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Quantum electrodynamics and fundamental constants

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ABSTRACT

The unprecedented precision achieved both in the experimental measurements as well as in the theoretical description of atomic bound states make them an ideal study object for fundamental physics and the determination of fundamental constants. This requires a careful study of the effects from quantum electrodynamics (QED) on the interaction between the electron and the nucleus.

The two theoretical approaches for the evaluation of QED corrections are presented and discussed. Due to the presence of two energy scales from the binding potential and the radiation field, an overlapping parameter has to be used in both approaches in order to separate the energy scales. The different choices for the overlapping parameter in the two methods are further illustrated in a model example.

With the nonrelativistic theory, relativistic corrections in order $(Z\alpha)^2$ to the two-photon decay rate of ionic states are calculated, as well as the leading radiative corrections of $\alpha(Z\alpha)^2 \ln[(Z\alpha)^{-2}]$. It is shown that the corrections is gauge-invariant under a "hybrid" gauge transformation between Coulomb and Yennie gauge.

Furthermore, QED corrections for Rydberg states in one-electron ions are investigated. The smallness of the corrections and the absence of nuclear size corrections enable very accurate theoretical predictions. Measuring transition frequencies and comparing them to the theoretical predictions, QED theory can be tested more precisely. In turn, this could yield a more accurate value for the Rydberg constant. Using a transition in a nucleus with a well determined mass, acting as a reference, a comparison to transition in other nuclei can even allow to determined nuclear masses.

Finally, in order to avoid an additional uncertainty in nuclei with non zero nuclear spin, QED self-energy corrections to the hyperfine structure up to order $\alpha(Z\alpha)^2\Delta E_{\mathrm{HFS}}$ are determined for highly excited Rydberg states.

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1. INTRODUCTION

This work investigates the fundamentals of the electromagnetic interactions. Already since the formulation of the mathematical foundations of classical electrodynamics by Maxwell, its theoretical investigation lead to a lot of discoveries in many different fields of physics. For example, the appearance of a velocity independent of the reference system namely the speed of light, required a new theory of relativity, Einstein's theory of special and later general relativity.

An especially interesting subsection of electrodynamics is studied: bound-states. This means that two oppositely charged objects form a stable system. The usual lay man's example would be the planets circling the sun in the case of the gravitational interaction. Interestingly, in electrodynamics on the first glance oppositely charged objects cannot form bound-state like that because a charge moving on a circle emits radiation. In turn, it therefore loses energy and would ultimately crash into the other object. Electromagnetic bound-states are only possible for quantum objects at small distances where their wave-like behavior allows standing-wave like states which are stable.

The focus is set on the most well-known electromagnetic bound-system, the atom. More specifically atoms with only one electron are considered. As the aim is to understand the fundamental interaction of the electron and the core, interactions between electrons would only lead to unnecessary perturbations. Moreover, in one-electron atoms not only numerical but also analytical methods can be employed, whereas it is mathematically impossible to solve three-body problems analytically. This can increase our understanding because analytical steps can offer a more detailed view on the systematics of the interaction.

Early in the development of quantum mechanics a solution for the bound-states of a one-electron atom was found by Schrödinger [1]. This solution was based upon a non relativistic approach as relativistic effects are small in hydrogen. It not only explained why the bound-states are stable but also allowed to predict the energy difference which is emitted as light if an electron changes from one state to another. This specific spectral emission of atoms still is one of the most important tools to

experimentally investigate atomic physics. While relativistic effects were included shortly afterwards by Dirac [2], precise spectroscopical measurements by Lamb and Retherford [3] observed slight differences from the theoretical prediction.

So what was missing? So far the same Coulomb potential as in classical electrodynamics was used. In it light is describe as a wave and a wave alone. However, from Einstein's famous work on the photo-effect [4] and initial work by Planck on the Black body radiation [5], it is known that light is also quantized and also behaves like a particle. This is not yet included in the theory, even though some effects can be calculated with a fluctuating classical field. It seems, however, better to go all the way and use a fully quantized theory for the electromagnetic interaction. So fundamentally the photon nature of light also has to be included to gain a deeper understanding of the electromagnetic interaction.

One of these quantum effects of electrodynamics is the interaction of an electron with its own radiation field. This cannot be solved in classical electrodynamics. Even in the quantum theory the mass of the electron has to be chosen to already include this interaction because it is not possible to observe an electron without its radiation field. However, for a bound state this effect is in fact observable and contributes a major part to the Lamb shift [6], which is the shift of the lines from the Dirac values as observed by Lamb and Retherford [3].

As this elucidates, may of the properties of the quantum world were discovered in atoms and much of the modern quantum field theories was partially derived in order to better understand the energy levels of the electrons in it. Even now because of the very precise predictions and experimental measurements atoms are one of the prime study objects for fundamental physics and specifically for quantum electrodynamics (QED).

There is one big complication, however, for the theoretical study of bound states compared to free particles in high-energy reaction and that is the presence of the binding potential. For a free electron the effects of the quantized field are calculated by a perturbative expansion in the number of interactions between the electron and the quantized field. As only electromagnetic interactions are considered, the coupling

strength is given by the strength of the electromagnetic interaction

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137.036}\,, \tag{1}$$

the so-called fine-structure constant. The results are consequently obtained as a series expansion in α. Because the fine-structure constant is relatively small, this series is naturally ordered in so far as the higher-order corrections diminish in magnitude due to the higher order in α.

For a bound electron on the other hand, the expansion in interactions with the radiation field is still carried out but it is complicated by the fact that each order of interaction with the quantized field receives contributions from all orders of interactions with the binding potential. Since the nucleus can consist of a number of positive charges, the strength of the interaction with the binding potential is given by $Z\alpha$, where Z is the nuclear charge number. As the result, the natural order in the series expansion is lost.

Mohr in Refs. [7, 8] developed a method using the fully relativistic formalism of QED to obtain results in the first order of interaction with the radiation field but to all orders of interaction with the binding coulomb potential. It is based upon a separation of energy scales in the expression into two parts. In the first part, the low-energy part, the binding energy is the dominant scale while in the second part, the high-energy part, the energy of the radiation field dominates. The resulting expression in both parts can then be evaluated numerically. The exact procedure is explained in detail in Sec. 3.

Alternatively, the ordered structure of the resulting series can be restored using the formalism explained in Sec. 4. For this purpose the expression is also split into a low- and high-energy part, though this time with an infinitesimal overlapping parameter. In the low-energy part a nonrelativistic expansion of the fully relativistic expression is carried out using the Foldy-Wouthuysen transformation. In the high-energy part a perturbative expansion in the binding potential is employed. While it is fairly apparent that the expansion in the high-energy part is an expansion in the binding strength $Z\alpha$, interestingly, the expansion in the low-energy part is as well. The reason lies in the scaling of the velocity of a bound electron such that the

nonrelativistic expansion parameter $v/c \approx Z\alpha$. Consequently, the result is given as a double series in α for the interaction with the radiation field and in $Z\alpha$ for the binding potential.

For further illustration of the application of the overlapping parameter, in Sec. 5 the method is studied by considering a model example.

The question now arises which are the most interesting systems for a study of fundamental physics using the known methods. Following the idea that new effects are more likely to be discovered at high energies, it would appear that it is preferable to study strong binding fields. Due to the dependence of the binding field i.e. the electric field of the nucleus on the nuclear charge number Z which is depicted in Fig. 1.1, it would appear that ions with a large Z are favorable.

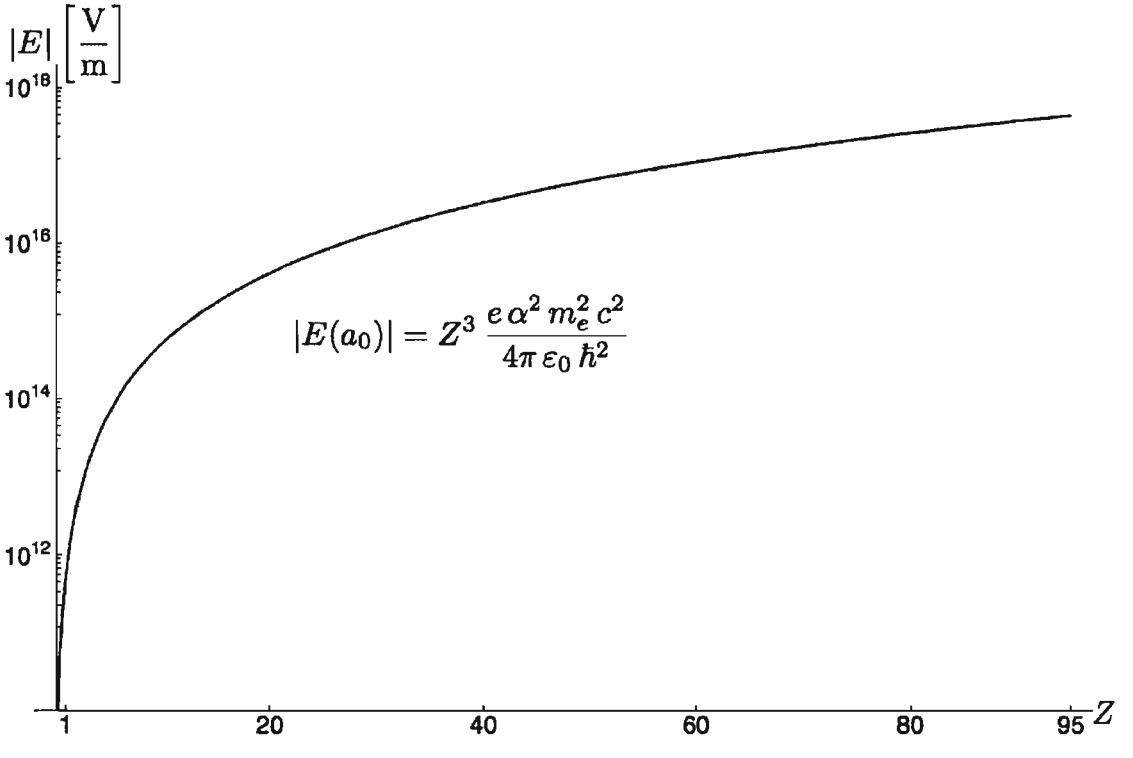

Figure 1.1. Magnitude of the electric field of the nucleus at the Bohr radius as a function of the nuclear charge number Z.

Nevertheless, such an investigation can only lead to a better understanding if experimental results can be obtained with a comparable accuracy thus allowing to check whether the theoretical prediction is actually realized in nature. The experimental precision achieved in measurements of transition frequencies is shown in Fig. 1.2.

