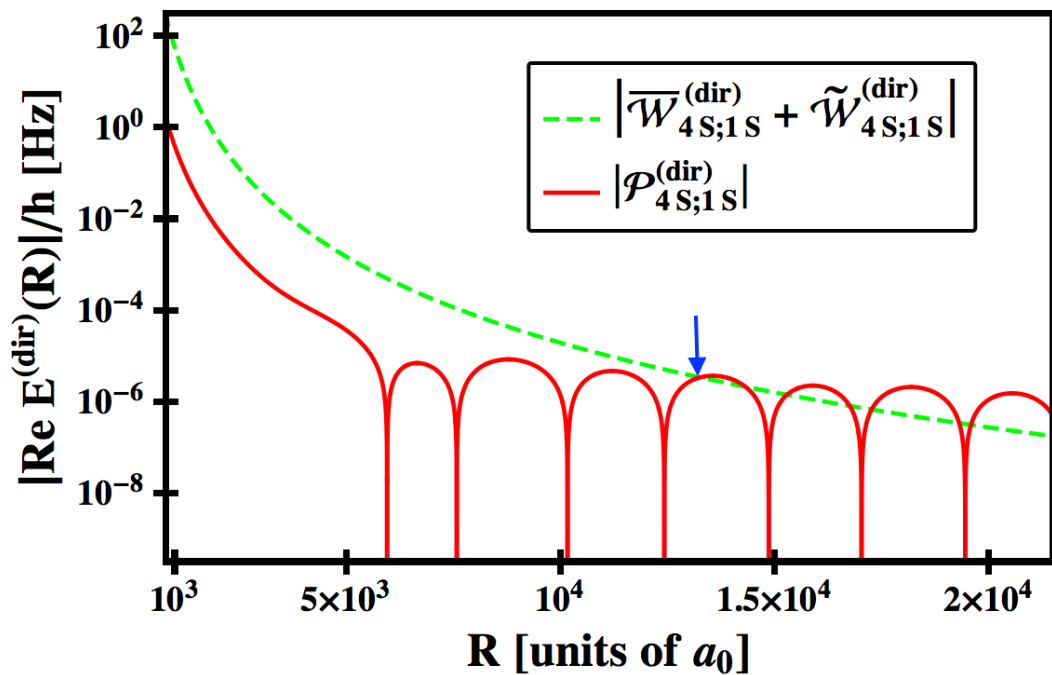


Figure 8.2: Distance dependent direct-type interaction energy in the 4S-1S system in the CP range. The vertical axis is an absolute value of the interaction energy divided by the Plank constant. We have used the logarithmic scale on the vertical axis. The horizontal axis is the interatomic separation in units of Bohr's radius. The arrow indicates the point where the pole term becomes comparable to the Wick-rotated term.

We follow the same procedure as we did in the 4S-1S system to evaluate the pole term contribution of the 5S-1S system, which yields

$$\begin{aligned}
\mathcal{P}_{5S;1S}^{\text{direct}}(\rho) = & -\frac{2^{23} \times 5^{10} \times 1447^2 E_h}{3^{40}} \frac{1}{\rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{9 E_h}{800 \hbar} \right) \left\{ \cos \left(\frac{9\alpha\rho}{400} \right) \left[3 - \right. \right. \\
& \left. \left. 5 \left(\frac{9\alpha\rho}{800} \right)^2 + \left(\frac{9\alpha\rho}{800} \right)^4 \right] + \frac{9\alpha\rho}{400} \sin \left(\frac{9\alpha\rho}{400} \right) \left[3 - \left(\frac{9\alpha\rho}{800} \right)^2 \right] \right\} \\
& - \frac{3^6 \times 5^9 \times 11^2 E_h}{2^{38}} \frac{1}{\rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{8 E_h}{225 \hbar} \right) \left\{ \cos \left(\frac{16\alpha\rho}{225} \right) \left[3 - \right. \right. \\
& \left. \left. 5 \left(\frac{8\alpha\rho}{225} \right)^2 + \left(\frac{8\alpha\rho}{225} \right)^4 \right] + \frac{16\alpha\rho}{225} \sin \left(\frac{16\alpha\rho}{225} \right) \left[3 - \left(\frac{8\alpha\rho}{225} \right)^2 \right] \right\} \\
& - \frac{2^{16} \times 3^2 \times 5^9 E_h}{7^{16}} \frac{1}{\rho^6} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{21 E_h}{200 \hbar} \right) \left\{ \cos \left(\frac{21\alpha\rho}{100} \right) \left[3 - 5 \left(\frac{21\alpha\rho}{200} \right)^2 \right. \right. \\
& \left. \left. + \left(\frac{21\alpha\rho}{200} \right)^4 \right] + \frac{21\alpha\rho}{100} \sin \left(\frac{21\alpha\rho}{100} \right) \left[3 - \left(\frac{21\alpha\rho}{200} \right)^2 \right] \right\}. \tag{8.63}
\end{aligned}$$

See Figure 8.3 for a comparison between the Wick-Rotated and the pole term for direct type contribution of the 5S-1S system.

Recall that the total interaction energy is the sum

$$E_{nS;1S}^{\text{direct}}(R) = \mathcal{W}_{nS;1S}^{\text{direct}}(R) + \mathcal{P}_{nS;1S}^{\text{direct}}(R). \tag{8.64}$$

The Wick-rotated term is the sum of the degenerate part which follows R^{-6} and the nondegenerate part which follows R^{-7} power law. The degenerate part dominates over the nondegenerate one. On the other hand, the pole term has terms obeying R^{-2} , R^{-3} , R^{-4} , R^{-5} , and R^{-6} power law. The pole term can also be expressed as a sum of a cosine and a sine term. Notice that the contribution due to the pole at $\omega = -E_{2P,nS}/\hbar + i\epsilon$ is larger than the other pole at $\omega = -E_{mP,nS}/\hbar + i\epsilon$ due to the presence of low lying virtual mP -levels. So far the comparison between the Wick-rotated term and the pole term is concerned, initially, the Wick-rotated term

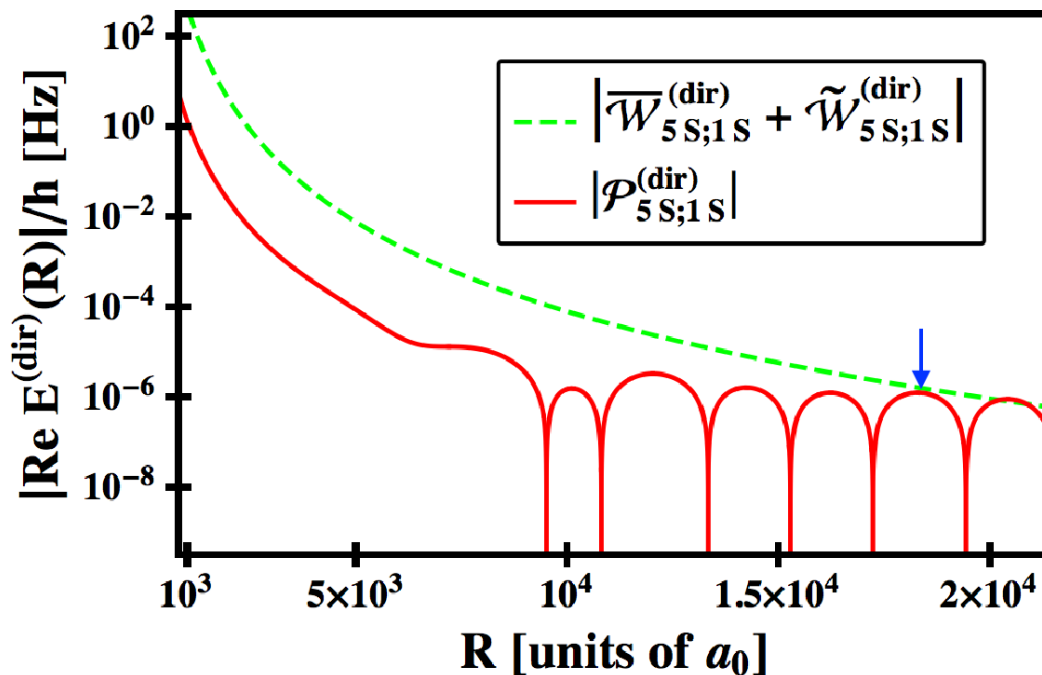


Figure 8.3: Distance dependent direct-type interaction energy in the $5S$ - $1S$ system in the CP range. The vertical axis is an absolute value of the interaction energy divided by the Plank constant. We have used the logarithmic scale on the vertical axis. The horizontal axis is the interatomic separation in units of Bohr's radius. The arrow indicates the point where the pole term becomes comparable to the Wick-rotated term.

dominates the pole term. However, as the interatomic separation increases, the pole term gradually becomes larger the Wick-rotated term as shown in Figures 8.1, 8.2 and 8.3. Not only nS - $1S$ systems but also nD - $1S$ systems have the same behavior of Wick-rotated versus pole term dominance [79]. Notice the position of arrows in Figures 8.1, 8.2 and 8.3. The arrow shifted to the larger value of R as the principal quantum number of the atom interacting with the ground state increases. This leads us to the conclusion that larger the value of n in nS - $1S$ system longer it takes for the pole term to dominate over the Wick-rotated term.

8.4. MIXING INTERACTION ENERGY IN THE CP RANGE

Similar to the direct term contribution, the degenerate contribution, $\overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R)$, calculated in the vdW range is still valid in the CP range as well. However, the non-degenerate contribution, $\widetilde{E}_{nS;1S}^{\text{maxing}}(R)$, and the pole term, $\mathcal{P}_{nS;1S}^{\text{direct}}(R)$, are different than the values in the vdW range. The approximation used for the nondegenerate polarizabilities for the direct term holds true also for the mixing term, i.e.,

$$\alpha_{nS1S}(\omega) \approx \alpha_{nS1S}(\omega = 0), \quad \tilde{\alpha}_{nS1S}(\omega) = \tilde{\alpha}_{nS1S}(\omega = 0). \quad (8.65)$$

Thus the non-degenerate contribution, $\widetilde{\mathcal{W}}_{nS;1S}^{\text{maxing}}(R)$, reads

$$\begin{aligned} \widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{nS1S}(\omega = 0) \tilde{\alpha}_{nS1S}(\omega = 0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \times \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ &= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{nS1S}(\omega = 0) \tilde{\alpha}_{nS1S}(\omega = 0). \end{aligned} \quad (8.66)$$

Writing

$$\alpha_{nS1S}(\omega = 0) = \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \langle \alpha_{nS1S} \rangle_{a.u.}(\omega = 0), \quad (8.67a)$$

$$\tilde{\alpha}_{nS1S}(\omega = 0) = \frac{e^2 \hbar^2}{\alpha^4 m^3 c^4} \langle \tilde{\alpha}_{nS1S}(0) \rangle_{a.u.}, \quad (8.67b)$$

where $\langle \tilde{\alpha}_{nS1S}(0) \rangle_{a.u.}$ is the static nondegenerate the polarizability $\tilde{\alpha}_{nS1S}(0)$ in atomic units, Eq. (8.66) leads to

$$\widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) = -\frac{23}{4\pi\alpha} \langle \alpha_{nS1S} \rangle_{a.u.}(\omega = 0) \langle \tilde{\alpha}_{nS1S}(0) \rangle_{a.u.} E_h \left(\frac{a_0}{R} \right)^7. \quad (8.68)$$

Substituting the corresponding polarizabilities, we have

$$\begin{aligned}\widetilde{\mathcal{W}}_{3S;1S}^{\text{mixing}}(R) &= -\frac{23}{4\pi\alpha} \left(-\frac{621\sqrt{3}}{512} \right) \frac{18225\sqrt{3}}{512} E_h \left(\frac{a_0}{R} \right)^7 \\ &= \frac{3^{10} \times 5^2 \times 23^2}{2^{20}} \frac{E_h}{\pi\alpha} \left(\frac{a_0}{R} \right)^7,\end{aligned}\quad (8.69)$$

$$\begin{aligned}\widetilde{\mathcal{W}}_{4S;1S}^{\text{mixing}}(R) &= -\frac{23}{4\pi\alpha} \left(-\frac{442368}{390625} \right) \frac{49348608}{390625} E_h \left(\frac{a_0}{R} \right)^7 \\ &= \frac{2^{28} \times 3^4 \times 23 \times 251}{5^{16}} \frac{E_h}{\pi\alpha} \left(\frac{a_0}{R} \right)^7,\end{aligned}\quad (8.70)$$

$$\begin{aligned}\widetilde{\mathcal{W}}_{5S;1S}^{\text{mixing}}(R) &= -\frac{23}{4\pi\alpha} \left(-\frac{4375\sqrt{5}}{13122} \right) \frac{1296875\sqrt{5}}{13122} E_h \left(\frac{a_0}{R} \right)^7 \\ &= \frac{5^{11} \times 7 \times 23 \times 83}{2^4 \times 3^{16}} \frac{E_h}{\pi\alpha} \left(\frac{a_0}{R} \right)^7.\end{aligned}\quad (8.71)$$

The total Wick-rotated contribution to the mixing term interaction is the sum

$$\mathcal{W}_{nS;1S}^{\text{mixing}}(R) = \overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) + \widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R).\quad (8.72)$$

Thus, we have

$$\mathcal{W}_{3S;1S}^{\text{mixing}}(\rho) = -\frac{3^9 \times 23}{2^{15}} \frac{E_h}{\rho^6} + \frac{3^{10} \times 5^2 \times 23^2}{2^{20}} \frac{E_h}{\pi\alpha\rho^7},\quad (8.73a)$$

$$\mathcal{W}_{4S;1S}^{\text{mixing}}(\rho) = -\frac{2^{26} \times 3^6}{5^{14}} \frac{E_h}{\rho^6} + \frac{2^{28} \times 3^4 \times 23 \times 251}{5^{16}} \frac{E_h}{\pi\alpha\rho^7},\quad (8.73b)$$

$$\mathcal{W}_{5S;1S}^{\text{mixing}}(\rho) = -\frac{2 \times 5^9 \times 7}{3^{14}} \frac{E_h}{\rho^6} + \frac{5^{11} \times 7 \times 23 \times 83}{2^4 \times 3^{16}} \frac{E_h}{\pi\alpha\rho^7}.\quad (8.73c)$$

Notice that the degenerate part which depends on ρ^{-6} dominates the nondegenerate part which follows R^{-7} power law. Determination of mixing type pole term, $\mathcal{P}_{nS;1S}^{\text{mixing}}(R)$, follows the same type of algebra we used for the direct type pole term $\mathcal{P}_{nS;1S}^{\text{direct}}(R)$. For the 3S-1S system, the mixing type pole term $\mathcal{P}_{3S;1S}^{\text{mixing}}(R)$ is given by

$$\mathcal{P}_{3S;1S}^{\text{mixing}}(R) = -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} \langle 3S|e\vec{r}|2P(m=\mu)\rangle \langle 2P(m=\mu)|e\vec{r}|1S\rangle$$

$$\begin{aligned} & \times \alpha_{3S1S} \left(\frac{E_{2P,3S}}{\hbar} \right) \left\{ \cos \left(\frac{2E_{2P,3S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,3S}R}{\hbar c} \right)^2 \right. \right. \\ & \left. \left. + \left(\frac{E_{2P,3S}R}{\hbar c} \right)^4 \right] + \frac{2E_{2P,3S}R}{\hbar c} \sin \left(2 \frac{E_{2P,3S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{2P,3S}R}{\hbar c} \right)^2 \right] \right\}. \end{aligned} \quad (8.74)$$

Substituting $\sum_{\mu} \langle 3S | \vec{r} | 2P(m = \mu) \rangle \langle 2P(m = \mu) | \vec{r} | 1S \rangle = -\frac{32768}{46875\sqrt{3}} a_0^2$ and carrying out few steps of algebra we get,

$$\begin{aligned} \mathcal{P}_{3S;1S}^{\text{mixing}}(R) &= \frac{2^{15} \sqrt{3}}{3^2 \times 5^6} \frac{E_h}{\rho^6} \alpha_{3S1S}^{\text{dl}} \left(\frac{5 E_h}{72 \hbar} \right) \left\{ \cos \left(\frac{5 \alpha \rho}{36} \right) \left[3 - 5 \left(\frac{5 \alpha \rho}{72} \right)^2 \right. \right. \\ & \left. \left. + \left(\frac{5 \alpha \rho}{72} \right)^4 \right] + \frac{5 \alpha \rho}{36} \sin \left(\frac{5 \alpha \rho}{36} \right) \left[3 - \left(\frac{5 \alpha \rho}{72} \right)^2 \right] \right\}. \end{aligned} \quad (8.75)$$

The mixing type contribution to the pole term for 4S-1S system, $\mathcal{P}_{4S;1S}^{\text{mixing}}(R)$, reads

$$\begin{aligned} \mathcal{P}_{4S;1S}^{\text{mixing}}(R) &= -\frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} \langle 4S | e \vec{r} | 3P(m = \mu) \rangle \langle 3P(m = \mu) | e \vec{r} | 1S \rangle \\ & \times \alpha_{4S1S} \left(\frac{E_{3P,4S}}{\hbar} \right) \left\{ \cos \left(\frac{2E_{3P,4S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,4S}R}{\hbar c} \right)^2 \right. \right. \\ & \left. \left. + \left(\frac{E_{3P,4S}R}{\hbar c} \right)^4 \right] + \frac{2E_{3P,4S}R}{\hbar c} \sin \left(2 \frac{E_{3P,4S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{3P,4S}R}{\hbar c} \right)^2 \right] \right\} \\ & - \frac{2}{3(4\pi\epsilon_0)^2 R^6} \sum_{\mu} \langle 4S | e \vec{r} | 2P(m = \mu) \rangle \langle 2P(m = \mu) | e \vec{r} | 1S \rangle \\ & \times \alpha_{4S1S} \left(\frac{E_{2P,4S}}{\hbar} \right) \left\{ \cos \left(\frac{2E_{2P,4S}R}{\hbar c} \right) \left[3 - 5 \left(\frac{E_{2P,4S}R}{\hbar c} \right)^2 \right. \right. \\ & \left. \left. + \left(\frac{E_{2P,4S}R}{\hbar c} \right)^4 \right] + \frac{2E_{2P,4S}R}{\hbar c} \sin \left(2 \frac{E_{2P,4S}R}{\hbar c} \right) \left[3 - \left(\frac{E_{2P,4S}R}{\hbar c} \right)^2 \right] \right\}. \end{aligned} \quad (8.76)$$

Substituting

$$\begin{aligned} \sum_{\mu} \langle 4S | \vec{r} | 3P(m = \mu) \rangle \langle 3P(m = \mu) | \vec{r} | 1S \rangle &= \frac{7278336}{5764801} a_0^2, \\ \sum_{\mu} \langle 4S | \vec{r} | 2P(m = \mu) \rangle \langle 2P(m = \mu) | \vec{r} | 1S \rangle &= \frac{262144}{531441} a_0^2, \end{aligned}$$

and carrying out few steps of algebra, we find

$$\begin{aligned}
\mathcal{P}_{4S;1S}^{\text{mixing}}(\rho) = & -\frac{2^9 \times 3^6 \times 13 E_h}{7^8} \frac{1}{\rho^6} \langle \alpha_{4S1S} \rangle_{a.u.} \left(\frac{7 E_h}{288 \hbar} \right) \left\{ \cos \left(\frac{7\alpha\rho}{144} \right) \left[3 - 5 \left(\frac{7\alpha\rho}{288} \right)^2 \right. \right. \\
& + \left. \left. \left(\frac{7\alpha\rho}{288} \right)^4 \right] + \frac{7\alpha\rho}{144} \sin \left(\frac{7\alpha\rho}{144} \right) \left[3 - \left(\frac{7\alpha\rho}{288} \right)^2 \right] \right\} \\
& - \frac{2^{19} E_h}{3^{13} \rho^6} \langle \alpha_{4S1S} \rangle_{a.u.} \left(\frac{3 E_h}{32 \hbar} \right) \left\{ \cos \left(\frac{3\alpha\rho}{16} \right) \left[3 - 5 \left(\frac{3\alpha\rho}{32} \right)^2 \right. \right. \\
& + \left. \left. \left(\frac{3\alpha\rho}{32} \right)^4 \right] + \frac{3\alpha\rho}{16} \sin \left(\frac{3\alpha\rho}{16} \right) \left[3 - \left(\frac{3\alpha\rho}{32} \right)^2 \right] \right\}. \tag{8.77}
\end{aligned}$$

Similarly, for the 5S-1S system, we have,

$$\begin{aligned}
\mathcal{P}_{5S;1S}^{\text{mixing}}(\rho) = & -\frac{2^{23} \times 1447 E_h}{3^{19} \times 5\sqrt{5} \rho^6} \langle \alpha_{5S1S} \rangle_{a.u.} \left(\frac{9 E_h}{800 \hbar} \right) \left\{ \cos \left(\frac{9\alpha\rho}{400} \right) \left[3 - \right. \right. \\
& 5 \left(\frac{9\alpha\rho}{800} \right)^2 + \left. \left. \left(\frac{9\alpha\rho}{800} \right)^4 \right] + \frac{9\alpha\rho}{400} \sin \left(\frac{9\alpha\rho}{400} \right) \left[3 - \left(\frac{9\alpha\rho}{800} \right)^2 \right] \right\} \\
& - \frac{3^6 \times 5^4 \times 11\sqrt{5} E_h}{2^{25} \rho^6} \langle \alpha_{5S1S} \rangle_{a.u.} \left(\frac{8 E_h}{225 \hbar} \right) \left\{ \cos \left(\frac{16\alpha\rho}{225} \right) \left[3 - \right. \right. \\
& 5 \left(\frac{8\alpha\rho}{225} \right)^2 + \left. \left. \left(\frac{8\alpha\rho}{225} \right)^4 \right] + \frac{16\alpha\rho}{225} \sin \left(\frac{16\alpha\rho}{225} \right) \left[3 - \left(\frac{8\alpha\rho}{225} \right)^2 \right] \right\} \\
& - \frac{2^{16} \times 5^4 \times \sqrt{5} E_h}{3^4 \times 7^8 \rho^6} \langle \alpha_{5S1S} \rangle_{a.u.} \left(\frac{21 E_h}{200 \hbar} \right) \left\{ \cos \left(\frac{21\alpha\rho}{100} \right) \left[3 - 5 \left(\frac{21\alpha\rho}{200} \right)^2 \right. \right. \\
& + \left. \left. \left(\frac{21\alpha\rho}{200} \right)^4 \right] + \frac{21\alpha\rho}{100} \sin \left(\frac{21\alpha\rho}{100} \right) \left[3 - \left(\frac{21\alpha\rho}{200} \right)^2 \right] \right\}. \tag{8.78}
\end{aligned}$$

The mixing type contribution for nS -1S system decreases as n increases.

8.5. OSCILLATORY TAILS IN THE DIRECT TERM IN THE LAMB SHIFT RANGE

We devote this subsection to the calculation of the interaction energy in the long range of interatomic distance. By the long range interatomic distance, we mean

the interatomic distances such that $R \gg \hbar c/\mathcal{L}$, where \mathcal{L} is the Lamb-shift energy. At this interatomic range, the integrand in the Wick-rotated the interaction energy

$$\mathcal{W}_{nS;1S}^{\text{direct}}(R) = -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \int_0^\infty d\omega \alpha_{1S}(i\omega) \alpha_{nS}(i\omega) \frac{\omega^4 e^{-2\omega R/c}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \quad (8.79)$$

is damped by oscillations in ω . The contribution of the non vanishing frequencies in the polarizabilities is exponentially suppressed, which yields

$$\begin{aligned} \mathcal{W}_{nS;1S}^{\text{direct}}(R) &= -\frac{\hbar}{\pi c^4 (4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{nS}(0) \int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \\ &\quad \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] \\ &= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \alpha_{nS}(0). \end{aligned} \quad (8.80)$$

Here, we have substituted the value of the integral

$$\int_0^\infty d\omega \frac{\omega^4 e^{-2\omega R/c}}{R^2} \left[1 + 2 \left(\frac{c}{\omega R} \right) + 5 \left(\frac{c}{\omega R} \right)^2 + 6 \left(\frac{c}{\omega R} \right)^3 + 3 \left(\frac{c}{\omega R} \right)^4 \right] = \frac{23c^5}{4R^7}. \quad (8.81)$$

The static polarizability $\alpha_{nS}(0)$ is the sum

$$\alpha_{nS}(0) = \bar{\alpha}_{nS}(0) + \tilde{\alpha}_{nS}(0), \quad (8.82)$$

where $\bar{\alpha}_{nS}(0)$ is the degenerate and the $\tilde{\alpha}_{nS}(0)$ is the nondegenerate polarizability.