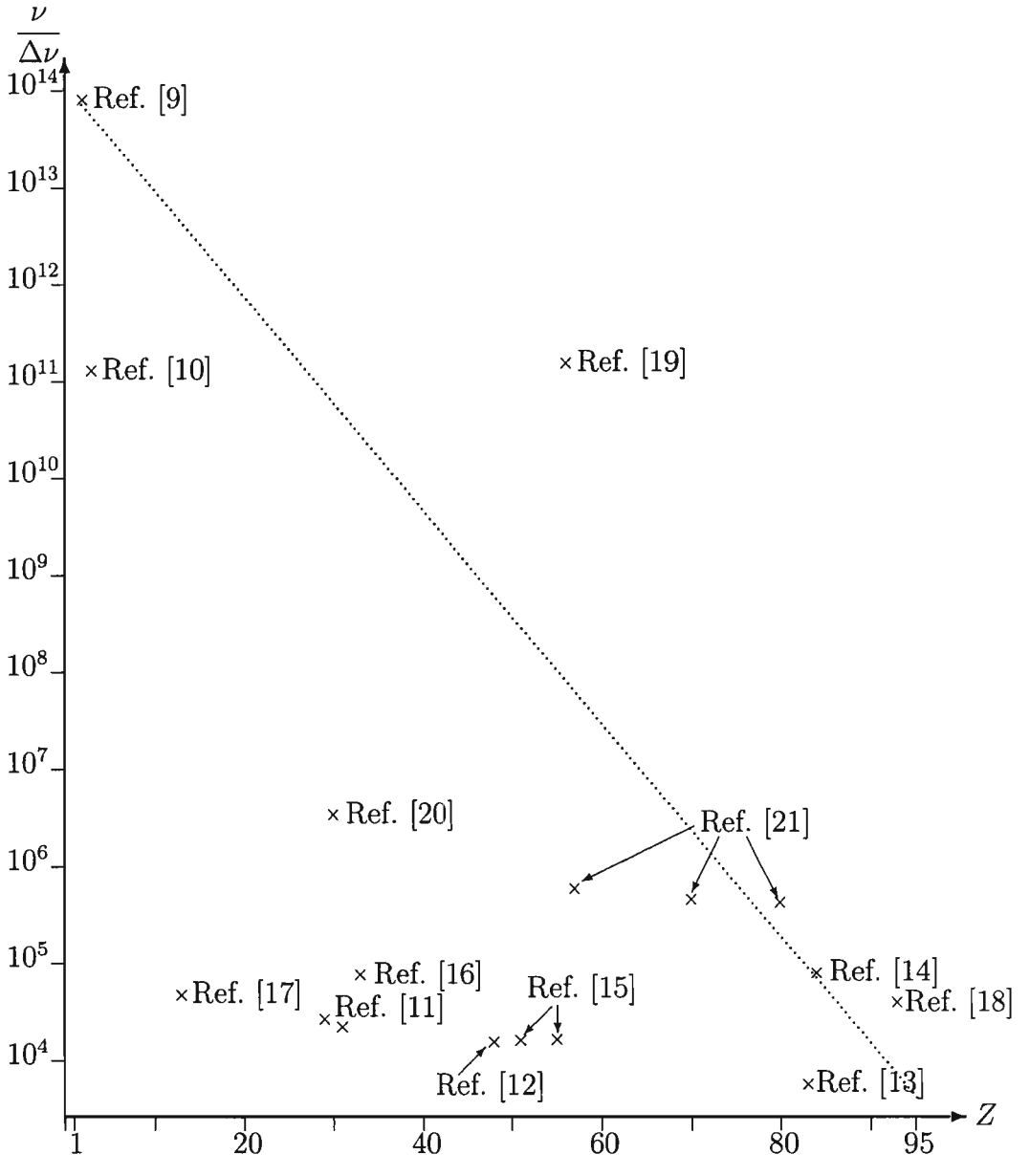

Figure 1.2. Relative accuracy $\nu/\Delta\nu$ of the experimental measurements of the transition frequency for a selected number of nuclear charge number Z with the corresponding references.

Unfortunately, this provides that the experimental accuracy reached for heavy atoms is significantly less than for ions with a low nuclear charge. The especially astonishing ultra-high precision results in Fig. 1.2 from Refs. [9, 10, 19] have been obtained using optical frequency combs which require transitions in the optical and near optical range. Hence, systems should be studied where there are transitions suited for an interrogation with optical frequency combs.

The experimental accuracy is, in fact, not the only argument for light atoms as being favorable for the study of the basis of QED. There is a problem with heavy nuclei and that is the nuclear size. At the high level of precision in the theoretical description, it can no longer be assumed that the nucleus is point-like. While the shift of the transition frequencies this introduces has been calculated, the large uncertainties of the experimentally determined radii make it the by far largest theoretical uncertainty. The ratio of the energy shift due to the QED self-energy correction to the energy shift because of the nuclear size is shown in Fig. 1.3. The figure makes it clear that the QED effects, which are studied here, are much larger compared to the spurious nuclear size correction for low Z.

Even though the nuclear size correction in hydrogen is small, it is still the major reason why the theoretical predictions in it are on the same level as the experimental accuracy. The problem can be avoided by considering so-called highly excited Rydberg states. In these states the electron is highly excited and thus so far away from the nucleus that the nuclear size correction becomes negligibly small. With the right choice for a combination of small to medium nuclear charge number and principal quantum number, transitions between such Rydberg states can be in the optical and near-optical regime and consequently accessible to measurements using optical frequency combs. Hence, Rydberg states are the ideal study object for the fundamental electromagnetic interaction because they constitute a nearly pure QED system as well as allow for very accurate experimental measurements.

Such experimental measurements of transition frequencies often employ two-photon transitions like for example the $1S$–$2S$ transition in Ref. [9]. The accuracy thereby is limited by the decay width of the line. For this reason, as a first application of the method of the nonrelativistic expansion of the fully relativistic theory

described in Sec. 4, relativistic corrections to the two-photon decay width for lower-lying states are calculated in Sec. 6. The calculation also turns out to be conceptually interesting because it illustrates how the nonrelativistic theory allows to identify the physical origin of corrections. Moreover, the invariance of the corrections under gauge transformations of the quantized field is shown explicitly.

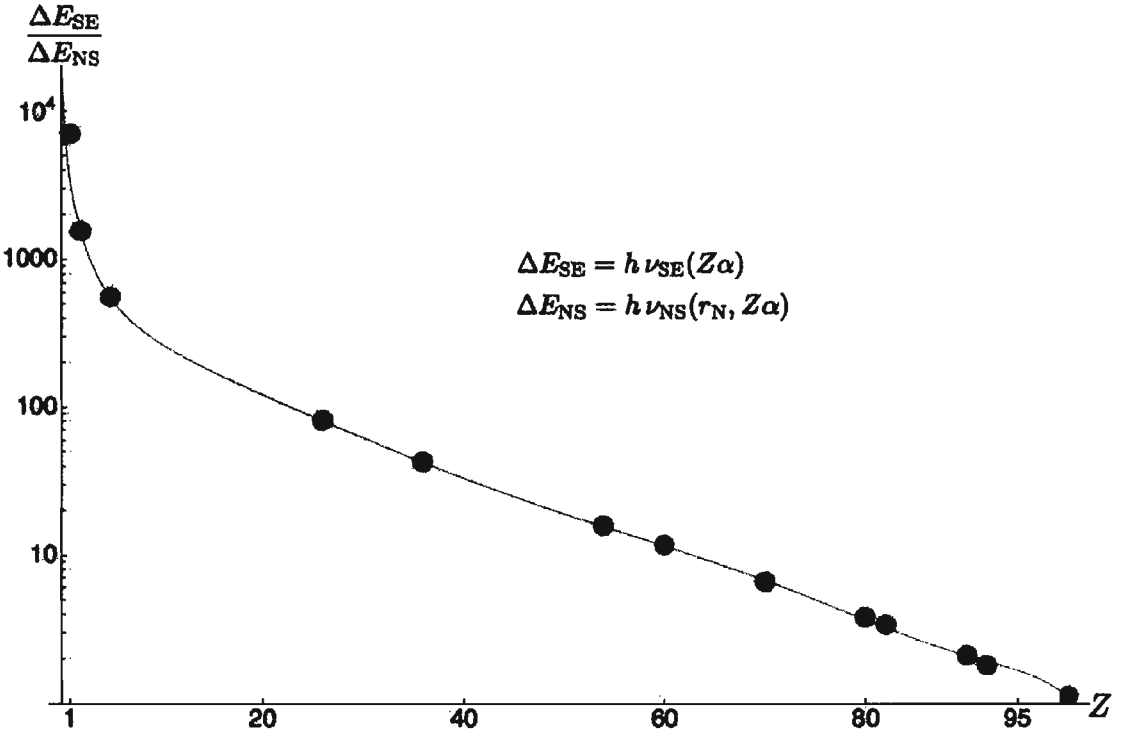

Figure 1.3. Ratio of the energy shift because of the QED self-energy correction to the energy shift due to the nuclear size correction shown in dependence of the nuclear charge number Z. r_N is the radius of the nucleus.

In order to reduce theoretical uncertainties in the QED predictions for Rydberg states, in Sec. 7 QED self-energy correction of order $\alpha(Z\alpha)^6$ are determined for a number of highly excited Rydberg states within the framework of the nonrelativistic theory from Sec. 4. This does not only allow to test the theory up to very high accuracy but also to use a comparison of theory and experiment under the assumption that the theory is correct to obtain very accurate values for fundamental constants.

These are constants which cannot be determined by theory but rather have to be experimentally measured. The most accurately known of the fundamental constants is the Rydberg constant [22]. It is specifically interesting because it appears in every spectroscopic prediction. A comparison of theory and experiment in Rydberg states might allow to deduce a more accurate value for the Rydberg constant. All necessary as well as some experimental considerations are also discussed in this section.

For nuclei with non zero nuclear spin, the hyperfine interaction between the nuclear spin and the total angular momentum of the electron leads to a further shift of energy levels. Because this could introduce additional uncertainties into the determination of the Rydberg constant, QED self-energy corrections to the hyperfine splitting up to order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$ are determined for highly excited Rydberg states in Sec. 8.

This work is organized as follows. The theoretical methods are presented and explained in Secs. 3, 4, and 5. Calculations which have been carried out using the nonrelativistic expansion of the fully relativistic theory are then presented in the Secs. 6, 7, and 8. In Sec. 6 relativistic corrections to the two-photon decay rate are determined and the gauge invariance of the theory is shown explicitly. QED self-energy corrections to the Lamb shift of Rydberg states are calculated in Sec. 7 where also possible applications of these results for a determination of the Rydberg constant and nuclear masses are presented. For these highly excited states QED self-energy corrections to the hyperfine splitting are then calculated in Sec. 8. Finally, conclusions are drawn in Sec. 9.

2. UNITS AND CONVENTIONS

In this section an overview over all conventions and units is given which will be used in this work, in order to prevent any confusion.

- In the analytic part of the calculation the Heaviside-Lorentz unit system is used. In it the speed of light c, the Planck quantum $\hbar$ and the electric constant ϵ_0 are set equal to one ($\epsilon_0 = \hbar = c = 1$). With this the one remaining physical dimension is chosen to be the length which is labeled as λ_e.

- For the numerical part of the calculation atomic units are used.

- The common index notation is employed in which Greek indices go through the values of $0 \ldots 3$, while Arabic indices go from $1 \ldots 3$.

- Contravariant indices are placed as superscripts. Therefore $k^0 = \omega$ denotes the 0th component of the four-vector k.

- The metric tensor in this work is

$$g_{\mu\nu} = \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix},$$

  where the blank spaces are zero.

- x is used for the four-vector $(t, \vec{x})$. In spherical coordinates $\hat{x}$ stands for the two angular coordinates θ, φ and r for the radial coordinate.

- Whenever Greek or Arabic indices are repeated, the Einstein summation convention is employed.

- Tr denotes taking the trace of a matrix.

The Heaviside-Lorentz Unit System. Here, a short look is taken at the transition from the SI to the Heaviside-Lorentz unit system, which starts from Coulomb's law

$$F = k_0 \frac{q_1 q_2}{r^2} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2} .$$

As mentioned above the units are chosen in such a way that $\epsilon_0 = 1$. Also the units of length and time are set so that $c = 1$. Finally, the unit of energy is set in order to have $\hbar = 1$ in these units. Consequently, Coulomb's law takes the form

$$e^2 = \frac{e^2}{\epsilon_0 \hbar c} = 4\pi \frac{k_0 e^2}{\hbar c} = 4\pi\alpha, \text{ because } \epsilon_0 = \hbar = c = 1 .$$

The advantage of these units is that the electric charge is now a dimensionless quantity. For later reference the Coulomb potential of an electron attracted by a number Z of positive charges in the origin is rewritten in the form

$$V(\vec{r}) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} = -\frac{1}{4\pi\epsilon_0} \frac{4\pi Z\alpha}{r} = -\frac{Z\alpha}{r} .$$

Accordingly, the inhomogeneous Maxwell equation in covariant formulation in the Heaviside-Lorentz unit system takes the simple form

$$\partial_\mu F^{\mu\nu} = j^\nu .$$

Atomic Units. As the name suggest, atomic units are used almost exclusively in atomic physics. In it the scale of units are chosen in such a way that they are oriented on the hydrogen atom. Starting from the Gaussian unit system, the charge of the electron e, the mass of the electron m_e and the Planck quantum $\hbar$ are chosen as the units. From these units the other units can be derived, which are

- The unit of length is obtained to be the Bohr radius a_0.
- As unit of energy one has the atomic binding energy $(Z\alpha)^2 m_e$.