Thus, Eq. (8.80), can be expressed as

$$\begin{aligned} \mathcal{W}_{nS;1S}^{\text{direct}}(R) &= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \bar{\alpha}_{nS}(0) - \frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \tilde{\alpha}_{nS}(0) \\ &= \overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) + \widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R), \end{aligned} \quad (8.83)$$

where

$$\overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \overline{\alpha}_{nS}(0) \quad (8.84)$$

is the degenerate contribution to the direct interaction energy and

$$\widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \widetilde{\alpha}_{nS}(0) \quad (8.85)$$

is the nondegenerate contribution to the direct interaction energy. The static polarizability due to the degenerate states, $\overline{\alpha}_{nS}(0)$, can be expressed as

$$\overline{\alpha}_{nS}(0) = \frac{2e^2}{9} \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle nS|x^j|nP(m=\mu)\rangle|^2 \left(\frac{1}{-\mathcal{L}_n} + \frac{2}{\mathcal{F}_n} \right). \quad (8.86)$$

Substituting $\alpha_{1S}(0) = 9e^2\hbar^2/(2\alpha^4 m^3 c^4)$ and $\overline{\alpha}_{nS}(0)$ from Eq. (8.86), Eq. (8.84) yields

$$\begin{aligned} \overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R) &= -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{1S}(0) \overline{\alpha}_{nS}(0) \\ &= -\frac{23}{4\pi R^7} \frac{9\hbar^2}{2\alpha^4 m^3 c^4} \left(\frac{e^2}{4\pi\epsilon_0\hbar c} \right)^2 \frac{2\hbar^3 c^3}{9} \\ &\quad \times \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle nS|x^j|nP(m=\mu)\rangle|^2 \left(-\frac{1}{\mathcal{L}_n} + \frac{2}{\mathcal{F}_n} \right) \\ &= -\frac{23}{4\pi\alpha R^7} \left(\frac{\hbar}{\alpha mc} \right)^5 (\alpha^2 mc^2)^2 \\ &\quad \times \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle nS|x^j|nP(m=\mu)\rangle|^2 \left(-\frac{1}{\mathcal{L}_n} + \frac{2}{\mathcal{F}_n} \right) \\ &= -\frac{23 a_0^5}{4\pi\alpha R^7} E_h^2 \sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle nS|x^j|nP(m=\mu)\rangle|^2 \left(-\frac{1}{\mathcal{L}_n} + \frac{2}{\mathcal{F}_n} \right). \quad (8.87) \end{aligned}$$

Substituting

$$\sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 3S|x^j|3P(m=\mu)\rangle|^2 = 162 a_0^2, \quad (8.88a)$$

$$\sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 4S|x^j|4P(m=\mu)\rangle|^2 = 540 a_0^2, \quad (8.88b)$$

$$\sum_{j=1}^3 \sum_{\mu=-1}^1 |\langle 5S|x^j|5P(m=\mu)\rangle|^2 = 1350 a_0^2, \quad (8.88c)$$

in Eq. (8.87), $\overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$ results

$$\overline{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -\frac{3726}{4\pi\alpha} \left(-\frac{E_h}{\mathcal{L}_3} + \frac{2E_h}{\mathcal{F}_3} \right) E_h \left(\frac{a_0}{R} \right)^7, \quad (8.89a)$$

$$\overline{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -\frac{12420}{4\pi\alpha} \left(-\frac{E_h}{\mathcal{L}_4} + \frac{2E_h}{\mathcal{F}_4} \right) E_h \left(\frac{a_0}{R} \right)^7, \quad (8.89b)$$

$$\overline{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -\frac{31050}{4\pi\alpha} \left(-\frac{E_h}{\mathcal{L}_5} + \frac{2E_h}{\mathcal{F}_5} \right) E_h \left(\frac{a_0}{R} \right)^7. \quad (8.89c)$$

On the other hand, the nondegenerate polarizabilities $\tilde{\alpha}_{nS}(0)$ are given by

$$\tilde{\alpha}_{3S}(0) = \frac{2025 e^2 \hbar^2}{2 \alpha^4 m^3 c^4}, \quad \tilde{\alpha}_{4S}(0) = \frac{4992 e^2 \hbar^2}{\alpha^4 m^3 c^4}, \quad \tilde{\alpha}_{5S}(0) = \frac{35625 e^2 \hbar^2}{2 \alpha^4 m^3 c^4}. \quad (8.90)$$

Substituting nondegenerate polarizabilities from Eq. (8.90) and $\alpha_{1S}(0) = 9e^2\hbar^2/(2\alpha^4 m^3 c^4)$

in Eq. (8.85), we get

$$\widetilde{\mathcal{W}}_{3S;1S}^{\text{direct}}(R) = -\frac{419175}{16\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7, \quad (8.91a)$$

$$\widetilde{\mathcal{W}}_{4S;1S}^{\text{direct}}(R) = -\frac{129168}{\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7, \quad (8.91b)$$

$$\widetilde{\mathcal{W}}_{5S;1S}^{\text{direct}}(R) = -\frac{7374375}{16\pi\alpha} E_h \left(\frac{a_0}{R} \right)^7. \quad (8.91c)$$

Thus the Wick-rotated part, $\mathcal{W}_{nS;1S}^{\text{direct}}(R)$, which is the sum of the degenerate contribution $\overline{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$ and the nondegenerate contribution $\widetilde{\mathcal{W}}_{nS;1S}^{\text{direct}}(R)$ are given by

$$\mathcal{W}_{3S;1S}^{\text{direct}}(\rho) = -\left[\frac{419175}{4} + 3726 \left(-\frac{E_h}{\mathcal{L}_3} + \frac{2E_h}{\mathcal{F}_3} \right) \right] \frac{E_h}{4\pi\alpha\rho^7}, \quad (8.92a)$$

$$\mathcal{W}_{4S;1S}^{\text{direct}}(\rho) = -\left[\frac{516672}{4} + 12420 \left(-\frac{E_h}{\mathcal{L}_4} + \frac{2E_h}{\mathcal{F}_4} \right) \right] \frac{E_h}{4\pi\alpha\rho^7}, \quad (8.92b)$$

$$\mathcal{W}_{5S;1S}^{\text{direct}}(\rho) = - \left[\frac{7374375}{4} + 31050 \left(-\frac{E_h}{\mathcal{L}_5} + \frac{2E_h}{\mathcal{F}_5} \right) \right] \frac{E_h}{4\pi\alpha\rho^7}. \quad (8.92c)$$

Both the degenerate and nondegenerate parts obey ρ^{-7} power law. However, the degenerate part dominates the nondegenerate one. The Wick-rotated contours enclosed the low lying virtual P -states which are available for a dipole transition from the reference state. The contribution of the pole in the long range limit can be written as

$$\begin{aligned} \mathcal{P}_{nS;1S}^{\text{direct}}(R) &= -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^2} \sum_{m=2}^n \langle nS|\vec{r}|mP\rangle \cdot \langle mP|\vec{r}|nS\rangle \\ &\times \alpha_{1S} \left(\frac{E_{mP,nS}}{\hbar} \right) \left(\frac{E_{mP,nS}}{\hbar c} \right)^4 \cos \left(2 \frac{E_{mP,nS} R}{\hbar c} \right). \end{aligned} \quad (8.93)$$

For $n = 3, 4, 5$, the direct pole terms are given as

$$\mathcal{P}_{3S;1S}^{\text{direct}}(\rho) = -\frac{2^3 \alpha^4 E_h}{5^8 \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{5 E_h}{72\hbar} \right) \cos \left(\frac{5\alpha\rho}{36} \right), \quad (8.94)$$

$$\begin{aligned} \mathcal{P}_{4S;1S}^{\text{direct}}(\rho) &= -\frac{2^{22} \times 3^2 \times 13^2 \alpha^4 E_h}{7^{12} \times 19^4 \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{7 E_h}{288\hbar} \right) \cos \left(\frac{7\alpha\rho}{144} \right) \\ &- \frac{2^2 \alpha^4 E_h}{3^{12} \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{3 E_h}{32\hbar} \right) \cos \left(\frac{3\alpha\rho}{16} \right), \end{aligned} \quad (8.95)$$

$$\begin{aligned} \mathcal{P}_{5S;1S}^{\text{direct}}(\rho) &= -\frac{2^3 \times 5^2 \times 1447^2 \alpha^4 E_h}{3^{32} \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{9 E_h}{800\hbar} \right) \cos \left(\frac{9\alpha\rho}{400} \right) \\ &- \frac{5 \times 11^2 \alpha^4 E_h}{2^{26} \times 3^2 \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{8 E_h}{225\hbar} \right) \cos \left(\frac{16\alpha\rho}{225} \right) \\ &- \frac{2^4 \times 3^6 \times 5 \alpha^4 E_h}{7^{12} \rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{21 E_h}{200\hbar} \right) \cos \left(\frac{21\alpha\rho}{100} \right). \end{aligned} \quad (8.96)$$

See Figure 8.4 for a comparison between the Wick-rotated and pole type contributions to the direct term in the Lamb-shift range for the $3S-1S$ system. The energy curves of the $4S-1S$ and the $5S-1S$ systems are similar to that of the $3S-1S$ system. The pole term contains an oscillatory cosine term whose amplitude goes as ρ^{-2} . In this range, the direct term of interaction energy for the $nS-1S$ system is larger for the

large value of n . As shown in Figure 8.4, in the very long range of inter atomic distance, the pole type contribution dominates over Wick-rotated contribution.

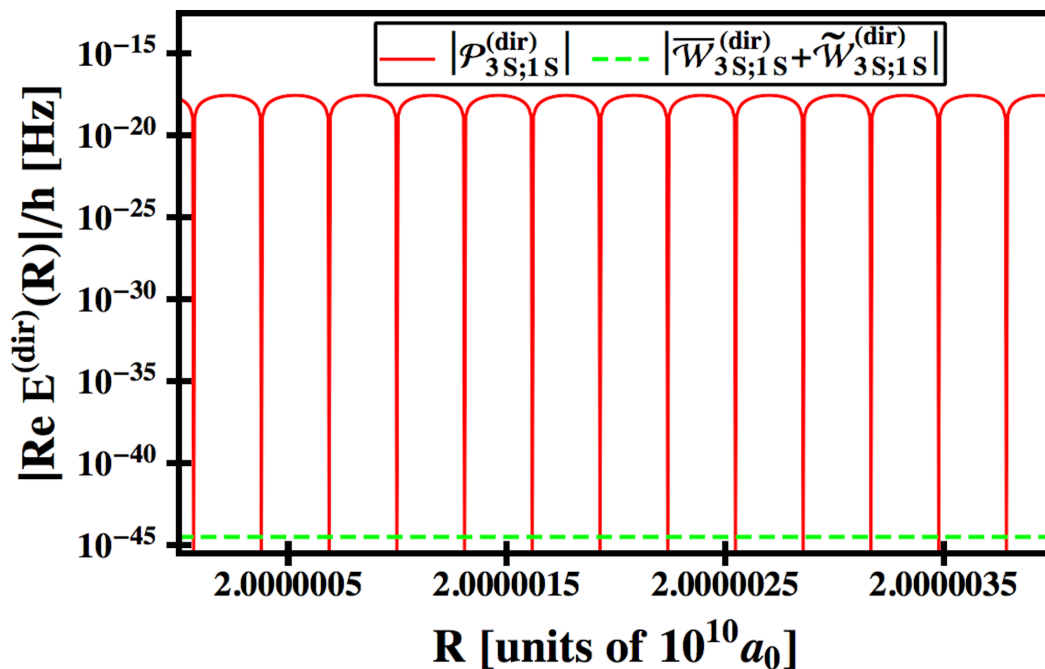


Figure 8.4: Distance dependent direct-type interaction energy in the $3S$ - $1S$ system in the very long range. This is a semi-log plot. The vertical axis is an absolute value of the interaction energy divided by the Plank constant. We have used the logarithmic scale on the vertical axis. The pole-type contribution approaches to $-\infty$ upon the change of sign of the pole term contribution.

8.6. OSCILLATORY TAILS IN THE MIXING TERM IN THE LAMB SHIFT RANGE

Similar to the direct term contribution, the mixing term contribution to the Wick-rotated part of interaction energy can also be written as

$$\mathcal{W}_{nS;1S}^{\text{mixing}}(R) = \overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) + \widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R), \quad (8.97)$$

where

$$\overline{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{nS\underline{1S}}(0) \overline{\alpha}_{nS\underline{1S}}(0) \quad (8.98)$$

is the degenerate contribution to the mixing interaction energy and

$$\widetilde{\mathcal{W}}_{nS;1S}^{\text{mixing}}(R) = -\frac{23}{4\pi R^7} \frac{\hbar c}{(4\pi\epsilon_0)^2} \alpha_{nS\underline{1S}}(0) \widetilde{\alpha}_{nS\underline{1S}}(0) \quad (8.99)$$

is the nondegenerate contribution to the mixing interaction energy. Here, the degenerate part of the static polarizability, $\overline{\alpha}_{nS\underline{1S}}(0)$, is

$$\overline{\alpha}_{nS\underline{1S}}(0) = \frac{2e^2}{9} \sum_{j=1}^3 \langle 1S|x^j|nP\rangle \cdot \langle nP|x^j|nS\rangle \left(-\frac{1}{\mathcal{L}_n} + \frac{2}{\mathcal{F}_n} \right). \quad (8.100)$$

We have,

$$\sum_{j=1}^3 \langle 1S|x^j|3P\rangle \cdot \langle 3P|x^j|3S\rangle = -\frac{243\sqrt{3}}{64} a_0^2, \quad (8.101a)$$

$$\sum_{j=1}^3 \langle 1S|x^j|4P\rangle \cdot \langle 4P|x^j|4S\rangle = -\frac{110592}{15625} a_0^2, \quad (8.101b)$$

$$\sum_{j=1}^3 \langle 1S|x^j|5P\rangle \cdot \langle 5P|x^j|5S\rangle = -\frac{2500\sqrt{5}}{729} a_0^2. \quad (8.101c)$$

The static polarizability, $\alpha_{nS\underline{1S}}(0)$, with E_{1S} as the reference energy are given as

$$\alpha_{3S\underline{1S}}(0) = -\frac{621\sqrt{3}}{512} \frac{e^2\hbar^2}{\alpha^4 m^3 c^4}, \quad (8.102a)$$

$$\alpha_{4S\underline{1S}}(0) = -\frac{442368}{390625} \frac{e^2\hbar^2}{\alpha^4 m^3 c^4}, \quad (8.102b)$$

$$\alpha_{5S\underline{1S}}(0) = -\frac{4375\sqrt{5}}{13122} \frac{e^2\hbar^2}{\alpha^4 m^3 c^4}. \quad (8.102c)$$