3. THEORY: FULLY RELATIVISTIC QED

3.1. RELATIVISTIC DESCRIPTION OF THE ELECTRON

The fully relativistic equation which describes the behavior of the electron wave function $\psi(x)$ in a Coulomb potential has been found by Dirac in Ref. [2]. In contrast to the well known Schrödinger equation it is based on the relativistic energy-momentum relation. Moreover, it also contains an inherent description of the spin. The solution can be obtained in basically the same way as shown in textbooks for the nonrelativistic Schrödinger equation, by first separating off the time-dependent part because the equation is time-independent to give

$$|\psi, t\rangle = e^{-\mathrm{i}E_D t} |\psi, 0\rangle \ . \tag{2}$$

The remaining part of the wave function can then be found by solving the equation

$$H_D |\psi\rangle = \left(-\mathrm{i}\vec{\alpha} \cdot \vec{\nabla} - \frac{Z\alpha}{r} + \beta m_e\right) |\psi\rangle = E_D |\psi\rangle \ , \tag{3}$$

where the matrices $\vec{\alpha}$ and β are given in the representation here as

$$\vec{\alpha} = \gamma^0 \vec{\gamma} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \ , \tag{4}$$

$$\beta = \gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ . \tag{5}$$

A further separation into a radial and an angular part allows to obtain for the wave function in position space

$$\psi(\vec{x}) = \begin{pmatrix} \sqrt{\frac{\ell-m+\frac{1}{2}}{2\ell+1}} Y_{\ell,m-\frac{1}{2}}(\hat{x}) g(r) \\ \sqrt{\frac{\ell+m+\frac{1}{2}}{2\ell+1}} Y_{\ell,m+\frac{1}{2}}(\hat{x}) g(r) \\ -\sqrt{\frac{\ell+m-\frac{1}{2}}{2\ell-1}} Y_{\ell-1,m-\frac{1}{2}}(\hat{x}) \mathrm{i} f(r) \\ \sqrt{\frac{\ell-m-\frac{1}{2}}{2\ell-1}} Y_{\ell-1,m+\frac{1}{2}}(\hat{x}) \mathrm{i} f(r) \end{pmatrix} \tag{6}$$

with the radial functions

$$\begin{aligned} g(r) = & -\frac{\sqrt{\Gamma(2\gamma+(n-|\kappa|)+1)}}{\Gamma(2\gamma+1)\sqrt{(n-|\kappa|)!}} \sqrt{\frac{1+\epsilon}{4N(N-\kappa)}} \left(\frac{2Z}{Na_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{Na_0}} \left(\frac{2Zr}{Na_0}\right)^{\gamma-1} \\ & \times \left[-(n-|\kappa|) F\left(-(n-|\kappa|)+1, 2\gamma+1, \frac{2Zr}{Na_0}\right) \right. \\ & \left. + (N-\kappa) F\left(-(n-|\kappa|), 2\gamma+1, \frac{2Zr}{Na_0}\right) \right], \end{aligned} \tag{7}$$

and

$$\begin{aligned} f(r) = & -\frac{\sqrt{\Gamma(2\gamma+(n-|\kappa|)+1)}}{\Gamma(2\gamma+1)\sqrt{(n-|\kappa|)!}} \sqrt{\frac{1-\epsilon}{4N(N-\kappa)}} \left(\frac{2Z}{Na_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{Na_0}} \left(\frac{2Zr}{Na_0}\right)^{\gamma-1} \\ & \times \left[(n-|\kappa|) F\left(-(n-|\kappa|)+1, 2\gamma+1, \frac{2Zr}{Na_0}\right) \right. \\ & \left. + (N-\kappa) F\left(-(n-|\kappa|), 2\gamma+1, \frac{2Zr}{Na_0}\right) \right], \end{aligned} \tag{8}$$

where $a_0 = 1/m_e\alpha$ is the Bohr radius and $Y_{\ell,m}(\hat{x})$ the spherical harmonics as defined in Ref. [23]. These equations are given in terms of the Dirac quantum number κ with

$$\kappa = (-1)^{j-\ell+1/2}(j+\tfrac{1}{2}), \tag{9}$$

the sometimes called "apparent principal quantum number" N

$$N = \sqrt{n^2 - 2(n-|\kappa|)(|\kappa|-\gamma)}, \tag{10}$$

the parameter ϵ, which is the eigenenergy divided by the rest mass of the electron,

$$\epsilon = \left[1 + \frac{(Z\alpha)^2}{(n - |\kappa| + \gamma)^2}\right]^{-\frac{1}{2}}, \tag{11}$$

and γ

$$\gamma = \sqrt{\kappa^2 - (Z\alpha)^2}\,. \tag{12}$$

A detailed derivation can be found in Ref. [24]. The resulting energies of the states are then

$$E = m_e\epsilon = m_e\left[1 + \frac{(Z\alpha)^2}{(n - |\kappa| + \gamma)^2}\right]^{-\frac{1}{2}}. \tag{13}$$

In contrast to the experimental measurements of Lamb and Retherford [3], the solution of the Dirac equation predicts that states with the same absolute value of κ, which means equal total angular momentum $\vec{j} = \vec{\ell} + \vec{s}$, have the same energy. This Lamb shift can only be explained by including the quantization of the electromagnetic field [6] into our considerations of the electron. This quantized theory of electromagnetism is called quantum electrodynamics (QED). In the next section, the quantization of the electromagnetic field is discussed. Afterwards, it will be shown how to combine QED with the Dirac theory of the electron and show how the quantized field alters the energy levels of Dirac theory.

3.2. QUANTIZED FIELD

So far, the electron has been treated in all its detail but kept the electromagnetic field like in the classical Maxwell theory. The next step is to quantize the electromagnetic field in order to include the particle nature of the photon as well as its wave nature which is contained in classical electrodynamics. Because the quantum theory has to agree Maxwell's theory in the classical limit (high energies, many photons), Maxwell's equations in covariant formulation are recalled, which in this unit system

are given as

$$\partial_\mu F^{\mu\nu} = j^\nu \,, \tag{14}$$

$$\epsilon_{\mu\nu\rho\sigma}\partial^\rho F^{\mu\nu} = 0 \,, \tag{15}$$

where $F^{\mu\nu}$ is defined by

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu \,. \tag{16}$$

The four-vector potential A^μ is combined of the scalar potential ψ and the vector potential $\vec{A}$

$$A^\mu = \left(\phi, \vec{A}\right) \,. \tag{17}$$

Similarly, the four-vector current is

$$j^\mu = \left(\rho, \vec{j}\right) \,. \tag{18}$$

Using the Hamiltonian principle and the Euler-Lagrange equation similar to classical mechanics the inhomogeneous Maxwell equation (14) can be obtained from the Lagrange density

$$\mathcal{L}_{\text{em}} = -\frac{1}{4} F^{\mu\nu} F_{\mu\nu} - j^\mu A_\mu \,. \tag{19}$$

The homogeneous Maxwell equation (15) is automatically fulfilled by the use of the four-vector potential. Following the Noether theorem invariance of the action

$$S = \int d^4x \, \mathcal{L}_{\text{em}} \tag{20}$$

under a transformation leads to a conserved quantity. In this way for example the conservation of the electromagnetic current or the continuity equation

$$\partial_\mu j^\mu = 0 \tag{21}$$

can be shown. As one might recall from electrodynamics the four-vector potentials can be gauge transformed according to

$$A_\mu \rightarrow A'_\mu = A_\mu + \partial_\mu \Lambda \tag{22}$$

while the electric and magnetic field are invariant under this gauge transformation [25]. Now, this gauge transformation is applied to the Lagrange density in Eq. (19), which gives

$$\mathcal{L}' = -\left[\frac{1}{4}F^{\mu\nu}F_{\mu\nu} + j^\mu A_\mu + j^\mu \partial_\mu \Lambda\right] . \tag{23}$$

Because the current is conserved and, therefore, $\partial_\mu j^\mu = 0$, the term $\partial_\mu j^\mu \Lambda = 0$ can be added to the Lagrangian which yields

$$\mathcal{L}'_{\text{em}} = -\left[\frac{1}{4}F^{\mu\nu}F_{\mu\nu} + j^\mu A_\mu + \partial_\mu (j^\mu \Lambda)\right] . \tag{24}$$

The last term is a total derivative which does not change the action in Eq. (20). This means that the action is invariant under the gauge transformation. Although this gauge freedom can be very useful for the actual calculations, it complicates the quantization of the theory as a specific gauge has to be chosen prior to quantization. Here, Coulomb gauge is used

$$\vec{\nabla} \cdot \vec{A} = 0 \tag{25}$$

even though it is not Lorentz-invariant. However, this gauge will mainly be used in this work and moreover its quantization developed by Gupta and Bleuler is very instructive.

In quantum mechanics momentum and position are elevated to operators, which have to fulfill the commutation relation

$$[x_i, p_j] = \mathrm{i}\delta_{ij} . \tag{26}$$

For the quantization of the electromagnetic field, the procedure is similar and the vector potential is elevated into an operator. In order to get an similar commutation

relation the conjugate momentum is required. This conjugate momentum is denoted as π and is obtained in a similar way as in classical mechanics with a derivative of the Lagrangian with respect to the time-derivative of the field

$$\pi^{\mu} = \frac{\partial \mathcal{L}}{\partial(\partial^0 A_{\mu})} . \tag{27}$$

The Lagrangian, of which the derivative is taken, in Coulomb gauge takes the form

$$\mathcal{L} = \frac{1}{2}\partial^0 A_i \partial_0 A^j - \frac{1}{2}(\partial_j A_i)^2 + j_i A_i + \frac{1}{2}\partial_i A_j \partial_j A_i + \partial^0 A_i \partial_i A^0 + \frac{1}{2}(\partial_i A^0)^2 - j_0 A^0 . \tag{28}$$

So, the conjugate momenta are obtained as

$$\pi^0 = \frac{\partial \mathcal{L}}{\partial(\partial^0 A_0)} = 0 , \tag{29}$$

$$\pi^i = \frac{\partial \mathcal{L}}{\partial(\partial^0 A_i)} = -\partial_0 A^i - \partial_i A^0 = E^i . \tag{30}$$

Here, the advantage of our choice of gauge also can be elucidated. The potential has no dynamics of its own and is given entirely by the charge distribution. This allows to continue to work with the classical Coulomb potential of the electron proton interaction and only quantize the vector potential.

With the conjugate momenta a Legendre transformation can be used to receive the Hamilton density for the free field with $j_i = 0$

$$\mathcal{H}_{\text{free}} = \pi^k A_k - \mathcal{L} = \frac{1}{2}\left(\vec{E}^2 + \vec{B}^2\right) . \tag{31}$$

It has the form of a harmonic oscillator but as it is a density, it is in fact a continuous chain of massless harmonic oscillators. Accordingly, the quantization is nearly the same as for the normal harmonic oscillator. Therefore, it will not be reiterated here. A detailed derivation can for example be found in Ref. [26]. Just discuss the commutation relations are investigated which are

$$\left[\hat{A}^i(t,\vec{x}), \hat{A}^j(t,\vec{x}')\right] = 0 , \tag{32}$$

$$\left[\hat{\pi}^i(t,\vec{x}), \hat{\pi}^j(t,\vec{x}')\right] = 0 , \tag{33}$$

where the hat is used to make clear that one is dealing with operators now. It is important to note here that these relations are always for equal times. Normally, the commutation relation between A and π are expected to look like

$$\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right] = \mathrm{i}\delta^{ij}\delta(\vec{x}-\vec{x}')\,. \tag{34}$$

Unfortunately, this is not correct because of the gauge condition, which can be seen by taking the divergence of the commutator

$$\partial_i\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right] = \left[\partial_i\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right] = \left[0,\hat{\pi}^j(t,\vec{x}')\right] = 0\,, \tag{35}$$

while

$$\partial_i\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right] = \mathrm{i}\partial_j\delta(\vec{x}-\vec{x}') \neq 0\,. \tag{36}$$

The right idea can be envisioned by looking at a certain choice to fulfill the gauge condition of the vector potential $\partial_i A_i = 0$ which can be imposed by a projection operator

$$A_i(t,\vec{x}) \rightarrow \left(\delta_{ij} - \frac{\partial_i\partial_j}{\partial^2}\right) A_j(t,\vec{x})\,. \tag{37}$$

Applying this projection operator on the δ distribution gives us

$$\left(\delta_{ij} - \frac{\partial_i\partial_j}{\partial^2}\right)\delta(\vec{x}-\vec{x}') = \int \frac{d^3k}{(2\pi)^3}\left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) e^{\mathrm{i}\vec{k}\cdot(\vec{x}-\vec{x}')} = \delta^{\perp,ij}(\vec{x}-\vec{x}')\,. \tag{38}$$

This transverse δ distribution now gives the right commutation relation

$$\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right] = \mathrm{i}\delta^{\perp,ij}(\vec{x}-\vec{x}')\,. \tag{39}$$

All this leads us to the quantized vector potential for a free field [27]

$$\vec{A}(t,\vec{x}) = \int \frac{d^3k}{(2\pi)^3}\frac{1}{\sqrt{2\omega_{\vec{k}}}}\sum_{\lambda=1}^{2}\left(a^\lambda(\vec{k})\vec{\epsilon}^{\,\lambda}(\vec{k})e^{-\mathrm{i}k\cdot x} + a^{\lambda\dagger}(\vec{k})\vec{\epsilon}^{\,\lambda}(\vec{k})e^{\mathrm{i}k\cdot x}\right) \tag{40}$$

where the polarization vectors $\vec{\epsilon}^{\,\lambda}(\vec{k})$ fulfill the relations

$$\vec{\epsilon}^{\,\lambda}(\vec{k}) \cdot \vec{\epsilon}^{\,\lambda'}(\vec{k}) = \delta^{\lambda\lambda'} , \tag{41}$$

$$\vec{k} \cdot \vec{\epsilon}^{\,\lambda}(\vec{k}) = 0 \tag{42}$$

$$\sum_{\lambda=1}^{2} \epsilon_i^{\lambda}(\vec{k})\epsilon_j^{\lambda}(\vec{k}) = \delta_{ij} - \frac{k_i k_j}{\vec{k}^{\,2}} . \tag{43}$$

which accounts for the fact that there are no longitudinal photons i.e. light is a transversal wave. Plugging in the obtained quantized $\vec{A}(x)$ into the Hamiltonian in Eq. (31) leads to a Hamiltonian of the same form as for the harmonic oscillator

$$H_{\text{free}} = \frac{1}{2}\sum_{\lambda=1}^{2} \int d^3k\, \omega_{\vec{k}} \left(a^{\lambda,\dagger}(\vec{k}) a^{\lambda}(\vec{k}) + \frac{1}{2}\delta^3(0) \right) . \tag{44}$$

The δ distribution is usually neglected even though it represents an infinite energy shift. Still, it is not observable because the energy of a photon cannot be measured without it.