Substituting the values of $\bar{\alpha}_{nS1S}(0)$ and $\alpha_{nS1S}(0)$ in Eq. (8.98), we get

$$\bar{\mathcal{W}}_{3S;1S}^{\text{mixing}}(\rho) = -\frac{3^7 \times 23^2}{2^{16}} \left(-\frac{E_h}{\mathcal{L}_3} + \frac{2E_h}{\mathcal{F}_3} \right) \frac{E_h}{\pi\alpha\rho^7}, \quad (8.103a)$$

$$\bar{\mathcal{W}}_{4S;1S}^{\text{mixing}}(\rho) = -\frac{2^{25} \times 3^4 \times 23}{5^{14}} \left(-\frac{E_h}{\mathcal{L}_4} + \frac{2E_h}{\mathcal{F}_4} \right) \frac{E_h}{\pi\alpha\rho^7}, \quad (8.103b)$$

$$\bar{\mathcal{W}}_{5S;1S}^{\text{mixing}}(\rho) = -\frac{5^9 \times 7 \times 23}{3^{16}} \left(-\frac{E_h}{\mathcal{L}_5} + \frac{2E_h}{\mathcal{F}_5} \right) \frac{E_h}{\pi\alpha\rho^7}. \quad (8.103c)$$

As we calculated in the CP range, the nondegenerate contribution to the Wick-rotated part of the interaction energy for 3S-1S, 4S-1S, and 5S-1S systems are given as

$$\widetilde{\mathcal{W}}_{3S;1S}^{\text{mixing}}(\rho) = \frac{3^{10} \times 5^2 \times 23^2}{2^{20}} \frac{E_h}{\pi\alpha\rho^7}, \quad (8.104a)$$

$$\widetilde{\mathcal{W}}_{4S;1S}^{\text{mixing}}(\rho) = \frac{2^{28} \times 3^4 \times 23 \times 251}{5^{16}} \frac{E_h}{\pi\alpha\rho^7}, \quad (8.104b)$$

$$\widetilde{\mathcal{W}}_{5S;1S}^{\text{mixing}}(\rho) = \frac{5^{11} \times 7 \times 23 \times 83}{2^4 \times 3^{16}} \frac{E_h}{\pi\alpha\rho^7}. \quad (8.104c)$$

Thus the total Wick-rotated part given by

$$\mathcal{W}_{nS1S}^{\text{mixing}}(\rho) = \bar{\mathcal{W}}_{nS1S}^{\text{mixing}}(\rho) + \widetilde{\mathcal{W}}_{nS1S}^{\text{mixing}}(\rho), \quad (8.105)$$

for $nS-1S$ system with $n = 3, 4, 5$ reads

$$\mathcal{W}_{3S;1S}^{\text{mixing}}(\rho) = -\left[\frac{3^7 \times 23^2}{2^{16}} \left(-\frac{E_h}{\mathcal{L}_3} + \frac{2E_h}{\mathcal{F}_3} \right) - \frac{3^{10} \times 5^2 \times 23^2}{2^{20}} \right] \frac{E_h}{\pi\alpha\rho^7}, \quad (8.106a)$$

$$\mathcal{W}_{4S;1S}^{\text{mixing}}(\rho) = -\left[\frac{2^{25} \times 3^4 \times 23}{5^{14}} \left(-\frac{E_h}{\mathcal{L}_4} + \frac{2E_h}{\mathcal{F}_4} \right) - \frac{2^{28} \times 3^4 \times 23 \times 251}{5^{16}} \right] \frac{E_h}{\pi\alpha\rho^7}, \quad (8.106b)$$

$$\mathcal{W}_{5S;1S}^{\text{mixing}}(\rho) = -\left[\frac{5^9 \times 7 \times 23}{3^{16}} \left(-\frac{E_h}{\mathcal{L}_5} + \frac{2E_h}{\mathcal{F}_5} \right) - \frac{5^{11} \times 7 \times 23 \times 83}{2^4 \times 3^{16}} \right] \frac{E_h}{\pi\alpha\rho^7}. \quad (8.106c)$$

An extra contribution comes from the poles present in the Wick-rotated contours. The mixing pole term, in the long range limit, can be written as

$$\begin{aligned} \mathcal{P}_{nS;1S}^{\text{mixing}}(R) &= -\frac{2e^2}{3(4\pi\epsilon_0)^2 R^2} \sum_{m=2}^n \langle nS|\vec{r}|mP\rangle \cdot \langle mP|\vec{r}|1S\rangle \\ &\times \alpha_{nS1S} \left(\frac{E_{mP,nS}}{\hbar}\right) \left(\frac{E_{mP,nS}}{\hbar c}\right)^4 \cos\left(2\frac{E_{mP,nS}R}{\hbar c}\right). \end{aligned} \quad (8.107)$$

Substituting the corresponding matrix elements and the values of $E_{mP,nS}$ for $n = 3, 4, 5$, we have

$$\mathcal{P}_{3S;1S}^{\text{mixing}}(\rho) = \frac{2^3\sqrt{3}}{3^{10} \times 5^2} \frac{\alpha^4 E_h}{\rho^2} \alpha_{3S1S}^{\text{dl}} \left(\frac{5E_h}{72\hbar}\right) \cos\left(\frac{5\alpha\rho}{36}\right), \quad (8.108a)$$

$$\begin{aligned} \mathcal{P}_{4S;1S}^{\text{mixing}}(\rho) &= -\frac{2 \times 3^2 \times 13}{7^4 \times 19^4} \frac{\alpha^4 E_h}{\rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{7E_h}{288\hbar}\right) \cos\left(\frac{7\alpha\rho}{144}\right) \\ &\quad - \frac{1}{2 \times 3^9} \frac{\alpha^4 E_h}{\rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{3E_h}{32\hbar}\right) \cos\left(\frac{3\alpha\rho}{16}\right), \end{aligned} \quad (8.108b)$$

$$\begin{aligned} \mathcal{P}_{5S;1S}^{\text{mixing}}(\rho) &= -\frac{2^3 \times 1447}{3^{11} \times 5^9 \times \sqrt{5}} \frac{\alpha^4 E_h}{\rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{9E_h}{800\hbar}\right) \cos\left(\frac{9\alpha\rho}{400}\right) \\ &\quad - \frac{11\sqrt{5}}{2^{13} \times 3^2 \times 5^4} \frac{\alpha^4 E_h}{\rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{8E_h}{225\hbar}\right) \cos\left(\frac{16\alpha\rho}{225}\right) \\ &\quad - \frac{2^4 \times \sqrt{5}}{5^4 \times 7^4} \frac{\alpha^4 E_h}{\rho^2} \langle \alpha_{1S} \rangle_{a.u.} \left(\frac{21E_h}{200\hbar}\right) \cos\left(\frac{21\alpha\rho}{100}\right). \end{aligned} \quad (8.108c)$$

The mixing part of the total interaction energy is the sum of the Wick-rotated term and the pole term. The Wick-rotated term follows ρ^{-7} power law while the pole term contains a cosine term whose magnitude falls off as ρ^{-2} . Notice that the contribution of the pole at $\omega = -E_{2P,nS}/\hbar + i\epsilon$ is significantly larger than the other pole at $\omega = -E_{mP,nS}/\hbar + i\epsilon$ with $m > 2$.

9. CONCLUSION

To study the long-range interaction between two neutral hydrogen atoms, we have used the time ordered perturbation theory. We observed that the odd order perturbations vanish and the second order terms correspond to the self-energy contribution and talk only about the Lamb shift of the individual atoms. Thus, what we care about here is the fourth order perturbation term, which finally gives the CP interaction.

The functional form of the interatomic interaction depends on the range of the interatomic distance. If both the interacting atoms are in the ground state, the interaction follows the usual $C_6(1S; 1S)/R^6$ functional form for $a_0 \leq R \leq a_0/\alpha$. The distance R , which ranges from the Bohr radius a_0 to the wavelength of the typical optical transition a_0/α is the so-called vdW range. For the $1S$ - $1S$ system, we find $C_6(1S; 1S) = 6.499\,026\,705 E_h a_0^6$, which agrees with the previously reported result [53; 80; 81; 82]. The interatomic interaction has the well known R^{-7} functional form if the distance is larger than the wavelength of optical transition i.e. $a_0/\alpha \leq R$. Thus, when both atom are in ground state fourth-order time-ordered perturbation theory is applied and retardation regime is achieved for $a_0/\alpha \ll R$

The situation is different if the atom interacting with the ground state atom is in an excited state. For excited reference states, we match the scattering amplitude and the effective Hamiltonian of the system. If the atom interacting with the ground state atom is in the first excited state, quasi-degenerate levels are present. In this case, we have to differentiate three ranges for the interatomic distance: vdW range ($a_0 \leq R \leq a_0/\alpha$), CP range ($a_0/\alpha \leq R \leq \hbar c/\mathcal{L}$), and Lamb shift range ($R \geq \hbar c/\mathcal{L}$). In the vdW range, the interatomic interaction between the atoms A and B can be formulated in the functional form $-C_6(2S; 1S)/R^6$. A complication

arises as $|1S\rangle_A|2S\rangle_B$ and $|2S\rangle_A|1S\rangle_B$ are energetically degenerate. Thus, we have the mixing term contribution as well. We have thus expressed the vdW interaction as the sum, $C_6(2S; 1S) = D_6(2S; 1S) \pm M_6(2S; 1S)$, where $D_6(2S; 1S)$ represents the direct term and $M_6(2S; 1S)$ depicts the mixing term contributions. For the $2S$ - $1S$ system, there is a clear discrepancy in the literature among various results. In Ref [80], Tang and Chan reported that the direct coefficient $D_6(2S; 1S)$ is $56.7999E_h a_0^6$ and they did not calculate mixing terms contribution. In Ref [53], Chibisov presented the calculation of both the direct and the mixing term. Chibisov claimed that $D_6(2S; 1S) = 55.5(0.5) E_h a_0^6$ and $M_6(2S; 1S) = 27.9819(2) E_h a_0^6$. In Ref. [83], Deal and Young reported that $D_6(2S; 1S) = 176.7523E_h a_0^6$ and $M_6(2S; 1S) = 27.9832E_h a_0^6$. Our finding, ignoring the relativistic correction, shows $C_6(2S; 1S) = (176.752266285 \pm 27.983245543) E_h a_0^6$. We confirm all the significant figures of the result reported in Ref [83], and we add few more significant figures. We noticed that in both publications [80] and [53], authors did not include the contribution of the quasi-degenerate $2P$ levels of the excited atom. In the CP range, the interaction is still of the R^{-6} functional form. We find $C_6(2S; 1S) = (243/2 \mp 46.614032414) E_h a_0^6$, which is smaller than that of $C_6(2S; 1S)$ coefficient in the vdW range. For the very large interatomic distance, the interaction energy is the sum of the CP type $-C_7(2S; 1S)/R^{-7}$ term and the pole term which has an oscillatory distance dependence whose amplitude falls off as R^{-2} . The pole term arises as the Wick-rotated contour of the complex ω -plane picks up a pole at $\omega = \mathcal{L}_2 + i\epsilon$, where $\mathcal{L}_2 = E(2S_{1/2}) - E(2P_{1/2})$ is the Lamb shift.

We have examined the Dirac- δ perturbation to the interaction energy of the $1S$ - $1S$ and $2S$ - $1S$ system. The Dirac- δ perturbation is a local potential which is non-zero only at the origin. It is the first time that the δ -perturbation to the interaction energy for S -states have been studied. The Dirac- δ modification of the interaction energy is of great interest as the fine structure, the hyperfine correction, and the

leading radiative correction to the vdW interaction for S -states [84] are of Dirac- δ type. The δ -perturbation has vanishing contribution to the Hamiltonian of the system as the probability density of the P -states vanish at the origin. However, it modifies both the energy and the wave function of the system. The Dirac- δ correction to the interaction energy is in the order of α^2 times the plain interaction. If both atoms are in the ground state, there is no degenerate state to consider. The δ -perturbed interaction energy for the $1S$ - $1S$ system ignoring the relativistic correction is found to be $\delta E(1S; 1S) = -34.685\,544\,399 \left(\frac{a_0}{R}\right)^6 E_h$. In the CP region, where the contribution is chiefly due to the degenerate one, both the energy part and the wave function part of the $1S$ - $1S$ follow $1/R^7$ behavior which is negligible. On the other hand, the energy part and the wave function part of perturbed interaction energy in the Lamb shift range are found to be

$$\delta E_{1S;1S}^{(E)}(R) = -\frac{387}{8} \frac{\alpha}{\pi} \left(\frac{a_0}{R}\right)^7 E_h \quad \text{and} \quad \delta E_{1S;1S}^{(\psi)}(R) = -\frac{729}{16} \frac{\alpha}{\pi} \left(\frac{a_0}{R}\right)^7 E_h. \quad (9.1)$$

For $2S$ - $1S$ system, we observed that the δ -perturbed interaction energy, in the vdW range, is

$$\begin{aligned} \delta E(2S; 1S) &= -\frac{\delta D_6(2S; 1S) \pm \delta M_6(2S; 1S)}{R^6} \\ &= (367.914605710 \mp 58.095351093) \alpha^2 E_h \left(\frac{a_0}{R}\right)^6, \end{aligned} \quad (9.2)$$

which is clearly in the $1/R^6$ functional form. A very peculiar behavior is observed as the δ perturbed interaction energy follows the $1/R^5$ power law in the CP range. The energy type contribution, $\delta E^{(E)}(2S; 1S)$, and the wave function type correction, $\delta E^{(\psi)}(2S; 1S)$, both of them are solely the contributions given by the quasi-degenerate

states, which are

$$\begin{aligned}\delta E^{(E)}(2S; 1S) &= -\frac{\delta D_5^{(E)}(2S; 1S) \pm \delta M_5^{(E)}(2S; 1S)}{R^5} \\ &= -\left(\frac{891}{32} \pm 10.682382428\right) \frac{\alpha^3}{\pi} E_h \left(\frac{a_0}{R}\right)^5, \quad (9.3)\end{aligned}$$

$$\begin{aligned}\delta E^{(\psi)}(2S; 1S) &= -\frac{\delta D_6^{(\psi)}(2S; 1S) \pm \delta M_6^{(\psi)}(2S; 1S)}{R^6} \\ &= -\left(\frac{81}{4} \mp 58.439051900\right) \alpha^2 E_h \left(\frac{a_0}{R}\right)^6. \quad (9.4)\end{aligned}$$

It is observed that, in the van der Waals range, the dominant contribution comes from the wave function type correction, however, in the CP range, the energy type correction is the dominant one. In the Lamb shift range, the interaction energy is the sum of the CP term which follows a R^{-7} power law and the long range cosine term with amplitude falling off as R^{-2} and it is in the order of 10^{-36} Hz. From the experimental point of view, this is too small quantity to consider.