For completeness, all the four-vector potentials for other gauges are given which appear in this work. The corresponding derivations can be found in the literature [28]. A general expression for the four-vector potential is

$$A_\mu(x) = \int \frac{d^3k}{(2\pi)^3} \frac{1}{\sqrt{2\omega_{\vec{k}}}} \sum_{r=0}^{3} \left(a^r(\vec{k})\epsilon_\mu^r(k) e^{-\mathrm{i}k\cdot x} + a^{r\dagger}(\vec{k})\epsilon_\mu^{r*}(k) e^{\mathrm{i}k\cdot x} \right) , \tag{45}$$

where

$$\sum_{r=0}^{3} \epsilon_\mu^r(k)\epsilon_\nu^{r*}(k) = \left(g^{\mu\nu} - (1-\xi)\frac{k^\mu k^\nu}{k^2} \right) . \tag{46}$$

The two cases which are important in this work are Feynman gauge ($\xi = 1$) which is commonly used in QED for free unbound particles and Yennie gauge [29] with $\xi = 3$ as the length gauge which can allow some simplifications. This will be encountered in the treatment of the two-photon decay which will be studied in Sec. 6.

Unfortunately, it is not possible to just use this quantized vector potential in the Dirac equation and obtain another analytical solution. Similar to quantum electrodynamics for free electrons a perturbative approach to include the interactions with the quantize field is required. In the next section the formal derivation for a perturbative treatment of bound-state QED will be shown and explained.

3.3. FULLY RELATIVISTIC QED AND ENERGY SHIFTS

After the quantization of the electromagnetic field, it is time to show how its effects can be included into the Dirac equation for the electron. The simple ansatz would be to add the electromagnetic interaction term $j^\mu A_\mu$, which couples the electron's current to the quantized radiation field, to the Dirac Hamiltonian from Eq. (3). This yields

$$H = -\mathrm{i}\vec{\alpha}\cdot\vec{\nabla} - \frac{Z\alpha}{r} + \beta m_e + \int d^3x j^\mu(x) A_\mu(x)\,. \tag{47}$$

It would be nice if this equation could be solved like the Dirac equation without the interaction. However, this is not possible because the current $j^\mu(x)$ depends on the electron's wave function. It is assumed that this interaction term constitutes only a small perturbation, since it only slightly shifts the energy levels. So, perturbation theory is used and it is treated as a perturbation to the bound eigenstates of the Dirac equation. The unperturbed Hamiltonian is then

$$H_0\,|\psi\rangle = (-\mathrm{i}\vec{\alpha}\cdot\vec{\nabla} - \frac{Z\alpha}{r} + \beta m_e)\,|\psi\rangle = E_0\,|\psi\rangle\ . \tag{48}$$

and its eigenfunctions are the unperturbed states. The aim is to solve the full Hamiltonian

$$H\,|\Psi\rangle = E\,|\Psi\rangle\ , \tag{49}$$

so the interaction Hamiltonian is added to the unperturbed problem which is done by adiabatic damping

$$H_\varepsilon(t) = H_0 + g e^{-\varepsilon|t|} H_1(t)\,. \tag{50}$$

The interaction is slowly turned on in the infinite past and damps out again in the infinite future. That means that at infinite times the eigenfunctions of the unperturbed Dirac Hamiltonian are also eigenfunctions of the full problem and one has

$$H_\varepsilon(t=0) = H = H_0 + gH_1\,, \quad \lim_{t\to\pm\infty} H_\varepsilon(t) = H_0\,. \tag{51}$$

As can be seen here, the perturbation is time-dependent and makes a time-dependent treatment necessary. The tool used is time-ordered perturbation theory based on the formalism outlined by Dyson (see for example Ref. [30]). The interaction between the electron's current and the QED radiative field is then included perturbatively by the interaction Hamiltonian

$$\mathcal{H}_1(x) = j^\mu(x)A_\mu(x)\,. \tag{52}$$

The dependence on the spatial variables can be integrated out to give

$$H_1(t) = \int d^3x\, \mathcal{H}_1(x)\,. \tag{53}$$

The interaction picture [31] is employed for the calculations which when using the bound-state Dirac Hamiltonian as H_0 is commonly called the Furry picture [32], accordingly one has the equations

$$\mathrm{i}\frac{\partial}{\partial t}\,|\Psi_\varepsilon(t)\rangle = ge^{-\varepsilon|t|}H_1(t)\,|\Psi_\varepsilon(t)\rangle\,, \tag{54}$$

with

$$H_1(t) = e^{\mathrm{i}H_0t}H_1(t=0)e^{-\mathrm{i}H_0t}\,. \tag{55}$$

With this Hamiltonian, the equation for the time evolution operator can be written as

$$\mathrm{i}\frac{\partial}{\partial t}U_\varepsilon(t,t_0) = ge^{-\varepsilon|t|}H_1(t)U_\varepsilon(t,t_0)\,. \tag{56}$$

As evident, the exponential becomes equal to unity in the limit $\varepsilon \to 0$ and also the perturbed eigenfunctions are equal to the unperturbed solutions of the Coulomb-Dirac equation in the infinite past and future. This allows to write

$$|\Psi_\varepsilon\rangle = |\Psi_\varepsilon(t=0)\rangle = U_\varepsilon(0,\infty)\,|\psi\rangle\ . \tag{57}$$

However, it is not possible to just take the limit $\varepsilon \to 0$ in order to obtain the interacting bound states as this limit does not exist [33]. The way to obtain the right limit has been shown by Gell-Mann and Low in Ref. [34]. Following the derivation in Ref. [33], the equation

$$(H_0 - E_0)\,|\Psi_\varepsilon\rangle = (H_0 - E_0)U_\varepsilon(0,\infty)\,|\psi\rangle = [H_0, U_\varepsilon(0,\infty)]\,|\psi\rangle \tag{58}$$

is considered. Using the known Dyson series for the time evolution operator yields

$$\begin{aligned}[H_0, U_\varepsilon(0,\infty)] &= \left[H_0, \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} g^n \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n\, e^{\varepsilon t_1 + \ldots + t_n}\, T(H_1(t_1)\ldots H_1(t_n))\right] \\ &= \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} g^n \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_1 + \ldots + t_n}\, [H_0, T(H_1(t_1)\ldots H_1(t_n))]\ .\end{aligned} \tag{59}$$

The commutator can now be evaluated with the help of the Heisenberg equation

$$-\mathrm{i}\frac{\partial}{\partial t} H_1(t,t_0) = [H_0, H_1(t)]\,, \tag{60}$$

to give

$$\begin{aligned}&[H_0, T(H_1(t_1)\ldots H_1(t_n))] = [H_0, H_1(t_{i_1})\ldots H_1(t_{i_n})] \\ &= [H_0, H_1(t_{i_1})] H_1(t_{i_2})\ldots H_1(t_{i_n}) + \ldots + H_1(t_{i_1})\ldots H_1(t_{i_{n-1}})[H_0, H_1(t_{i_n})] \\ &= (-\mathrm{i})\frac{\partial H_1(t_{i_1})}{\partial t_{i_1}} H_1(t_{i_2})\ldots H_1(t_{i_n}) + \ldots + H_1(t_{i_1})\ldots H_1(t_{i_{n-1}})(-\mathrm{i})\frac{\partial H_1(t_{i_n})}{\partial t_{i_n}} \\ &= (-\mathrm{i})\sum_{i=0}^{n} \frac{\partial}{\partial t_i} H_1(t_{i_1})\ldots H_1(t_{i_n}) \\ &= (-\mathrm{i})\sum_{i=0}^{n} \frac{\partial}{\partial t_i} T(H_1(t_1)\ldots H_1(t_n))\,.\end{aligned} \tag{61}$$

This means for Eq. (58)

$$\begin{aligned}(H_0 - E_0)\,|\Psi_\varepsilon\rangle &= \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} g^n \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_1 + \ldots + t_n} \\ &\quad \times (-\mathrm{i}) \sum_{i=0}^{n} \frac{\partial}{\partial t_i} T(H_1(t_1) \ldots H_1(t_n))\,|\psi\rangle \\ &= -g \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^{n-1}}{(n-1)!} g^{n-1} \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_1 + \ldots + t_n} \\ &\quad \times \frac{\partial}{\partial t_1} T(H_1(t_1) \ldots H_1(t_n))\,|\psi\rangle\ ,\end{aligned} \tag{62}$$

because all derivatives are equivalent as the integrand is symmetric under permutation of the time arguments. The remaining time derivative can be integrated out using partial integration

$$\begin{aligned}&\int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{\partial}{\partial t_1} T(H_1(t_1) \ldots H_1(t_n)) = \\ &= e^{\varepsilon t_1} T(H_1(t_1) \ldots H_1(t_n))\Big|_{-\infty}^{0} - \int_{-\infty}^{0} dt_1 (\frac{\partial}{\partial t_1} e^{\varepsilon t_1}) T(H_1(t_1) \ldots H_1(t_n)) \\ &= H_1(0) T(H_1(t_2) \ldots H_1(t_n)) - \varepsilon \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} T(H_1(t_1) \ldots H_1(t_n))\,.\end{aligned} \tag{63}$$

Plugging this result into Eq. (62) yields

$$\begin{aligned}(H_0 - E_0)\,|\Psi_\varepsilon\rangle &= -gH_1(0) \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^{n-1}}{(n-1)!} g^{n-1} \int_{-\infty}^{0} dt_2 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_2 + \ldots + t_n} \\ &\quad \times T(H_1(t_2) \ldots H_1(t_n))\,|\psi\rangle + \varepsilon g \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^{n-1}}{(n-1)!} g^{n-1} \\ &\quad \times \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_1 + \ldots + t_n} T(H_1(t_1) \ldots H_1(t_n))\,|\psi\rangle \\ &= -gH_1(0) U_\varepsilon(0, -\infty)\,|\psi\rangle + \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} g^n \\ &\quad \times \int_{-\infty}^{0} dt_1 \ldots \int_{-\infty}^{0} dt_n e^{\varepsilon t_1 + \ldots + t_n} T(H_1(t_1) \ldots H_1(t_n))\,|\psi\rangle \\ &= -gH_1(0) U_\varepsilon(0, -\infty)\,|\psi\rangle + \mathrm{i}\varepsilon g \frac{\partial}{\partial g} U_\varepsilon(0, -\infty)\,|\psi\rangle \\ &= -gH_1(0)\,|\Psi_\varepsilon\rangle + \mathrm{i}\varepsilon g \frac{\partial}{\partial g}\,|\Psi_\varepsilon\rangle\ .\end{aligned} \tag{64}$$

With the full Hamiltonian this equation can be shortened to give

$$(H - E_0)\,|\Psi_\varepsilon\rangle = \mathrm{i}\varepsilon g \frac{\partial}{\partial g}\,|\Psi_\varepsilon\rangle\ . \tag{65}$$

As mentioned earlier, it is not possible to just take the limit of the wave function. This point can be elucidated here because in the limit $\varepsilon \to 0$ the full and the unperturbed state in Eq. (65) would have the same energy which in turn would imply that there is no energy shift. Since this is not the case, something is done wrong here. The correct solution can be obtained by dividing Eq. (65) by the overlap of the unperturbed and the perturbed state $\langle\psi|\Psi_\varepsilon\rangle$. With some manipulations

$$\begin{aligned}(H - E_0)\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} &= \mathrm{i}\varepsilon g \frac{\frac{\partial}{\partial g}|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} \\ &= \mathrm{i}\varepsilon g \left[\frac{\partial}{\partial g}\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} + \frac{\left(\frac{\partial}{\partial g}\langle\psi|\Psi_\varepsilon\rangle\right)|\Psi_\varepsilon\rangle}{(\langle\psi|\Psi_\varepsilon\rangle)^2}\right] \\ &= \mathrm{i}\varepsilon g \left[\frac{\partial}{\partial g}\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} + \frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle}\frac{\partial}{\partial g}\ln\langle\psi|\Psi_\varepsilon\rangle\right]\end{aligned} \tag{66}$$

is obtained, which can also be written as

$$\left(H - E_0 - \mathrm{i}\varepsilon g \frac{\partial}{\partial g}\ln\langle\psi|\Psi_\varepsilon\rangle\right)\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} = \mathrm{i}\varepsilon g \frac{\partial}{\partial g}\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle}\,. \tag{67}$$

As requirement for the application of the Gell-Mann Low theorem the limit

$$\lim_{\varepsilon\to 0}\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle}$$

has to be well defined in all orders of the perturbative expansion. If this is the case, then the situation is not altered by the derivative with respect to g. In turn, this means that because of the linear factor of ε the right hand side of Eq. (67) vanishes in the limit $\varepsilon \to 0$. So, one finds

$$\begin{aligned}\left(H - E_0 - \lim_{\varepsilon\to 0}\mathrm{i}\varepsilon g \frac{\partial}{\partial g}\ln\langle\psi|\Psi_\varepsilon\rangle\right)\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} &= 0 \\ (H - E)\frac{|\Psi_\varepsilon\rangle}{\langle\psi|\Psi_\varepsilon\rangle} &= 0\,.\end{aligned} \tag{68}$$

Thus, the constructed state is an eigenvector of H with eigenvalue E as intended. Consequently, this also gives the energy shift between the energy of the unperturbed state and the real eigenstate of the perturbed system, which can be read off Eq. (68) to be

$$\Delta E = E - E_0 = E_0 + \lim_{\varepsilon \to 0} \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \ln \langle \psi | \Psi_\varepsilon \rangle - E_0 = \lim_{\varepsilon \to 0} \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \ln \langle \psi | \Psi_\varepsilon \rangle \ . \tag{69}$$

This result can also be expressed in different ways using the time-evolution operator

$$\Delta E = \lim_{\varepsilon \to 0} \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \ln \langle \psi \, | U_\varepsilon(0, -\infty) | \, \psi \rangle = - \lim_{\varepsilon \to 0} \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \ln \langle \psi \, | U_\varepsilon(0, \infty) | \, \psi \rangle \tag{70}$$

$$= \frac{1}{2} \lim_{\varepsilon \to 0} \mathrm{i}\varepsilon g \frac{\partial}{\partial g} \ln \langle \psi \, | U_\varepsilon(\infty, -\infty) | \, \psi \rangle \ . \tag{71}$$

The time-evolution operator from $-\infty$ to ∞ is generally called the S matrix [35]

$$S_{\varepsilon,g} = U_{\varepsilon,g}(\infty, -\infty) \, . \tag{72}$$

Furthermore, all disconnected diagrams can also be dropped from the S matrix, this means diagrams which have no connection to the in and out states do not have to be considered. Thus, when also the logarithmic derivate is expanded, the energy shift can be written as

$$\Delta E_g = \lim_{\varepsilon \to 0} \frac{\mathrm{i}\varepsilon g}{2} \frac{\frac{\partial}{\partial g} \langle \psi \, | S_{\varepsilon,g} | \, \psi \rangle}{\langle \psi \, | S_{\varepsilon,g} | \, \psi \rangle} \, . \tag{73}$$

In this case, the energy shift still depends on the value introduced for the coupling parameter, as it is not good to change or vary the electric charge, the parameter g is used and the limit $g \to 1$ is taken at the end of the calculation.

In order to be able to evaluate the expression for the energy shift now, the perturbative expansion of the S matrix has to be used

$$S_{\varepsilon,g} = 1 + \sum_{k=1}^{\infty} S_{\varepsilon,g}^{(k)} \tag{74}$$

with

$$S_{\varepsilon,g}^{(k)} = \frac{(-\mathrm{i}g)^k}{k!} \int d^4x_1 \ldots \int d^4x_k e^{-\varepsilon|t_1|} \ldots e^{-\varepsilon|t_k|} T(H_1(x_1) \ldots H_1(x_k)) \,, \tag{75}$$

as it has been defined in Ref. [36]. With this now a perturbative expansion for the energy shift of the bound system is found [36]

$$\begin{aligned}
\frac{\frac{\partial}{\partial g} \langle\psi| S_{\varepsilon,g} |\psi\rangle}{\langle\psi| S_{\varepsilon,g} |\psi\rangle}\bigg|_{g=1} &= \frac{\left\langle\psi\middle| S_\varepsilon^{(1)} \middle|\psi\right\rangle + 2\left\langle\psi\middle| S_\varepsilon^{(2)} \middle|\psi\right\rangle + 3\left\langle\psi\middle| S_\varepsilon^{(3)} \middle|\psi\right\rangle + \ldots}{1 + \left\langle\psi\middle| S_\varepsilon^{(1)} \middle|\psi\right\rangle + \left\langle\psi\middle| S_\varepsilon^{(2)} \middle|\psi\right\rangle + \left\langle\psi\middle| S_\varepsilon^{(3)} \middle|\psi\right\rangle + \ldots} \\
&= \langle\psi| S_\varepsilon^{(1)} |\psi\rangle + 2\langle\psi| S_\varepsilon^{(2)} |\psi\rangle - \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^2 \\
&\quad + 3\langle\psi| S_\varepsilon^{(3)} |\psi\rangle - 3\langle\psi| S_\varepsilon^{(1)} |\psi\rangle \langle\psi| S_\varepsilon^{(2)} |\psi\rangle \\
&\quad + \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^3 + 4\langle\psi| S_\varepsilon^{(4)} |\psi\rangle \\
&\quad - 4\langle\psi| S_\varepsilon^{(1)} |\psi\rangle \langle\psi| S_\varepsilon^{(3)} |\psi\rangle - 2\langle\psi| S_\varepsilon^{(2)} |\psi\rangle^2 \\
&\quad + 4\langle\psi| S_\varepsilon^{(1)} |\psi\rangle^2 \langle\psi| S_\varepsilon^{(2)} |\psi\rangle - \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^4 + \ldots \,.
\end{aligned} \tag{76}$$

For the energy shift this leads to

$$\begin{aligned}
\Delta E_n = \lim_{\varepsilon\to 0} \frac{\mathrm{i}\varepsilon}{2} \Big[&\langle\psi| S_\varepsilon^{(1)} |\psi\rangle + 2\langle\psi| S_\varepsilon^{(2)} |\psi\rangle - \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^2 + 3\langle\psi| S_\varepsilon^{(3)} |\psi\rangle \\
&- 3\langle\psi| S_\varepsilon^{(1)} |\psi\rangle \langle\psi| S_\varepsilon^{(2)} |\psi\rangle + \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^3 + 4\langle\psi| S_\varepsilon^{(4)} |\psi\rangle \\
&- 4\langle\psi| S_\varepsilon^{(1)} |\psi\rangle \langle\psi| S_\varepsilon^{(3)} |\psi\rangle - 2\langle\psi| S_\varepsilon^{(2)} |\psi\rangle^2 \\
&+ 4\langle\psi| S_\varepsilon^{(1)} |\psi\rangle^2 \langle\psi| S_\varepsilon^{(2)} |\psi\rangle - \langle\psi| S_\varepsilon^{(1)} |\psi\rangle^4 + \ldots \Big] \,.
\end{aligned} \tag{77}$$

In this way, a perturbative expansion has been found which allows to compute the level shift in every order of perturbation theory.

3.4. APPLICATION OF THE GELL–MANN LOW THEOREM

After the general expression for the energy shift of a bound-state due to an interaction has been derived. It will be applied to the problem under study. The method outlined in Refs. [7, 8, 36, 37] is explained which will lead to fully relativistic equations for the energy shift for a bound electron due to its interaction with its own radiation field. This is called the self-energy. In addition, the methods employed there

to transform the resulting equations into a form suited for a numerical calculation are shown.

In the beginning the quantities from the last section have to be chosen according to the problem at hand. Following the derivation in Ref. [36] the electron mass can be extracted from the Dirac equation. This simplifies the calculation. Consequently, Eq. (3) takes the form

$$\left[-\mathrm{i}\vec{\alpha}\cdot\vec{\nabla}-\frac{Z\alpha}{r}+\beta-E_n\right]\psi_n(\vec{x})=0\,, \tag{78}$$

where the time dependence of the solutions is given by

$$\psi_n(x)=\psi_n(\vec{x})e^{-\mathrm{i}E_nt}\,. \tag{79}$$

The electron mass will be reintroduced in the end of the calculation. For the further calculation, however, the fully quantized electron-positron field operator is required to account for all the effects the radiation field has on the electron. It can be expressed in terms of electron and positron annihilation and creation operators and the eigenfunctions of the Dirac equation as

$$\Psi(x)=\sum_{E_n>0}a_n\psi_n(x)+\sum_{E_m<0}b_m^\dagger\psi_m(x)\,. \tag{80}$$

Here, a_n is the annihilation operator for an electron in state n with $E_n>0$. $b_m^\dagger$ is the creation operator for a positron in the state m with $E_m<0$. These operators fulfill the usual anti-commutation relations for fermion operators

$$\left\{a_n,a_m^\dagger\right\}=\delta_{n,m}\;;\quad\{a_n,a_m\}=0 \tag{81}$$

and analog relations for the positron operators. When these operators act on the vacuum, the unperturbed states can be obtained

$$|n\rangle=a_n^\dagger\,|0\rangle\;. \tag{82}$$

For such states the unperturbed energy operator is given by the normal ordered expression

$$H_0 = \int d^3x \, :\Psi^\dagger(x) H_D \Psi(x): = \sum_{E_n>0} E_n a_n^\dagger a_n - \sum_{E_m<0} E_m b_m^\dagger b_m \, . \tag{83}$$

Normal ordering means that all creation operators are to the left of all annihilation operators. In this way, the vacuum expectation value of a normal ordered expression is 0.

After defining the Hamiltonian and field operators, now also the interaction Hamiltonian, which introduces the level shift, needs to be defined. As discussed earlier, the electron-positron field in the external potential is now coupled to the radiative QED photon field which can be achieved by the interaction Hamiltonian

$$H_1(x) = j^\mu(x) A_\mu(x) - \delta M(x) \tag{84}$$

with the current operator

$$j^\mu(x) = -\tfrac{1}{2} e \left[\bar{\Psi}(x)\gamma^\mu, \Psi(x)\right] \, , \tag{85}$$

which couples to the quantized photon field operator $A_\mu(x)$. The commutator is defined to only commute the operators and not the Dirac matrices, such that

$$\left[\bar{\Psi}(x)\gamma^\mu, \Psi(x)\right] \equiv \sum_{E_m>0, E_n>0} \bar{\psi}_m(x)\gamma^\mu \psi_n(x) \left[a_m^\dagger, a_n\right] + \ldots \, . \tag{86}$$

The last term $\delta M(x)$ is the mass renormalization term. It has to be included here to account for the fact that the electron mass cannot be measured without the effects of the quantized field and it is given by

$$\delta M(x) = \tfrac{1}{2} \delta m \left[\bar{\Psi}(x)\gamma^\mu, \Psi(x)\right] \, . \tag{87}$$

The magnitude of the mass counter term coefficient δm basically has to be fixed by the condition that without the Coulomb field the electron should have its known rest

mass or

$$\lim_{Z\alpha\to 0} \Delta E_n(Z\alpha) \to 0\,. \tag{88}$$

One may ask why the commutator is used here instead of the usual product. The reason is that also time-ordering at equal times has to be included because the Coulomb field is instantaneous and does not contain retardation. The equal time products cause the vacuum polarization which otherwise cannot be obtained [36].