In this work, we have also analyzed the hyperfine resolved $2S$ - $2S$ system composed of two electrically neutral hydrogen atoms. The analysis of the $2S$ - $2S$ system involves fascinating interplay of degenerate and nondegenerate perturbations theory with a full account of hyperfine splitting. Our approach to investigating the $2S$ - $2S$ system allows us to do the hyperfine calculation and to estimate the hyperfine pressure shift for the $2S$ hyperfine interval measurement.

Each hydrogen atom has four hyperfine states for S -states, namely the hyperfine singlet for $F = 0$ and the hyperfine triplet for $F = 1$ and similarly the four hyperfine states corresponding to P -states. Thus, the basis set of the two hydrogen atom system has 64 states. The 64-dimensional Hilbert space corresponding to the hyperfine resolved $2S$ - $2S$ system decomposes into five manifolds. We noticed that the adjacency graph serves as a great tool to study a higher dimensional matrix. Interestingly, each manifold further decomposes into two sub-manifolds of the same

dimension. In each of these sub-manifolds, the Hamiltonian matrix can be solved analytically. In these sub-manifolds, there are several degenerate subspaces which are first order in vdW shift, i.e., proportional to R^{-3} . However, the hyperfine transition where both atoms are in S -states undergoes the second order in vdW shift, i.e., proportional to R^{-6} . We also study the evolution of the energy levels, which are so-called the Born-Oppenheimer potential curves, in all the hyperfine subspaces. We observed a strange but a highly impressive feature of level crossings in the hyperfine resolved $2S$ - $2S$ system. In $F_z = +2$ and $F_z = -2$ manifolds, no level crossing occurs. However, in $F_z = +1$ and $F_z = -1$ manifolds, the level-crossings occur between the levels of different irreducible sub-manifolds, while in the $F_z = 0$ manifolds, the level-crossings present not only between the levels of different manifolds but also the levels of the same irreducible manifolds may cross. We reveal that the crossings are unavoidable, which repudiates the non-crossing theorem discussed in the literature so far. Thus, we can conclude that the system with two energy levels follows non-crossing theorem; however, the higher-dimensional irreducible matrices do not always follow the non-crossing rule. We are not much aware of the applicability of such phenomenon in spectroscopy; however, this certainly gives an insight understanding the Born-Oppenheimer potential curves.

We also studied higher excited S -states of the hydrogen atom interacting with the ground state atom. For excited reference states, interaction energy is calculated matching the scattering amplitude and the effective hamiltonian of the system. For mathematical simplicity, we have also employed the method of Wick-rotation, which is one of a standard calculation tricks of rotating the integration contour. The Wick-rotated integration contour enclosed poles at $\omega = -E_{mP,nS}/\hbar + i\epsilon$, where mP with $2 \leq m \leq n$ are the low lying virtual P -states of the atom which is at nS -state. The pole term contribution to the interaction energy thus arises naturally. In the vdW range, both the Wick-rotated and the pole terms of both the direct and the mixing

type contributions to the interaction energy are of R^{-6} type, although the dominant contribution comes from the Wick-rotated term. We notice that the higher principal quantum number of the atom, larger the direct contribution $E_{nS;1S}^{(\text{direct})}(R)$ and smaller the mixing contribution $E_{nS;1S}^{(\text{mixing})}(R)$ to the interaction energy. In the CP range, the Wick-rotated type input is the sum of the R^{-6} and R^{-7} terms, and the pole type contribution has cosine terms obeying the power law R^{-2} , R^{-4} , and R^{-6} and sine terms obeying power law R^{-3} and R^{-5} . An $nS-1S$ system for a particular value of n has $n - 2$ poles arising from the low-lying virtual mP -states, where $2P$ -states have the dominant contribution.

In the Lamb shift range, the Wick-rotated term follows the R^{-7} . In the case of pole term, the dominant contribution comes from the cosine term whose magnitude is of R^{-2} type. In this range, the Wick-rotated term and the pole term are of the same order of magnitude. The interaction energy of the $nS-1S$ systems in the vdW range is negative, which indicates that there exists the electrostatic force of attraction between the atoms which establishes a weak chemical bond between them in the vdW range. However, in the CP and Lamb shift ranges, the electrostatic force is not necessarily attractive. Indeed, its attractive and repulsive nature oscillates.

For excited reference states, in vdW range both the Wick-rotated and the pole term follow the same R^{-6} functional form, in Casimir-Polder range, there is a competition between Wick-rotated (R^{-6}) and the oscillatory pole term, and in the Lamb shift range, an oscillatory pole term whose magnitude falls off as R^{-2} dominates the Wick-rotated term. In short, if an atom interacting with the other atom in the ground state is in an excited state, the system never reach to the retardation regime.

APPENDIX A

DISCRETE GROUND STATE POLARIZABILITY

A.1. DISCRETE RADIAL GREEN FUNCTION

With the help of the completeness relation in discrete representation, one can write $\langle \vec{r}_1 | \vec{r}_2 \rangle$ as below:

$$\begin{aligned}
\langle \vec{r}_1 | \mathbb{1} | \vec{r}_2 \rangle &= \sum_{n\ell m} \langle \vec{r}_1 | n\ell m \rangle \langle n\ell m | \vec{r}_2 \rangle = \sum_{n\ell m} \psi_{n\ell m}(r_1, \theta_1, \varphi_1) \psi_{n\ell m}^*(r_2, \theta_2, \varphi_2) \\
&= \sum_{n\ell m} R_{n\ell}(r_1) R_{n\ell}(r_2) Y_{\ell m}(\theta_1, \varphi_1) Y_{\ell m}^*(\theta_2, \varphi_2) \\
&= \sum_{n\ell m} \frac{(n-\ell-1)!}{2n(n+\ell)!} \left(\frac{2}{na_0}\right)^3 \exp\left(-\frac{r_1+r_2}{na_0}\right) \left(\frac{2r_1}{na_0}\right)^\ell \left(\frac{2r_2}{na_0}\right)^\ell \\
&\quad L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_1}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_2}{na_0}\right). \tag{A.1}
\end{aligned}$$

Here, $\langle \vec{r} | n\ell m \rangle = \psi_{n\ell m}(r, \theta, \varphi)$ is the complete eigenfunction for Schrödinger-Coulomb Hamiltonian. We have used an ansatz which states that the total eigenfunctions can be expressed as the product of a radial part and an angular part as

$$\psi_{n\ell m}(r, \theta, \varphi) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi), \tag{A.2}$$

where the radial wave function $R_{n\ell}(r)$ is given by [85]

$$R_{n\ell}(r) = \left[\frac{(n-\ell-1)!}{(n+\ell)!} \right]^{1/2} \frac{2^{\ell+1}}{n^2} \frac{1}{a_0^{3/2}} \left(\frac{r}{na_0}\right)^\ell \exp\left(-\frac{r}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right), \tag{A.3}$$

and the angular part $Y_{\ell m}(\theta, \varphi)$ is the usual spherical harmonics given by

$$Y_{\ell m}(\theta, \varphi) = \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!} \right]^{1/2} P_\ell^m(\cos(\theta)) e^{im\varphi}. \tag{A.4}$$

Here, $L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ and $P_\ell^m(\cos(\theta))$ are respectively the associated Laguerre and the associated Legendre polynomials. In what follows, we generalize this concept to derive

discrete radial Green function. The total discrete Green function is given by

$$\begin{aligned}
G^{\text{dis}}(\vec{r}_1, \vec{r}_2, E) &= \langle \vec{r}_1 | \frac{\mathbb{1}}{H - E} | \vec{r}_2 \rangle = \sum_{n\ell m} \langle \vec{r}_1 | n\ell m \rangle \frac{1}{H - E} \langle n\ell m | \vec{r}_2 \rangle \\
&= \sum_{n\ell m} \frac{\psi_{n\ell m}(r_1, \theta_1, \varphi_1) \psi_{n\ell m}^*(r_2, \theta_2, \varphi_2)}{E_n - E} \\
&= \sum_{n\ell m} \frac{1}{E_n - E} \frac{(n - \ell - 1)!}{2n(n + \ell)!} \left(\frac{2}{na_0} \right)^3 \exp\left(-\frac{r_1 + r_2}{na_0}\right) \left(\frac{2r_1}{na_0} \right)^\ell \left(\frac{2r_2}{na_0} \right)^\ell \\
&\quad L_{n-\ell-1}^{2\ell+1} \left(\frac{2r_1}{na_0} \right) L_{n-\ell-1}^{2\ell+1} \left(\frac{2r_2}{na_0} \right) Y_{\ell m}(\theta_1, \varphi_1) Y_{\ell m}^*(\theta_2, \varphi_2). \tag{A.5}
\end{aligned}$$

Here, E_n is the energy eigenvalues corresponding to the eigenvalue equation

$$HR_{n\ell}(r) = \left(-\frac{\hbar^2}{2m_e} \vec{\nabla}^2 - \frac{\alpha\hbar c}{r} \right) R_{n\ell}(r) = E_n R_{n\ell}(r). \tag{A.6}$$

Let us rewrite $R_{n\ell}(r)$ as

$$R_{n\ell}(r) = C_{n\ell} r^\ell \exp\left(-\frac{r}{na_0}\right) L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na_0} \right), \tag{A.7}$$

where

$$C_{n\ell} = \left[\frac{(n - \ell - 1)!}{(n + \ell)!} \right]^{1/2} \frac{2^{\ell+1}}{n^2} \frac{1}{a_0^{3/2}} \left(\frac{1}{na_0} \right)^\ell, \tag{A.8}$$

is a constant independent of r . In the following derivation, we will be using \mathbb{L} in place of $L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na_0} \right)$ just to save some space. Now, we have

$$\begin{aligned}
HR_{n\ell}(r) &= \left(-\frac{\hbar^2}{2m_e} \vec{\nabla}^2 - \frac{\alpha\hbar c}{r} \right) C_{n\ell} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
&= \left[-\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\ell(\ell + 1)}{r^2} \right) - \frac{\alpha\hbar c}{r} \right] C_{n\ell} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
&= -\frac{\hbar^2}{2m_e} C_{n\ell} \frac{\partial}{\partial r} \left[\ell r^{\ell-1} \exp\left(-\frac{r}{na_0}\right) \mathbb{L} - \frac{r^\ell}{na_0} \exp\left(-\frac{r}{na_0}\right) \mathbb{L} + r^\ell \exp\left(-\frac{r}{na_0}\right) \frac{\partial}{\partial r} \mathbb{L} \right]
\end{aligned}$$

$$\begin{aligned}
& -\frac{\hbar^2}{2m_e} C_{nl} \frac{2}{r} \left[\ell r^{\ell-1} \exp\left(-\frac{r}{na_0}\right) \mathbb{L} - \frac{1}{na_0} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} + r^\ell \exp\left(-\frac{r}{na_0}\right) \frac{\partial}{\partial r} \mathbb{L} \right] \\
& -\frac{\hbar^2}{2m_e} C_{nl} \left[-\frac{\ell(\ell+1)}{r^2} + \frac{2m_e \alpha c}{\hbar r} \right] r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
& = -\frac{\hbar^2}{2m_e} C_{nl} \left[\frac{\ell(\ell-1)}{r^2} \mathbb{L} - \frac{\ell}{na_0 r} \mathbb{L} + \frac{\ell}{r} \frac{\partial}{\partial r} \mathbb{L} - \frac{\ell}{na_0 r} \mathbb{L} + \frac{1}{(na_0)^2} \mathbb{L} - \frac{1}{na_0} \frac{\partial}{\partial r} \mathbb{L} \right. \\
& \quad \left. + \frac{\ell}{r} \frac{\partial}{\partial r} \mathbb{L} - \frac{1}{na_0} \frac{\partial}{\partial r} \mathbb{L} + \frac{\partial^2}{\partial r^2} \mathbb{L} \right] r^\ell \exp\left(-\frac{r}{na_0}\right) - \frac{\hbar^2}{2m_e} C_{nl} \frac{2}{r} \left[\frac{\ell}{r} \mathbb{L} - \frac{1}{na_0} \mathbb{L} + \frac{\partial}{\partial r} \mathbb{L} \right] \\
& \quad \times r^\ell \exp\left(-\frac{r}{na_0}\right) - \frac{\hbar^2}{2m_e} C_{nl} \left[-\frac{\ell(\ell+1)}{r^2} + \frac{2m_e \alpha c}{\hbar r} \right] r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
& = -\frac{\hbar^2}{2m_e} C_{nl} r^{\ell-1} \exp\left(-\frac{r}{na_0}\right) \left\{ r \frac{\partial^2}{\partial r^2} \mathbb{L} + \left(2\ell + 2 - \frac{2r}{na_0}\right) \frac{\partial}{\partial r} \mathbb{L} + (n - \ell - 1) \mathbb{L} \right\} \\
& \quad - \frac{\hbar^2}{2m_e} C_{nl} \left[-\frac{2\ell}{na_0 r} - \frac{2}{na_0 r} + \frac{1}{(na_0)^2} + \frac{2m_e \alpha c}{\hbar r} - \frac{2n}{na_0 r} + \frac{2\ell}{na_0 r} + \frac{2}{na_0 r} \right] \\
& \quad \times r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L}. \tag{A.9}
\end{aligned}$$