3.4.1. Energy Shift. The energy shift of a level n in first order in α (second in e) can be read off Eq. (77) and gives

$$\Delta E^{(2)} = \lim_{\varepsilon\to 0} \frac{\mathrm{i}\varepsilon}{2} \left[\left\langle n \left| S_\varepsilon^{(1)} \right| m \right\rangle + 2 \left\langle n \left| S_\varepsilon^{(2)} \right| m \right\rangle \right] , \tag{89}$$

where the superscript on S denotes the order in perturbation theory the terms are mixed here because there is a contribution (i.e. the mass renormalization) which appears in first order and is of order e^2. This phenomenon is encountered later on as well. The first term is given as

$$\begin{aligned} \left\langle n \left| S_\varepsilon^{(1)} \right| m \right\rangle &= \mathrm{i} \int d^4x e^{-\varepsilon|t|} \left\langle n \left| \delta M(x) \right| m \right\rangle \\ &= \mathrm{i}\delta m \sum_{n'm'} \int dt e^{\mathrm{i}t(E_{n'}-E_{m'})-\varepsilon|t|} \int d^3x \bar{\psi}_{n'}(\vec{x})\psi_{m'}(\vec{x}) \left\langle n \left| \tfrac{1}{2}[a_{n'}^\dagger, a_{m'}] \right| m \right\rangle \\ &= \mathrm{i}\delta m \sum_{n'm'} \frac{2\varepsilon}{(E_{n'}-E_{m'})^2+\varepsilon^2} \int d^3x \psi_{n'}^\dagger(\vec{x})\gamma^0\psi_{m'}(\vec{x}) \left\langle n \left| \tfrac{1}{2}[a_{n'}^\dagger, a_{m'}] \right| m \right\rangle . \end{aligned} \tag{90}$$

In the limit $\varepsilon \to 0$ the replacement [36]

$$\lim_{\varepsilon\to 0} \frac{\varepsilon}{x^2+\varepsilon^2} = \frac{1}{\varepsilon}\delta(x)\,. \tag{91}$$

can be used to simplify the expression to

$$\left\langle n \left| S_\varepsilon^{(1)} \right| m \right\rangle = \frac{2\mathrm{i}}{\varepsilon}\delta m \sum_{n'm'} \int d^3x \psi_{n'}^\dagger(\vec{x})\gamma^0\psi_{m'}(\vec{x})\delta(E_{n'}, E_{m'}) \left\langle n \left| a_{n'}^\dagger a_{m'} \right| m \right\rangle , \tag{92}$$

where

$$\delta(E_{n'}, E_{m'}) = \begin{cases} 1 & \text{if } E_{n'} = E_{m'} \\ 0 & \text{if } E_{n'} \neq E_{m'} \end{cases} . \tag{93}$$

Before the second term can be considered, a closer look has to be taken at the states on which the operators act. While the fermion field operator $\psi(x)$ acts on the initial and final state of the electron, the electromagnetic field operator $A_\mu(x)$ acts on the photon vacuum. This means that the state $|n\rangle$ is actually the Fock-state $|n, 0\rangle$. So, this yields

$$\begin{aligned} \langle n \left| S_\varepsilon^{(2)} \right| m \rangle &= \left(\frac{\mathrm{i}e}{2}\right)^2 \int d^4x_1 \int d^4x_2 e^{-\varepsilon|t_1|} e^{-\varepsilon|t_2|} \langle n, 0| T\Big(\left[\bar{\Psi}(x_2)\gamma^\nu, \Psi(x_2)\right] \\ &\quad \times A_\nu(x_2) \left[\bar{\Psi}(x_1)\gamma^\mu, \Psi(x_1)\right] A_\mu(x_1) \Big) |m, 0\rangle \\ &= -\frac{e^2}{4} \int d^4x_1 \int d^4x_2 e^{-\varepsilon|t_1|} e^{-\varepsilon|t_2|} D_F(x_2 - x_1) \\ &\quad \times \langle n| T\Big(\left[\bar{\Psi}(x_2)\gamma_\mu, \Psi(x_2)\right] \left[\bar{\Psi}(x_1)\gamma^\mu, \Psi(x_1)\right] \Big) |m\rangle \ , \end{aligned} \tag{94}$$

with the photon propagator D_F defined by

$$\langle 0 \left| T\left(A_\nu(x_2) A_\mu(x_1)\right) \right| 0 \rangle = g_{\nu\mu} D_F(x_2 - x_1) \, . \tag{95}$$

It is given as

$$D_F(x_2 - x_1) = \frac{\mathrm{i}}{(2\pi)^4} \int d^4q \frac{e^{-\mathrm{i}q\cdot(x_2 - x_1)}}{q^2 + \mathrm{i}\delta} \, . \tag{96}$$

In this way, the photon degrees of freedom have been separated away. The Wick theorem [26] is applied for the fermion field operators, which means all possible contractions have to be constructed. In the case of bound state problems one has to be extra careful as equal time contraction have to be considered which are usually neglected in free field theory. In the bound theory these equal time contractions lead to vacuum polarization. In Ref. [36] this is explained in more detail. Here, it is just

mentioned that if equal times are not considered, the following identity holds

$$T\big[AB\tfrac{1}{2}(CD-DC)EF\big] = T[ABCDEF]\ . \tag{97}$$

This allows to simplify the current for unequal times while the commutator in its definition has to be used for equal times. This way the following contractions are obtained

$$\begin{aligned}
\big\langle n\,\big|S_\varepsilon^{(2)}\big|\,m\big\rangle = -\frac{e^2}{2}\int d^4x_1\int d^4x_2 e^{-\varepsilon|t_1|}e^{-\varepsilon|t_2|}D_F(x_2-x_1)\\
\times\Big\{\langle n,k|\,\bar\Psi(x_2)\gamma_\mu\Psi(x_2)\bar\Psi(x_1)\gamma^\mu\Psi(x_1)\,|l,m\rangle\\
+\langle n|\,\bar\Psi(x_2)\gamma_\mu\Psi(x_2)\bar\Psi(x_1)\gamma^\mu\Psi(x_1)\,|m\rangle\\
+\langle n|\,\bar\Psi(x_2)\gamma_\mu\Psi(x_2)\bar\Psi(x_1)\gamma^\mu\Psi(x_1)\,|m\rangle\\
-\langle n|\,\bar\Psi(x_2)\bar\Psi(x_2)\gamma_\mu\bar\Psi(x_1)\gamma^\mu\Psi(x_1)\,|m\rangle\\
-\langle n|\,\bar\Psi(x_2)\gamma_\mu\Psi(x_2)\Psi(x_1)\bar\Psi(x_1)\gamma^\mu\,|m\rangle\Big\}\ .
\end{aligned} \tag{98}$$

To evaluate this expression it is necessary to know what the contraction of two fermion field operators is equal to. This can be derived in the following [26]

$$\begin{aligned}
S_F(x_2,x_1) &= \big\langle 0\,\big|T\left(\Psi(x_2)\bar\Psi(x_1)\right)\big|\,0\big\rangle\\
&= \big\langle 0\,\big|{:}\Psi(x_2)\bar\Psi(x_1){:}\big|\,0\big\rangle + \langle 0|\,\bar\Psi(x_2)\bar\Psi(x_1)\,|0\rangle\\
&= 0+\begin{cases} +\left\{\Psi^+(x_2),\bar\Psi^-(x_1)\right\} & \text{if } t_2>t_1\\ -\left\{\bar\Psi^+(x_1),\Psi^-(x_2)\right\} & \text{if } t_2<t_1\end{cases}
\end{aligned} \tag{99}$$

with

$$\Psi^+(x)=\sum_{E_n>0}a_n\psi_n(x)\,,\quad \Psi^-(x)=\sum_{E_m<0}b_m^\dagger\psi_m(x)\,, \tag{100}$$

$$\bar\Psi^+(x)=\sum_{E_m<0}b_m\bar\psi_m(x)\,,\quad \bar\Psi^-(x)=\sum_{E_n>0}a_n^\dagger\bar\psi_n(x)\,, \tag{101}$$

and $\{\,,\,\}$ is the anti-commutator. Thus, the anti-commutators yield

$$\left\{\Psi^{+}(x_2),\bar{\Psi}^{-}(x_1)\right\} = \sum_{E_n,E_k>0} \psi_n(x_2)\bar{\psi}_k(x_1)\{a_n,a_k^{\dagger}\} = \sum_{E_n>0}\psi_n(x_2)\bar{\psi}_n(x_1)\,, \tag{102}$$

$$-\left\{\bar{\Psi}^{+}(x_1),\Psi^{-}(x_2)\right\} = -\sum_{E_m,E_l<0} \bar{\psi}_m(x_1)\psi_l(x_2)\{b_m,b_l^{\dagger}\} = -\sum_{E_m<0}\psi_m(x_2)\bar{\psi}_m(x_1)\,. \tag{103}$$

In order to use the propagator without explicitly looking at the time, use can be made of the time-evolution of the states. So, the propagator can be written as

$$\begin{aligned} S_F(x_2,x_1) &= \sum_{E_n>0} \psi_n(x_2)\bar{\psi}_n(x_1)\theta(t_2-t_1) - \sum_{E_m<0} \psi_m(x_2)\bar{\psi}_m(x_1)\theta(t_1-t_2) \\ &= \sum_{E_n>0} \psi_n(\vec{x}_2)\gamma^0\psi_n^{\dagger}(\vec{x}_1)e^{-\mathrm{i}E_n(t_2-t_1)}\theta(t_2-t_1) \\ &\quad - \sum_{E_m<0} \psi_m(\vec{x}_2)\gamma^0\psi_m^{\dagger}(\vec{x}_1)e^{-\mathrm{i}E_m(t_2-t_1)}\theta(t_1-t_2) \end{aligned} \tag{104}$$

This can also be expressed in terms of an integral over a dummy variable z in the complex plane using the Cauchy theorem. The function

$$f(z) = \frac{e^{-\mathrm{i}z(t_2-t_1)}}{E_n - z(1-\mathrm{i}\delta)} \tag{105}$$

has a pole at the energy of the states. If this energy is negative the pole is shifted into the (positive imaginary) upper half of the complex plane, while for positive energy the pole is shifted to the lower half of the plane. In a contour integration for $t_2 > t_1$ or $t_2 - t_1 > 0$ the circle has to be closed in the lower half to pick up a negative imaginary part for z so the exponent is always negative (negative argument in front of the Δt) so that the integral of the circle part vanishes. Using the Cauchy theorem, therefore only the enclosed poles are picked up which are ones with positive energy. For the case of $t_2 < t_1$ or $t_2 - t_1 < 0$, the circle has to closed in the upper half of the complex plane, in order to get a decaying exponential (positive argument in front of the Δt). So for this case all the negative energy poles are picked up. With these arguments,

thus, the fermion propagator is written as

$$\begin{aligned} S_F(x_2,x_1) &= \frac{1}{2\pi \mathrm{i}} \int\limits_{-\infty}^{\infty} dz \sum_n \frac{\psi_n(\vec{x}_2)\gamma^0\psi_n^\dagger(\vec{x}_1)}{E_n - z(1-\mathrm{i}\delta)} e^{-\mathrm{i}z(t_2-t_1)} \\ &= \frac{1}{2\pi \mathrm{i}} \int\limits_{-\infty}^{\infty} dz \frac{\gamma^0}{H - z(1-\mathrm{i}\delta)} e^{-\mathrm{i}z(t_2-t_1)} . \end{aligned} \tag{106}$$

After the contraction of the inner products, the expressions of Eq. (98) can be evaluated further

$$\begin{aligned} \left\langle n \left| S_\varepsilon^{(2)} \right| m \right\rangle = -\frac{e^2}{2} \int d^4x_1 \int d^4x_2 e^{-\varepsilon|t_1|} e^{-\varepsilon|t_2|} D_F(x_2 - x_1) \\ \times \Bigg\{ \sum_{n'm'} \bar{\psi}_{n'}(x_2)\gamma_\mu \psi_{m'}(x_2) \\ \times \sum_{k'l'} \bar{\psi}_{k'}(x_1)\gamma^\mu \psi_{l'}(x_1) \left\langle n,k \left| a_{n'}^\dagger a_{k'}^\dagger a_{l'} a_{m'} \right| l,m \right\rangle \\ + 2 \sum_{n'm'} \bar{\psi}_{n'}(x_2)\gamma_\mu S_F(x_2,x_1)\gamma^\mu \psi_{m'}(x_1) \left\langle n \left| a_{n'}^\dagger a_{m'} \right| m \right\rangle \\ - 2\,\mathrm{Tr}[\gamma_\mu S_F(x_2,x_2)] \sum_{n'm'} \bar{\psi}_{n'}(x_1)\gamma^\mu \psi_{m'}(x_1) \left\langle n \left| a_{n'}^\dagger a_{m'} \right| m \right\rangle \Bigg\} . \end{aligned} \tag{107}$$