Using the fact that $\mathbb{L} \equiv L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ satisfies the associated Laguerre differential equation:

$$r \frac{\partial^2}{\partial r^2} \mathbb{L} + \left(2\ell + 2 - \frac{2r}{na_0}\right) \frac{\partial}{\partial r} \mathbb{L} + (n - \ell - 1) \mathbb{L} = 0, \tag{A.10}$$

Eq. (A.9) reduces to

$$\begin{aligned}
HR_{nl}(r) &= -\frac{\hbar^2}{2m_e} \left[\frac{1}{(na_0)^2} + \frac{2m_e \alpha c}{\hbar r} - \frac{2}{a_0 r} \right] C_{nl} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
&= \left[-\frac{\hbar^2}{2m_e n^2 a_0^2} - \frac{\hbar \alpha c}{r} + \frac{\hbar^2}{m_e a_0 r} \right] C_{nl} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} \\
&= -\frac{\alpha^2 m_e c^2}{2n^2} C_{nl} r^\ell \exp\left(-\frac{r}{na_0}\right) \mathbb{L} = -\frac{\alpha^2 m_e c^2}{2n^2} R_{nl}(r). \tag{A.11}
\end{aligned}$$

Here, we have used $a_0 = \hbar/(\alpha m_e c)$. From Eq. (A.11), the eigenvalues E_n can be written as

$$E_n = -\frac{\alpha^2 m_e c^2}{2n^2}. \tag{A.12}$$

If we define a new quantum number k such that $k = n - \ell - 1$, the associated Laguerre polynomials $L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)$ becomes $L_k^{2\ell+1}\left(\frac{2r}{(k+\ell+1)a_0}\right)$ and the energy eigenvalues, in this condition, can be written as

$$E_{k\ell} = -\frac{\alpha^2 m_e c^2}{2(k+\ell+1)^2}. \quad (\text{A.13})$$

The energy difference $E_n - E$ in Eq. (A.5) is thus given by

$$\begin{aligned} E_n - E &= -\frac{\alpha^2 m_e c^2}{2n^2} - \left(-\frac{\alpha^2 m_e c^2}{2\nu^2}\right) \\ &= \frac{\alpha^2 m_e c^2}{2} \left(\frac{1}{\nu^2} - \frac{1}{n^2}\right) = \frac{\hbar^2}{2m_e a_0^2} \left(\frac{n^2 - \nu^2}{n^2 \nu^2}\right). \end{aligned} \quad (\text{A.14})$$

Substituting the value of the energy difference $E_n - E$ from Eq. (A.14) to Eq. (A.5), we get

$$\begin{aligned} G^{\text{dis}}(\vec{r}_1, \vec{r}_2, \nu) &= \frac{2m_e}{\hbar^2} \sum_{n\ell m} \frac{a_0^2 n^2 \nu^2}{n^2 - \nu^2} \frac{(n-\ell-1)!}{2n(n+\ell)!} \left(\frac{2}{na_0}\right)^3 \exp\left(-\frac{r_1+r_2}{na_0}\right) \left(\frac{2r_1}{na_0}\right)^\ell \\ &\quad \left(\frac{2r_2}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_1}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_2}{na_0}\right) Y_{\ell m}(\theta_1, \varphi_1) Y_{\ell m}^*(\theta_2, \varphi_2) \\ &= \frac{4m_e}{\hbar^2} \sum_{n\ell m} \frac{\nu^2}{n^2 - \nu^2} \frac{(n-\ell-1)!}{n(n+\ell)!} \left(\frac{2}{na_0}\right)^{2\ell+1} \exp\left(-\frac{r_1+r_2}{na_0}\right) (r_1 r_2)^\ell \\ &\quad L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_1}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_2}{na_0}\right) Y_{\ell m}(\theta_1, \varphi_1) Y_{\ell m}^*(\theta_2, \varphi_2). \end{aligned} \quad (\text{A.15})$$

The total discrete Green function is defined as

$$G^{\text{dis}}(\vec{r}_1, \vec{r}_2, \nu) = \sum_{n\ell m} g_\ell^{\text{dis}}(r_1, r_2, \nu) Y_{\ell m}(\theta_1, \varphi_1) Y_{\ell m}^*(\theta_2, \varphi_2). \quad (\text{A.16})$$

Comparing Eq. (A.16) with Eq. (A.15), we get the discrete radial Green function $g_\ell^{\text{dis}}(r_1, r_2, \nu)$ as

$$g_\ell^{\text{dis}}(r_1, r_2, \nu) = \frac{4m_e}{\hbar^2} \sum_{n=0}^{\infty} \frac{\nu^2}{n^2 - \nu^2} \frac{(n - \ell - 1)!}{n(n + \ell)!} \left(\frac{2}{na_0}\right)^{2\ell+1} \exp\left(-\frac{r_1 + r_2}{na_0}\right) (r_1 r_2)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_1}{na_0}\right) L_{n-\ell-1}^{2\ell+1}\left(\frac{2r_2}{na_0}\right). \quad (\text{A.17})$$

The ($\ell=1$)-component of the discrete radial Green function $g_{\ell=1}^{\text{dis}}(r_1, r_2, \nu)$ reads

$$g_{\ell=1}^{\text{dis}}(r_1, r_2, \nu) = \frac{4m_e}{\hbar^2} \sum_{n=2}^{\infty} \frac{\nu^2}{(n^2 - \nu^2) n^2 (n^2 - 1)} \left(\frac{2}{na_0}\right)^3 \exp\left(-\frac{r_1 + r_2}{na_0}\right) (r_1 r_2) L_{n-2}^3\left(\frac{2r_1}{na_0}\right) L_{n-2}^3\left(\frac{2r_2}{na_0}\right). \quad (\text{A.18})$$

The sum over n starts from 2 not from zero as $L_{-2}^3(x) = 0 = L_{-1}^3(x)$.

A.2. DISCRETE GROUND STATE POLARIZABILITY

The ground state static polarizability due to discrete energy levels is given by

$$\begin{aligned} \alpha_{1S}^{\text{dis}}(\omega = 0) &= 2P_{1S}^{\text{dis}}(\omega = 0) = 2\frac{e^2}{3} \left\langle 1S \left| r_1 \frac{1}{H - E} r_2 \right| 1S \right\rangle \\ &= \frac{2e^2}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R_{10}(r_1) r_1 g_{\ell=1}^{\text{dis}}(r_1, r_2, \nu) R_{10}(r_2) r_2 \\ &= \frac{32m_e e^2}{3\hbar^2 a_0^3} \int_0^\infty r_1^4 dr_1 \int_0^\infty r_2^4 dr_2 \exp\left(-\frac{r_1 + r_2}{a_0}\right) \sum_{n=2}^{\infty} \frac{1}{n^2 (n^2 - 1)^2} \\ &\quad \left(\frac{2}{na_0}\right)^3 \exp\left(-\frac{r_1 + r_2}{na_0}\right) L_{n-2}^3\left(\frac{2r_1}{na_0}\right) L_{n-2}^3\left(\frac{2r_2}{na_0}\right). \quad (\text{A.19}) \end{aligned}$$

Here, we have used the value of $g_{\ell=1}^{\text{dis}}(r_1, r_2, \nu)$ from Eq. (A.18) with $\nu = 1$ and substituted the radial part of ground state wave function of hydrogen which reads

$$R_{10}(r) = \frac{2e^{-r/a_0}}{\sqrt{a_0^3}}. \quad (\text{A.20})$$

Let us use dimensionless variables ρ defined as $\rho_i = 2r_i/(na_0)$. Then Eq. (A.19) becomes

$$\begin{aligned}\alpha_{1S}^{\text{dis}}(\omega = 0) &= \frac{32m_e e^2}{3\hbar^2 a_0^3} \sum_{n=2}^{\infty} \frac{1}{n^2 (n^2 - 1)^2} \left(\frac{na_0}{2}\right)^7 \int_0^{\infty} \rho_1^4 d\rho_1 \int_0^{\infty} \rho_2^4 d\rho_2 \\ &\quad \exp\left(-\frac{\rho_1 n + \rho_2 n}{2}\right) \exp\left(-\frac{\rho_1 + \rho_2}{2}\right) L_{n-2}^3(\rho_1) L_{n-2}^3(\rho_2) \\ &= \frac{a_0^4 m_e e^2}{12\hbar^2} \sum_{n=2}^{\infty} \frac{n^5}{(n^2 - 1)^2} \int_0^{\infty} \rho_1^4 \exp\left(-\frac{(1+n)\rho_1}{2}\right) L_{n-2}^3(\rho_1) d\rho_1 \\ &\quad \int_0^{\infty} \rho_2^4 \exp\left(-\frac{(1+n)\rho_2}{2}\right) L_{n-2}^3(\rho_2) d\rho_2.\end{aligned}\quad (\text{A.21})$$

Interestingly, the ρ_1 -integral is identical to the ρ_2 -integral. Hence, one can write Eq. (A.21) as

$$\alpha_{1S}^{\text{dis}}(\omega = 0) = \frac{e^2 a_0^2}{12 E_h} \sum_{n=2}^{\infty} \frac{n^5}{(n^2 - 1)^2} \left[\int_0^{\infty} u^4 e^{-(1+n)u/2} L_{n-2}^3(u) du \right]^2. \quad (\text{A.22})$$

Here, we have also used $\alpha = \hbar/(a_0 m_e c)$, and $E_h = \alpha^2 m_e c^2$, where α and E_h are respectively the fine-structure constant and the Hartree energy. We can evaluate the u -integral in Eq. (A.22) using the standard integral identity [43]

$$\int_0^{\infty} d\rho e^{s\rho} \rho^\gamma L_n^\mu(\rho) = \frac{\Gamma(\gamma + 1)\Gamma(n + \mu + 1)}{n!\Gamma(\mu + 1)} (-s)^{-(\gamma+1)} {}_2F_1\left(-n, \gamma + 1; \mu + 1; -\frac{1}{s}\right), \quad (\text{A.23})$$

which yields

$$\int_0^{\infty} u^4 e^{-(1+n)u/2} L_{n-2}^3(u) du = \frac{\Gamma(5)\Gamma(n+2)}{(n-2)!\Gamma(4)} \left(\frac{2}{1+n}\right)^5 {}_2F_1\left(2-n, 5; 4; \frac{2}{1+n}\right). \quad (\text{A.24})$$

Substituting the value of the integral in Eq. (A.22) and simplifying the expression using standard integral identity [43]

$${}_2F_1(-k, a+1; a; z) = (1-z)^k \frac{(z-1)a + kz}{a(z-1)}, \quad (\text{A.25})$$

we get

$$\alpha_{1S}^{\text{dis}}(\omega = 0) = \frac{e^2 a_0^2}{E_h} \sum_{n=2}^{\infty} \frac{1024}{3} \frac{n^9}{(n-1)^6 (n+1)^8} \left(\frac{n-1}{n+1} \right)^{2n}, \quad (\text{A.26})$$

which yields

$$\alpha_{1S}^{\text{dis}}(\omega = 0) = 0.362\,240\,952 \frac{e^2 a_0^2}{E_h}. \quad (\text{A.27})$$

Recalling the total ground state static polarizability of a hydrogen atom

$$\alpha_{1S}(\omega = 0) = \frac{9}{2} \frac{e^2 a_0^2}{E_h}, \quad (\text{A.28})$$

we come to the conclusion that, the major contribution in the ground state static polarizability comes from the continuum wave functions.