The trace has to be used when a propagator with two equal coordinates appears, since this is at least here a fermion loop [26]. The two times are transformed according to

$$a = t_2 - t_1 , \quad b = t_2 + t_1 \tag{108}$$

$$\rightarrow t_1 = \frac{b-a}{2} , \quad t_2 = \frac{a+b}{2} \tag{109}$$

which gives an additional factor of $-\frac{1}{2}$ from the Jacobian. With these variables Eq. (107) becomes

$$\begin{aligned}\left\langle n\left|S_\varepsilon^{(2)}\right|m\right\rangle = \frac{e^2}{4}\int d^3x_1\int d^3x_2\int da\int db\, e^{-\varepsilon|a|}e^{-\varepsilon|b|}D_F(x_2-x_1)\\ \times\sum_{n'm'}e^{\mathrm{i}\frac{a}{2}(E_{n'}+E_{m'})}\Bigg\{\bar\psi_{n'}(\vec x_2)\gamma_\mu\psi_{m'}(\vec x_2)\sum_{k'l'}\bar\psi_{k'}(\vec x_1)\gamma^\mu\psi_{l'}(\vec x_1)\\ \times\left\langle n,k\left|a^\dagger_{n'}a^\dagger_{k'}a_{l'}a_{m'}\right|l,m\right\rangle e^{\mathrm{i}\frac{b}{2}(E_{n'}+E_{k'}-E_{m'}-E_{l'})}e^{\mathrm{i}\frac{a}{2}(E_{k'}+E_{l'})}\\ +2\bar\psi_{n'}(\vec x_2)\gamma_\mu S_F(x_2,x_1)\gamma^\mu\psi_{m'}(\vec x_1)\left\langle n\left|a^\dagger_{n'}a_{m'}\right|m\right\rangle e^{\mathrm{i}\frac{b}{2}(E_{n'}-E_{m'})}\\ -2\,\mathrm{Tr}[\gamma_\mu S_F(x_2,x_2)]\,\bar\psi_{n'}(\vec x_1)\gamma^\mu\psi_{m'}(\vec x_1)\\ \times\left\langle n\left|a^\dagger_{n'}a_{m'}\right|m\right\rangle e^{\mathrm{i}\frac{b}{2}(E_n-E_m)}\Bigg\}.\end{aligned}\tag{110}$$

Only the integration with respect to the new variable b is carried out. In this case, it is not necessary to look into the time dependence of the propagators which depend on the time difference a alone and one finds

$$\begin{aligned}\left\langle n\left|S_\varepsilon^{(2)}\right|m\right\rangle = \frac{e^2}{4}\int d^3x_1\int d^3x_2\int da\, e^{-\varepsilon|a|}D_F(x_2-x_1)\\ \times\sum_{n'm'}e^{\mathrm{i}\frac{a}{2}(E_{n'}+E_{m'})}\Bigg\{\bar\psi_{n'}(\vec x_2)\gamma_\mu\psi_{m'}(\vec x_2)\sum_{k'l'}\bar\psi_{k'}(\vec x_1)\gamma^\mu\psi_{l'}(\vec x_1)\\ \times\left\langle n,k\left|a^\dagger_{n'}a^\dagger_{k'}a_{l'}a_{m'}\right|l,m\right\rangle e^{\mathrm{i}\frac{a}{2}(E_{k'}+E_{l'})}\\ \times\frac{8\varepsilon}{(E_{n'}+E_{k'}-E_{m'}-E_{l'})^2+4\varepsilon^2}\\ +\frac{8\varepsilon}{(E_{n'}-E_{m'})^2+4\varepsilon^2}\Bigg[2\bar\psi_{n'}(\vec x_2)\gamma_\mu S_F(x_2,x_1)\gamma^\mu\psi_{m'}(\vec x_1)\\ \times\left\langle n\left|a^\dagger_{n'}a_{m'}\right|m\right\rangle-2\,\mathrm{Tr}[\gamma_\mu S_F(x_2,x_2)]\,\bar\psi_{n'}(\vec x_1)\gamma^\mu\psi_{m'}(\vec x_1)\\ \times\left\langle n\left|a^\dagger_{n'}a_{m'}\right|m\right\rangle\Bigg]\Bigg\}.\end{aligned}\tag{111}$$

In the limit of $\varepsilon\to 0$ the integrals over the exponentials give

$$\lim_{\varepsilon\to0}\frac{8\varepsilon}{(E_{n'}+E_{k'}-E_{m'}-E_{l'})^2+4\varepsilon^2}=\frac{2}{\varepsilon}\delta(E_{n'}+E_{k'},E_{m'}+E_{l'})\tag{112}$$

$$\lim_{\varepsilon\to0}\frac{8\varepsilon}{(E_{n'}-E_{m'})^2+4\varepsilon^2}=\frac{2}{\varepsilon}\delta(E_{n'},E_{m'})\,.\tag{113}$$

Now, all the partial expressions have been obtained and Eq. (89) can be rewritten to give the energy shift

$$\begin{aligned}\Delta E_n^{(2)} = \frac{ie^2}{2}\int d^3x_1 \int d^3x_2 \int d(t_2-t_1) D_F(x_2-x_1) \\ \times \Bigg\{ \sum_{n'm'} \bar{\psi}_{n'}(x_2)\gamma_\mu \psi_{m'}(x_2) \sum_{k'l'} \bar{\psi}_{k'}(x_1)\gamma^\mu \psi_{l'}(x_1) \\ \times \left\langle n,k \left| a^\dagger_{n'} a^\dagger_{k'} a_{l'} a_{m'} \right| l,m \right\rangle \delta(E_{n'}+E_{k'}, E_{m'}+E_{l'}) \\ + \sum_{n'm'} \delta(E_{n'},E_{m'}) \Bigg[2\bar{\psi}_{n'}(x_2)\gamma_\mu S_F(x_2,x_1)\gamma^\mu \psi_{m'}(x_1) \left\langle n \left| a^\dagger_{n'} a_{m'} \right| m \right\rangle \\ - 2\,\mathrm{Tr}[\gamma_\mu S_F(x_2,x_2)]\, \bar{\psi}_{n'}(x_1)\gamma^\mu \psi_{m'}(x_1) \left\langle n \left| a^\dagger_{n'} a_{m'} \right| m \right\rangle \Bigg] \Bigg\} \\ - \delta m \sum_{n'm'} \int d^3x \bar{\psi}_{n'}(\vec{x})\psi_{m'}(\vec{x}) \delta(E_{n'},E_{m'}) \left\langle n \left| a^\dagger_{n'} a_{m'} \right| m \right\rangle .\end{aligned} \tag{114}$$

The first of the terms in Eq. (114) describes bound electron-electron scattering which vanishes here because only one-electron atoms are investigated here. This leaves the second term which describes the self-energy depicted in Fig. 3.1 and the third which describes vacuum polarization. The fourth term describes the mass renormalization which is included in the self-energy as it arises from the self-energy of a free electron. The focus is on the self-energy and vacuum polarization is discussed in short in a separate section later.

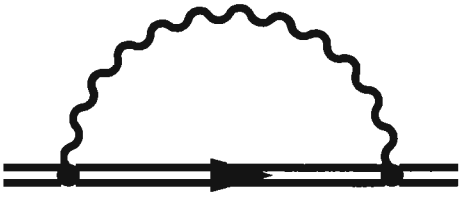

Figure 3.1. Feynman diagram of the self-energy of a bound electron. The double line represents the electron in the binding Coulomb potential and the wiggly line the virtual photon.

3.4.2. Self-energy. Starting from the just derived expression and Kronecker deltas are applied to the sums. In addition, it is used that $\bar{\psi}_n = \psi_n^\dagger \gamma^0$, as well as $e^2 = 4\pi\alpha$ in order to write the energy shift because of the self-energy as

$$\begin{aligned}\Delta E_n^{(2)\mathrm{SE}} = 4\pi \mathrm{i}\alpha \int d^3x_1 \int d^3x_2 \int d(t_2 - t_1) D_F(x_2 - x_1) \\ + \sum_{n'} \psi_{n'}^\dagger(x_2) \alpha_\mu S_F(x_2, x_1) \gamma^\mu \psi_{n'}(x_1) \left\langle n \left| a_{n'}^\dagger a_{n'} \right| n \right\rangle \\ - \delta m \sum_{n'} \int d^3x \psi_{n'}^\dagger(\vec{x}) \beta \psi_{n'}(\vec{x}) \left\langle n \left| a_{n'}^\dagger a_{n'} \right| n \right\rangle .\end{aligned} \tag{115}$$

Since $a_{n'}^\dagger a_{n'}$ is the number operator, there only is a contribution for the state in which the electron is sitting. This state is denoted as the reference state n, then

$$\sum_{n'} \left\langle n \left| a_{n'}^\dagger a_{n'} \right| n \right\rangle = \sum_{n'} \delta_{nn'} = 1 \tag{116}$$

and with this

$$\begin{aligned}\Delta E_n^{(2)\mathrm{SE}} = 4\pi \mathrm{i}\alpha \int d^3x_1 \int d^3x_2 \int d(t_2 - t_1) D_F(x_2 - x_1) \\ \times \psi_n^\dagger(x_2) \alpha_\mu S_F(x_2, x_1) \gamma^\mu \psi_n(x_1) - \delta m \int d^3x \psi_n^\dagger(\vec{x}) \beta \psi_n(\vec{x}) .\end{aligned} \tag{117}$$

In order to plug in the photon propagator from Eq. (96), this expression has to be regularized and with it the integral to avoid the divergences at large photon momentum. Pauli-Villars regularization [26] is employed so that the regularized photon propagator is given by

$$D_F(x_2 - x_1) = \frac{\mathrm{i}}{(2\pi)^4} \int d^4q \, e^{-\mathrm{i}q\cdot(x_2 - x_1)} \left[\frac{1}{q^2 + \mathrm{i}\epsilon} - \frac{1}{q^2 - \Lambda^2 + \mathrm{i}\epsilon} \right] . \tag{118}$$

This is the photon propagator which is plugged into Eq. (117) together with the bound fermion propagator from Eq. (106) to give

$$\begin{aligned}\Delta E_{n,\Lambda}^{(2)\mathrm{SE}} &= 4\pi \mathrm{i}\alpha \int d^3x_1 \int d^3x_2 \int d(t_2-t_1) \frac{\mathrm{i}}{(2\pi)^4} \int d^4q\, e^{-\mathrm{i}q\cdot(x_2-x_1)} \\ &\times \left[\frac{1}{q^2+\mathrm{i}\epsilon} - \frac{1}{q^2-\Lambda^2+\mathrm{i}\epsilon}\right] \psi_n^\dagger(x_2) \\ &\times \alpha_\mu \frac{1}{2\pi\mathrm{i}} \int dz \frac{\gamma^0}{H - z(1-\mathrm{i}\delta)} e^{-\mathrm{i}z(t_2-t_1)} \gamma^\mu \psi_n(x_1) \\ &- \delta m \int d^3x \psi_n^\dagger(\vec{x}) \beta \psi_n(\vec{x})\,. \end{aligned} \tag{119}$$

Using the time-evolution of the bound states leads to

$$\begin{aligned}\Delta E_{n,\Lambda}^{(2)\mathrm{SE}} &= \frac{2\mathrm{i}\alpha}{(2\pi)^4} \int d^3x_1 \int d^3x_2 \int d(t_2-t_1) \int_{C_F} dz \int d^4q\, e^{-\mathrm{i}q\cdot(x_2-x_1)} \\ &\times \left[\frac{1}{q^2+\mathrm{i}\epsilon} - \frac{1}{q^2-\Lambda^2+\mathrm{i}\epsilon}\right] \psi_n^\dagger(\vec{x}_2) \alpha_\mu \frac{e^{-\mathrm{i}z(t_2-t_1)}}{H - z(1-\mathrm{i}\delta)} \\ &\times \alpha^\mu \psi_n(\vec{x}_1) e^{\mathrm{i}E_n(t_2-t_1)} - \delta m \int d^3x \psi_n^\dagger(\vec{x}) \beta \psi_n(\vec{x}) \\ &= \frac{2\mathrm{i}\alpha}{(2\pi)^4} \int d^3x_1 \int d^3x_2 \int d(t_2-t_1) \int d^3q \int dq_0 \int_{C_F} dz \\ &\times e^{-\mathrm{i}\vec{q}\cdot(\vec{x}_2-\vec{x}_1)} \left[\frac{1}{q_0^2 - \vec{q}^2 + \mathrm{i}\epsilon} - \frac{1}{q_0^2 - \vec{q}^2 - \Lambda^2 + \mathrm{i}\epsilon}\right] \\ &\times \psi_n^\dagger(\vec{x}_2) \alpha_\mu \frac{1}{H - z(1-\mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1) \\ &\times \exp\left[\mathrm{i}\left(E_n - q_0 - z\right)(t_2-t_1)\right] - \delta m \int d^3x \psi_n^\dagger(\vec{x}) \beta \psi_n(\vec{x})\,. \end{aligned} \tag{120}$$