APPENDIX B

MAGIC WAVELENGTHS OF $nS-1S$ SYSTEMS

B.1. ORIENTATION

The AC Stark shift, which is the shifting of spectral lines in the presence of an oscillating electric field, can be used to trap neutral atoms. The AC Stark can also be useful in optical lattice clock experiments [86; 87; 88]. We here concentrate only in the trapping of the neutral hydrogen atoms. The AC Stark shift for the ground state is different to that of the excited states of the transition. The AC Stark shift vanishes if the trapping laser of particular wavelength called magic wavelength is turned on [86; 89; 90]. The calculation involves the determination of the point, where the AC Stark shift for the ground state is equal to that of the excited state, and the shifts due to the laser cancel. In other words, the atom does not feel the presence of light if the laser wavelength matches its magic wavelength value.

The AC Stark shift for the state $|\phi\rangle$ of an atom depends on the intensity of the laser field and the optical frequency of the photon which is given by

$$\Delta E_{AC} = -\frac{I_L}{2\epsilon_0 c} \alpha(\phi, \omega_L), \quad (\text{B.1})$$

where I_L stands for the intensity of the laser field. The I_L is proportional to the square of the amplitude of the electric field \mathcal{E}_L , mathematically, $I_L = \frac{1}{2}\epsilon_0 c \mathcal{E}_L^2$. $\alpha(\phi, \omega_L)$ in Eq. (B.1) represents the dipole polarizability of the state $|\phi\rangle$ [91; 92; 93].

The magic wavelengths corresponding to the $2S-1S$ transition of a hydrogen atom is computed in reference [94]. However, the author took only the discrete states of the hydrogen atom into account. The fact is the contribution of the continuum states can not be ignored. We already saw in Appendix A, for the ground state, the dominant contribution comes from the continuum states, not from the discrete one.

The following definition of the dipole polarizability

$$\alpha(\phi, \omega_L) = \frac{e^2}{3} \sum_{\pm} \left\langle \phi \left| \vec{r} \frac{1}{H_A - E \pm \hbar\omega_L} \vec{r} \right| \phi \right\rangle = \sum_{\pm} P_{\phi}(\pm\omega_L), \quad (\text{B.2})$$

includes the contributions of both discrete and continuous parts of the spectrum. The $H_A = \vec{p}^2/(2m_e) - (\alpha\hbar c)/r$, E , and P_{ϕ} in Eq. (B.2) are the atomic Hamiltonian of the system, the energy eigenvalues, and the P matrix element for the atomic reference state ϕ . The P_{1S} , P_{2S} , P_{3S} , P_{4S} , and P_{5S} matrix elements are given by Eqs. (3.44), (3.56), (3.66), (3.73), and (3.74) respectively. The P_{6S} matrix element reads

$$\begin{aligned} P(6S, t) = & \frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{432 t^2}{25(t-1)^{14} (t+1)^{12}} \left(39439108405 t^{24} - 3444722282 t^{23} \right. \right. \\ & - 113551229560 t^{22} + 9795349850 t^{21} + 135698822058 t^{20} - 11514250414 t^{19} \\ & - 87425932088 t^{18} + 7253828382 t^{17} + 33018970995 t^{16} - 2654366212 t^{15} \\ & - 7439943344 t^{14} + 569035620 t^{13} + 971507820 t^{12} - 65940540 t^{11} - 67724400 t^{10} \\ & + 1350940 t^9 + 2692555 t^8 + 1404750 t^7 - 509400 t^6 - 501150 t^5 + 200650 t^4 \\ & \left. + 99850 t^3 - 45400 t^2 - 9050 t + 4525 \right) - \frac{442368 t^9 (-1 + 36 t^2)}{25(-1 + t^2)^{14}} \\ & \times (2023 t^8 - 2932 t^6 + 1410 t^4 - 260 t^2 + 15)^2 {}_2F_1 \left(1, -6t; 1 - 6t; \frac{(t-1)^2}{(t+1)^2} \right) \\ & \left. - \frac{68040 t^2}{1 - t^2} \right]; \quad \text{where} \quad t = \left(1 + \frac{72 \hbar \omega}{\alpha^2 m c^2} \right)^{-1/2}. \quad (\text{B.3}) \end{aligned}$$

The contribution of the degenerate P -states has been excluded from $P(6S, t)$ subtracting $\frac{\hbar^2 e^2}{\alpha^4 m^3 c^4} \left[\frac{68040 t^2}{(1-t^2)} \right]$.

Work to the magic wavelengths for the $2S-1S$ and $3S-1S$ transitions in hydrogen atoms including the relativistic correction is presented in Ref. [95]. However, the relativistic correction, which is in the order of $\alpha^2 \sim 10^{-4}$ depends on the laser-field configuration. It is different for the different experimental setup. On the other hand,

the dominant correction to the magic wavelengths in the non-relativistic one-particle approximation comes from the reduced mass correction [96]. More explicitly, the reduced mass correction to the wavelength is of order $m_e/m_p \sim 10^{-3}$. The P matrix elements are proportional to the square of Bohr radius, $a_0 = \hbar/(\alpha mc)$, and inversely proportional to the Hartree energy, $E_h = \alpha^2 mc^2$. Thus, the reduced mass correction on the dipole polarizability and hence the AC Stark shift has overall factor of $(m_e/m_r)^3$, where the reduced mass m_r of the system is given by

$$m_r = \frac{m_e m_p}{m_e + m_p}, \quad (\text{B.4})$$

where m_e and m_p are the masses of an electron and a proton respectively. In this work, we also calculate the reduced mass correction of the magic wavelength, AC Stark shift, and the slope of the AC Stark shift at the magic wavelengths.

B.2. MAGIC WAVELENGTHS AND AC STARK SHIFT

Let us recall the AC Stark shift corresponding to the nS -state, which reads

$$\Delta E_{AC}(nS) = -\frac{I_L}{2\epsilon_0 c} \alpha(nS, \omega_L). \quad (\text{B.5})$$

Then the difference in AC Stark shift between an excited state and the ground state, i.e.,

$$\Delta E_{AC}(nS) - \Delta E_{AC}(1S) = -\frac{I_L}{2\epsilon_0 c} [\alpha(nS, \omega_L) - \alpha(1S, \omega_L)], \quad (\text{B.6})$$

can be written as

$$\Delta E_{AC}(nS) - \Delta E_{AC}(1S) = -\frac{I_L}{2\epsilon_0 c} f_{1S nS}(\omega_L), \quad (\text{B.7})$$

Table B.1: Influence of the reduced-mass correction (RMC) on the magic wavelengths λ_M , and the AC Stark shifts ΔE_M for $nS-1S$ transitions, where $n = 2, 3, 4, 5, 6$.

Quantity	condition	transitions				
		2S-1S	3S-1S	4S-1S	5S-1S	6S-1S
λ_M (in nm)	without RMC	514.366	1371.11	2811.24	4935.99	7588.47
	with RMC	514.646	1371.86	2812.77	4938.68	7592.60
ΔE_M (in $\frac{I_L}{\text{kW/cm}^2} \text{Hz}$)	without RMC	-221.222	-212.290	-211.249	-211.026	-210.964
	with RMC	-221.584	-212.637	-211.595	-211.371	-211.309

where

$$f_{1S nS}(\omega_L) = \alpha(nS, \omega_L) - \alpha(1S, \omega_L). \quad (\text{B.8})$$

The magic angular frequency satisfies the condition $f_{1S nS}(\omega_L = \omega_M) = 0$, which is the point of interaction of the polarizability of the ground state and that of the excited state of interest. Alternatively, this is the point where the difference of AC Stark shifts corresponding to the ground state, and the excited state vanishes nullifying the systematic uncertainties (see Figures (B.1) - (B.5))

The magic wavelength, λ_M , for the hydrogen $nS-1S$ transition is given as

$$\hbar \omega_M = E_M = \frac{hc}{\lambda_M} \implies \lambda_M = \frac{hc}{\hbar \omega_M}. \quad (\text{B.9})$$

The magic wavelengths, λ_M , and the AC Stark shifts, ΔE_{AC} , for the $2S-1S$, $3S-1S$, $4S-1S$, $5S-1S$, and $6S-1S$ transitions are listed in Table (B.1). The magic wavelength $\lambda_M = 514.646$ nm for the $2S-1S$ transition lies in between the $2S-3P$ transition (656.387 nm) and $2S-4P$ transition (486.213 nm) of a hydrogen atom. The magic wavelength $\lambda_M = 1371.86$ nm for the $3S-1S$ transition lies in between the $3S-4P$ transition (1875.39 nm) and $3S-5P$ transition (1282.01 nm) of a hydrogen atom. The magic wavelength $\lambda_M = 2812.77$ nm for the $4S-1S$ transition lies in between

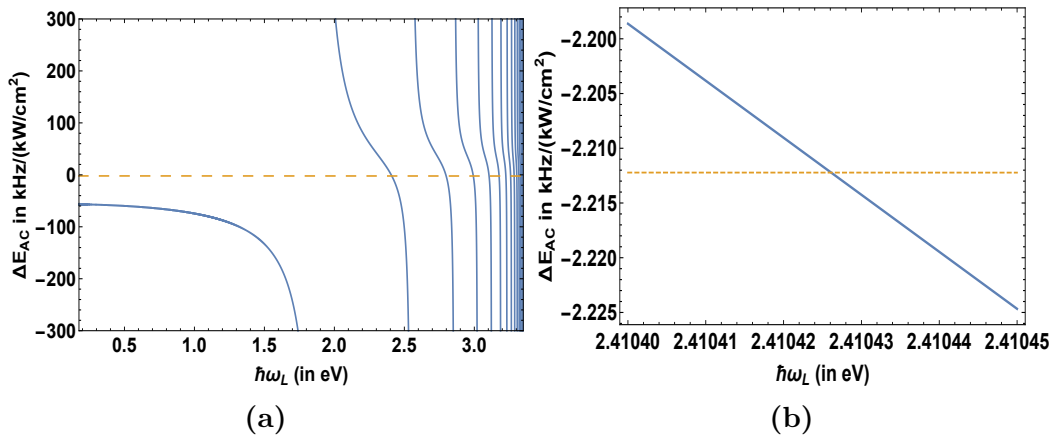


Figure B.1: AC Stark shift coefficients for the $1S$ - and $2S$ -states for intensity, $I_L = 10 \text{ kW/cm}^2$ as a function of laser photon energy $E_\gamma = \hbar\omega_L$. In Figure (a), the dashed line at $\Delta E_{AC} \approx 0$ represents the AC Stark shift coefficient of the $1S$ -state while the solid curved lines represent the AC Stark shift coefficient of the $2S$ -state. Figure (b) shows the AC Stark shifts near the magic wavelength, λ_M , for $2S$ - $1S$ transition. The AC Stark shifts of the $1S$ -state (dashed line) and the $2S$ -state (solid line) intersect at $(2.41043 \text{ eV}, -2.21222 \text{ kHz})$.

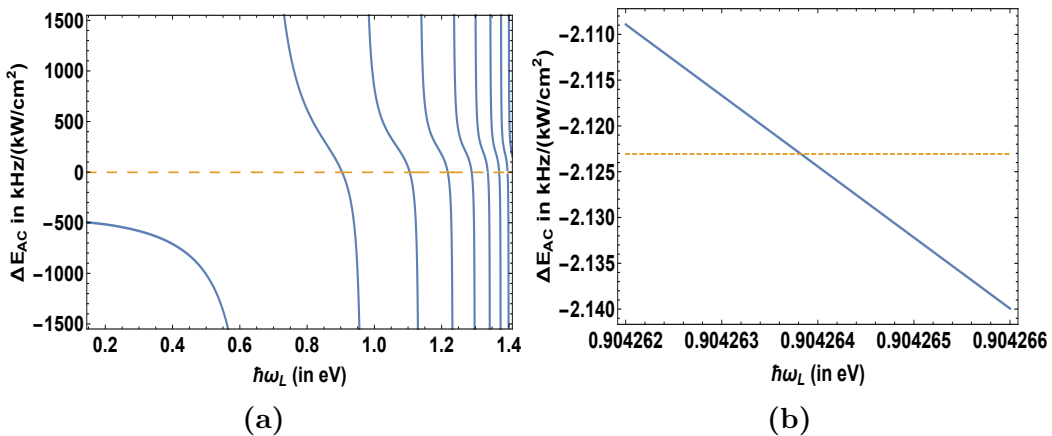


Figure B.2: AC Stark shift coefficients for the $1S$ - and $3S$ -states by a laser light of intensity, $I_L = 10 \text{ kW/cm}^2$ as a function of laser photon energy $E_\gamma = \hbar\omega_L$. In Figure (a), the dashed line at $\Delta E_{AC} \approx 0$ represents the AC Stark shift coefficient of the $1S$ -state while the solid curved lines represent the AC Stark shift coefficient of the $3S$ -state. Figure (b) shows the AC Stark shifts near the magic wavelength, λ_M , for $3S$ - $1S$ transition. The AC Stark shifts of the $1S$ -state (dashed line) and the $3S$ -state (solid line) intersect at $(0.904264 \text{ eV}, -2.12290 \text{ kHz/(kW/cm}^2))$.

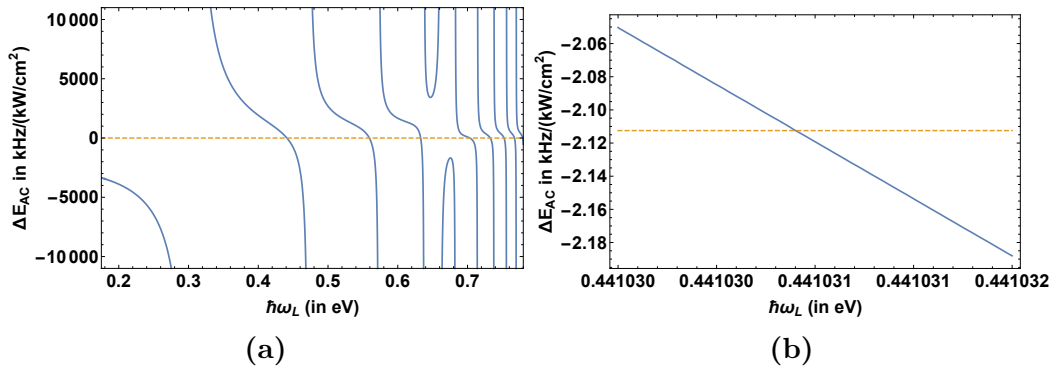


Figure B.3: AC Stark shift coefficients for the $1S$ - and $4S$ -states for intensity, $I_L = 10 \text{ kW/cm}^2$ as a function of laser photon energy $E_\gamma = \hbar\omega_L$. In Figure (a), the dashed line at $\Delta E_{AC} \approx 0$ represents the AC Stark shift coefficient of the $1S$ -state while the solid curved lines represent the AC Stark shift coefficient of the $4S$ -state. Figure (b) shows the AC Stark shifts near the magic wavelength λ_M , for $4S$ - $1S$ transition. The AC Stark shifts of the $1S$ -state (dashed line) and the $4S$ -state (solid line) intersect at $(0.441031 \text{ eV}, -2.11249 \text{ kHz}/(\text{kW}/\text{cm}^2))$.

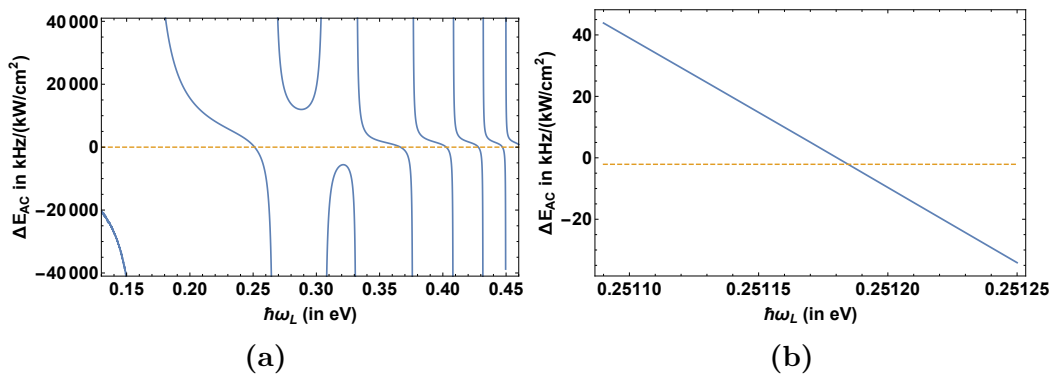


Figure B.4: AC Stark shift coefficients for the $1S$ - and $5S$ -states for intensity, $I_L = 10 \text{ kW/cm}^2$ as a function of laser photon energy $E_\gamma = \hbar\omega_L$. In Figure (a), the dashed line at $\Delta E_{AC} \approx 0$ represents the AC Stark shift coefficient of the $1S$ -state while the solid curved lines represent the AC Stark shift coefficient of the $5S$ -state. Figure (b) shows the AC Stark shifts near the magic wavelength λ_M , for $5S$ - $1S$ transition. The AC Stark shifts of the $1S$ -state (dashed line) and the $5S$ -state (solid line) intersect at $(0.251184 \text{ eV}, -2.11026 \text{ kHz}/(\text{kW}/\text{cm}^2))$.

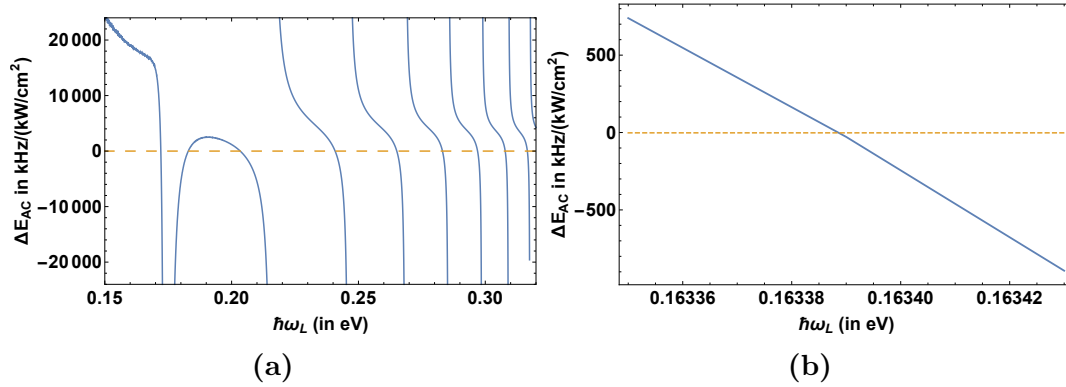


Figure B.5: AC Stark shift coefficients for the $1S$ - and $6S$ -states for intensity, $I_L = 10 \text{ kW/cm}^2$ as a function of laser photon energy $E_\gamma = \hbar\omega_L$. In Figure (a), the dashed line at $\Delta E_{AC} \approx 0$ represents the AC Stark shift coefficient of the $1S$ -state while the solid curved lines represent the AC Stark shift coefficient of the $6S$ -state. Figure (b) shows the AC Stark shifts near the magic wavelength λ_M , for $6S$ - $1S$ transition. The AC Stark shifts intersect at $(0.163385 \text{ eV}, -2.10964 \text{ kHz}/(\text{kW}/\text{cm}^2))$.

the $4S$ - $5P$ transition (4051.77 nm) and $4S$ - $6P$ transition (2625.55 nm) of a hydrogen atom. Similarly, the magic wavelength magic wavelength for $5S$ - $1S$, $\lambda_M = 4938.68 \text{ nm}$ lies between the $5S$ - $6P$ transition (7458.94 nm) and $5S$ - $7P$ transition (4653.21 nm) of a hydrogen atom. Likewise, the magic wavelength magic wavelength for $6S$ - $1S$, $\lambda_M = 7592.60 \text{ nm}$ lies between the $6S$ - $7P$ transition (12370.4 nm) and $6S$ - $8P$ transition (7501.57 nm) of a hydrogen atom. It is evident from Figures (B.1), (B.2), and (B.3) that, in addition to the magic wavelength tabulated above in Table ??, there are few other magic wavelength as well for each transition. For example, for the $2S$ - $1S$ transition, other magic wavelengths with reduced mass correction are 443.212 nm, 414.484 nm, 399.451 nm and so on with AC Stark shifts $-225.203 \frac{I_L}{(\text{kW}/\text{cm}^2)} \text{ Hz}$, $-227.404 \frac{I_L}{(\text{kW}/\text{cm}^2)} \text{ Hz}$, and $-228.776 \frac{I_L}{(\text{kW}/\text{cm}^2)} \text{ Hz}$ respectively.

As shown in Figures (B.1) - (B.5), the AC Stark shift for $1S$ -state is almost constant. The AC Stark shift for $1S$ -state, $\Delta E_{AC}(1S)$, is almost a horizontal line at

zero AC Stark shift. Numerically,

$$\Delta E_{AC}(1S) = -\frac{I_L}{2\epsilon_0 c} \alpha(1S, \omega_L). \quad (\text{B.10})$$

A lawful approximation to the dynamic polarizability of the ground state hydrogen is that it is roughly equal to its static polarizability, i.e., $\alpha(1S, \omega_L) \approx \alpha(1S, \omega_L = 0) = 9e^2 a_0^2 / (2E_h)$. Thus, Eq. (B.10) yields

$$\Delta E_{AC}(1S) \approx -210.921 \frac{I_L}{\text{kW/cm}^2} \text{Hz}. \quad (\text{B.11})$$

One of the most important features we observe in the AC Stark shift for the $4S$, $5S$, and $6S$ reference states is the double pole structures in their energy versus AC Stark shift plots. For the $4S$ -state, the AC Stark shift has a double pole at 0.661388 eV. Similarly, for the $5S$ - and $6S$ - states, poles appear respectively at 0.306128 eV and 0.166292 eV.

Let us now discuss the origin of such double pole structures. As given by Eq. (24) of Ref. [91], the AC Stark shift of the unperturbed state $|\phi, n_L\rangle$ reads

$$\Delta E_{AC}(\phi) = -\frac{e^2 \hbar \omega_L}{2\epsilon_0 \mathcal{V}} \sum_m \left[\frac{\langle \phi | z | m \rangle \langle m | z | \phi \rangle}{E_m - E_\phi - \hbar \omega_L} n_L + \frac{\langle \phi | z | m \rangle \langle m | z | \phi \rangle}{E_m - E_\phi + \hbar \omega_L} (n_L + 1) \right], \quad (\text{B.12})$$

which reduces to Eq. (B.5) in the classical limit, $n_L \rightarrow \infty$, $\mathcal{V} \rightarrow \infty$, and $n_L/\mathcal{V} = \text{constant}$. Here, ω_L , \mathcal{V} , E_m , and E_ϕ are the laser field frequency, normalization volume, energy corresponding to a virtual intermediate state $|m\rangle$, and energy corresponding to the reference state $|\phi\rangle$ respectively. If the laser frequency is same to the energy difference between the energy of the reference state and one of the virtual level, we observe the pole structures as seen in the Figures. (B.3), (B.4), and (B.5) in the Stark shifts. More interestingly, the double pole structure in the AC Stark shift of $4S$ -state

can be eliminated by subtracting the following term

$$-\frac{I_L}{2\epsilon_0 c} \frac{e^2}{3} \sum_{\mu} \sum_j \frac{\langle 4S|x^j|3P(m=\mu)\rangle \langle 3P(m=\mu)|x^j|4S\rangle}{(E_{3P} - E_{4S}) + \hbar\omega}. \quad (\text{B.13})$$

Similarly, the double pole structure in the AC Stark shift of 5S- and 6S- states gets eliminated if we subtract

$$-\frac{I_L}{2\epsilon_0 c} \frac{e^2}{3} \sum_{\mu} \sum_j \frac{\langle 5S|x^j|4P(m=\mu)\rangle \langle 4P(m=\mu)|x^j|5S\rangle}{(E_{4P} - E_{5S}) + \hbar\omega}, \quad (\text{B.14})$$

and

$$-\frac{I_L}{2\epsilon_0 c} \frac{e^2}{3} \sum_{\mu} \sum_j \frac{\langle 6S|x^j|5P(m=\mu)\rangle \langle 5P(m=\mu)|x^j|6S\rangle}{(E_{5P} - E_{6S}) + \hbar\omega}, \quad (\text{B.15})$$

respectively from the total AC Stark shifts of the respective states. This double pole structure suggests that there exist a resonant emission into the laser field. The emitted photon has energy,

$$\Delta E = \hbar\omega = E_{nS} - E_{(n-1)P}, \quad n \geq 4. \quad (\text{B.16})$$

Our investigation shows that Eq. (B.16) exactly predict the position of the double poles in the AC Stark shifts of 4S-, 5S-, and 6S- states.

B.3. SLOPE OF THE AC STARK SHIFTS

The slope η of the AC Stark shift at the magic wavelength is given by

$$\eta = \left. \frac{\partial}{\partial \omega_L} (\Delta E_{AC}(nS, \omega_L) - \Delta E_{AC}(1S, \omega_L)) \right|_{\omega_L = \omega_M}, \quad (\text{B.17})$$

which measures how fast the difference of AC Stark shifts between the nS -state and

Table B.2: Influence of the reduced-mass correction (RMC) on the slope of Stark shifts at the magic wavelengths in unit of $\frac{\text{Hz}}{\text{GHz}(\text{kW}/\text{cm}^2)}$ for $2S-1S$, $3S-1S$, $4S-1S$, $5S-1S$ and $6S-1S$ transitions.

condition	transitions				
	$2S-1S$	$3S-1S$	$4S-1S$	$5S-1S$	$6S-1S$
without RMC	-0.215044	- 3.20155	- 28.4212	- 201.627	-8036.57
with RMC	-0.215395	- 3.20679	- 28.4677	- 201.737	-8049.72

the $1S$ -state changes with the laser frequency. The slope of the AC Stark shifts at magic wavelengths are presented in Table (B.2). The magic wavelengths listed in Table (B.1) are the longest magic wavelengths for the corresponding transitions, and the slope of these transitions in Table (B.2) are the minimum slopes. The value of η with the reduced mass correction is 1.001637 times that of the η without the reduced mass correction. This factor comes from $(m_e/m_r)^3$. In the laser trapping process, a large slope of the AC Stark shift should be avoided. With no surprise, the slope of the AC Stark shift in $nS-1S$ transition is larger for the higher value of n . So far the feasibility of optical trapping [97] is concerned, difficulty increases as the value of n and hence the value of η increases.

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VITA

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