The time integration is carried out with the known identity

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp\left[\mathrm{i}k(x-a)\right] = \delta(x-a) \tag{121}$$

to obtain

$$\begin{aligned}
\Delta E^{(2)\mathrm{SE}}_{n,\Lambda} &= \frac{2\mathrm{i}\alpha}{(2\pi)^3}\int d^3x_1\int d^3x_2\int_{C_F} dz\int d^3q\int dq_0\, e^{-\mathrm{i}\vec{q}\cdot(\vec{x}_2-\vec{x}_1)} \\
&\quad\times\left[\frac{1}{q_0^2-\vec{q}^{\,2}+\mathrm{i}\epsilon}-\frac{1}{q_0^2-\vec{q}^{\,2}-\Lambda^2+\mathrm{i}\epsilon}\right] \\
&\quad\times\psi_n^\dagger(\vec{x}_2)\alpha_\mu\frac{1}{H-z(1-\mathrm{i}\delta)}\alpha^\mu\psi_n(\vec{x}_1)\delta((E_n-z)-q_0) \\
&\quad-\delta m\int d^3x\psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x}) \\
&= \frac{2\mathrm{i}\alpha}{(2\pi)^3}\int d^3x_1\int d^3x_2\int d^3q\int_{C_F} dz\, e^{-\mathrm{i}\vec{q}\cdot(\vec{x}_2-\vec{x}_1)} \\
&\quad\times\left[\frac{1}{(E_n-z)^2-\vec{q}^{\,2}+\mathrm{i}\epsilon}-\frac{1}{(E_n-z)^2-\vec{q}^{\,2}-\Lambda^2+\mathrm{i}\epsilon}\right] \\
&\quad\times\psi_n^\dagger(\vec{x}_2)\alpha_\mu\frac{1}{H-z(1-\mathrm{i}\delta)}\alpha^\mu\psi_n(\vec{x}_1) \\
&\quad-\delta m\int d^3x\psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x})\,.
\end{aligned} \tag{122}$$

The angle between $\vec{q}$ and $(\vec{x}_2-\vec{x}_1)$ is chosen to be θ_q (choosing $\vec{q}$ to be in the z direction) in order to compute the angular integral of q

$$\begin{aligned}
\Delta E^{(2)\mathrm{SE}}_{n,\Lambda} &= \frac{2\mathrm{i}\alpha}{(2\pi)^3}\int d^3x_1\int d^3x_2\int_{C_F} dz\int dqq^2\int d\psi_q\int d\theta_q\sin(\theta_q) \\
&\quad\times e^{-\mathrm{i}q|\vec{x}_2-\vec{x}_1|\cos(\theta_q)}\left[\frac{1}{(E_n-z)^2-q^2+\mathrm{i}\epsilon}-\frac{1}{(E_n-z)^2-q^2-\Lambda^2+\mathrm{i}\epsilon}\right] \\
&\quad\times\psi_n^\dagger(\vec{x}_2)\alpha_\mu\frac{1}{H-z(1-\mathrm{i}\delta)}\alpha^\mu\psi_n(\vec{x}_1)-\delta m\int d^3x\psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x}) \\
&= \frac{2\mathrm{i}\alpha}{(2\pi)^2}\int d^3x_1\int d^3x_2\int dqq^2\int_{C_F} dz\int_{-1}^{1} du\, e^{-\mathrm{i}qr_{21}u} \\
&\quad\times\left[\frac{1}{(E_n-z)^2-q^2+\mathrm{i}\epsilon}-\frac{1}{(E_n-z)^2-q^2-\Lambda^2+\mathrm{i}\epsilon}\right] \\
&\quad\times\psi_n^\dagger(\vec{x}_2)\alpha_\mu\frac{1}{H-z(1-\mathrm{i}\delta)}\alpha^\mu\psi_n(\vec{x}_1) \\
&\quad-\delta m\int d^3x\psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x})\,,
\end{aligned} \tag{123}$$

with $r_{21} = |\vec{x}_2 - \vec{x}_1|$. For further transformations of this equation the following relation is required

$$\begin{aligned}
&\frac{1}{(E_n - z)^2 - q^2 - \Lambda^2 + \mathrm{i}\epsilon} \\
&\quad = \frac{1}{2q}\left(\frac{1}{\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon} - q} - \frac{1}{\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon} + q}\right)
\end{aligned} \tag{124}$$

and the analogous relation for $\Lambda = 0$. Thus, Eq. (123) yields

$$\begin{aligned}
\Delta E_{n,\Lambda}^{(2)\mathrm{SE}} &= \frac{2\mathrm{i}\alpha}{(2\pi)^2}\int d^3x_1 \int d^3x_2 \int_{C_F} dz \int_0^\infty dq q^2 \frac{1}{\mathrm{i}qr_{21}} \frac{1}{2q} \left[e^{\mathrm{i}qr_{21}} - e^{-\mathrm{i}qr_{21}}\right] \\
&\quad \left[\frac{1}{\sqrt{(E_n - z)^2 + \mathrm{i}\epsilon} - q} - \frac{1}{\sqrt{(E_n - z)^2 + \mathrm{i}\epsilon} + q}\right. \\
&\quad \left. - \frac{1}{\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon} - q} + \frac{1}{\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon} + q}\right] \\
&\quad \times \psi_n^\dagger(\vec{x}_2)\alpha_\mu \frac{1}{H - z(1 - \mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1) - \delta m \int d^3x \psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x}) \\
&= -\frac{\alpha}{(2\pi)^2}\int d^3x_1 \int d^3x_2 \int_{C_F} dz \int_{-\infty}^\infty dq\, e^{\mathrm{i}qr_{21}} \frac{1}{r_{21}} \\
&\quad \left[\frac{1}{q - \sqrt{(E_n - z)^2 + \mathrm{i}\epsilon}} + \frac{1}{q + \sqrt{(E_n - z)^2 + \mathrm{i}\epsilon}}\right. \\
&\quad \left. - \frac{1}{q - \sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon}} - \frac{1}{q + \sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon}}\right] \\
&\quad \times \psi_n^\dagger(\vec{x}_2)\alpha_\mu \frac{1}{H - z(1 - \mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1) - \delta m \int d^3x \psi_n^\dagger(\vec{x})\beta\psi_n(\vec{x})\,.
\end{aligned} \tag{125}$$

This follows from

$$
\begin{aligned}
&\int_0^\infty dq \left(e^{\mathrm{i}qr} - e^{-\mathrm{i}qr}\right) \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] \\
&= \int_0^\infty dq e^{\mathrm{i}qr} \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] + \int_0^{-\infty} dq' e^{\mathrm{i}q'r} \left[\frac{1}{\sqrt{a}+q'} - \frac{1}{\sqrt{a}-q'}\right] \\
&= \int_0^\infty dq e^{\mathrm{i}qr} \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] - \int_{-\infty}^0 dq' e^{\mathrm{i}q'r}(-1) \left[\frac{1}{\sqrt{a}-q'} - \frac{1}{\sqrt{a}+q'}\right] \\
&= \int_0^\infty dq e^{\mathrm{i}qr} \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] + \int_{-\infty}^0 dq e^{\mathrm{i}qr} \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] \\
&= \int_{-\infty}^\infty dq e^{\mathrm{i}qr} \left[\frac{1}{\sqrt{a}-q} - \frac{1}{\sqrt{a}+q}\right] .
\end{aligned}
\tag{126}
$$

The integration with respect to q in Eq. (125) can now be carried out with the help of the Cauchy theorem. The contour is closed through the upper half of the complex plane to get a damping in the exponential. Therefore only poles above the real axis (those with $q - \sqrt{a}$) are picked up. This gives

$$
\begin{aligned}
\Delta E_{n,\Lambda}^{(2)\mathrm{SE}} = \frac{-\mathrm{i}\alpha}{2\pi} \int d^3x_1 \int d^3x_2 \int_{C_F} dz \Big(&\exp\left[\mathrm{i}\,|\vec{x}_2 - \vec{x}_1|\,\sqrt{(E_n - z)^2 + \mathrm{i}\epsilon}\right] \\
&- \exp\left[\mathrm{i}\,|\vec{x}_2 - \vec{x}_1|\,\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon}\right]\Big) \frac{1}{|\vec{x}_2 - \vec{x}_1|} \\
&\times \psi_n^\dagger(\vec{x}_2)\alpha_\mu \frac{1}{H - z(1 - \mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1) - \delta m \int d^3x \psi_n^\dagger(\vec{x}) \beta \psi_n(\vec{x}) \,,
\end{aligned}
\tag{127}
$$

As is well known, the complex square root has a certain ambiguity and normally a branch cut along the negative real axis to get rid of this ambiguity. Here, one has to deal with the root of a complex square displaced by a small imaginary part. For a real number, the square root of a square is defined by $\sqrt{x^2} = |x|$. Accordingly, the sign information present in x is lost, as both x and $-x$ get assigned the same value. Following this idea, it is adopted here for complex numbers by defining that the square root of the square of an imaginary number has positive imaginary part. Thus, the square root is chosen to always have a positive imaginary part, which leads

to the branch cut because the function has a non analytic point at $x = 0$. This choice is very useful for numerical calculation as it provides an exponential damping for the high-energy part and therefore allows to separate off the divergent parts as they need to have $r_{21} = 0$ [36]. As the x here is in fact more complicated a branch cut as shown in Fig. 3.2 is obtained. For simplicity, in accordance with Refs. [7,36,37] b and b' are defined by

$$b = -\mathrm{i}\sqrt{(E_n - z)^2 + \mathrm{i}\epsilon}\,, \tag{128}$$

$$b' = -\mathrm{i}\sqrt{(E_n - z)^2 - \Lambda^2 + \mathrm{i}\epsilon}\,, \tag{129}$$

which consequently always have a positive real part.

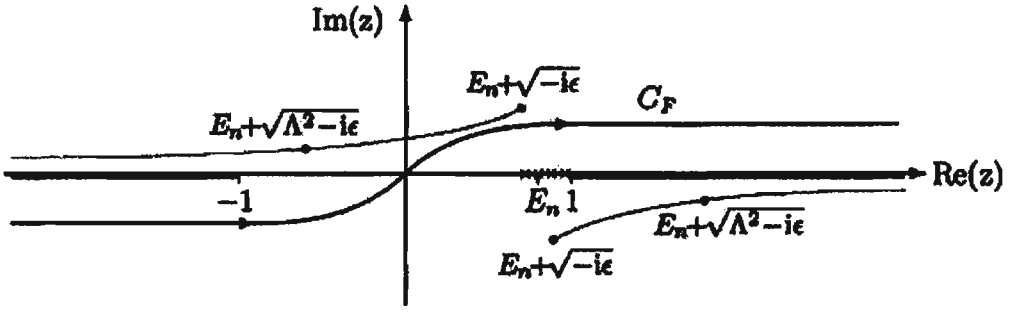

Figure 3.2. Integration contour C_F for the integration of the self-energy. The branch-cut closely below the real axis is due to the electron propagator, the other branch-cut is due to the square-roots b and b'. Bound state poles are denoted as $\times$.

The next step is to alter the path of the z integration. This is possible as the function which has to be integrated over is analytic. Following Ref. [36] the path is transformed as shown in Fig. 3.3 and split into two sections into a high-energy contour C_H and a low-energy contour C_L, which will be discussed separately. The separation is required because a low-energy photon leads to a change in the excitation of a bound electron, whereas a highly energetic photon can scatter the electron into a highly relativistic free state. This necessitates a different treatment for different

photon energies and constitutes a major complication of bound-state field theory over free field theory.

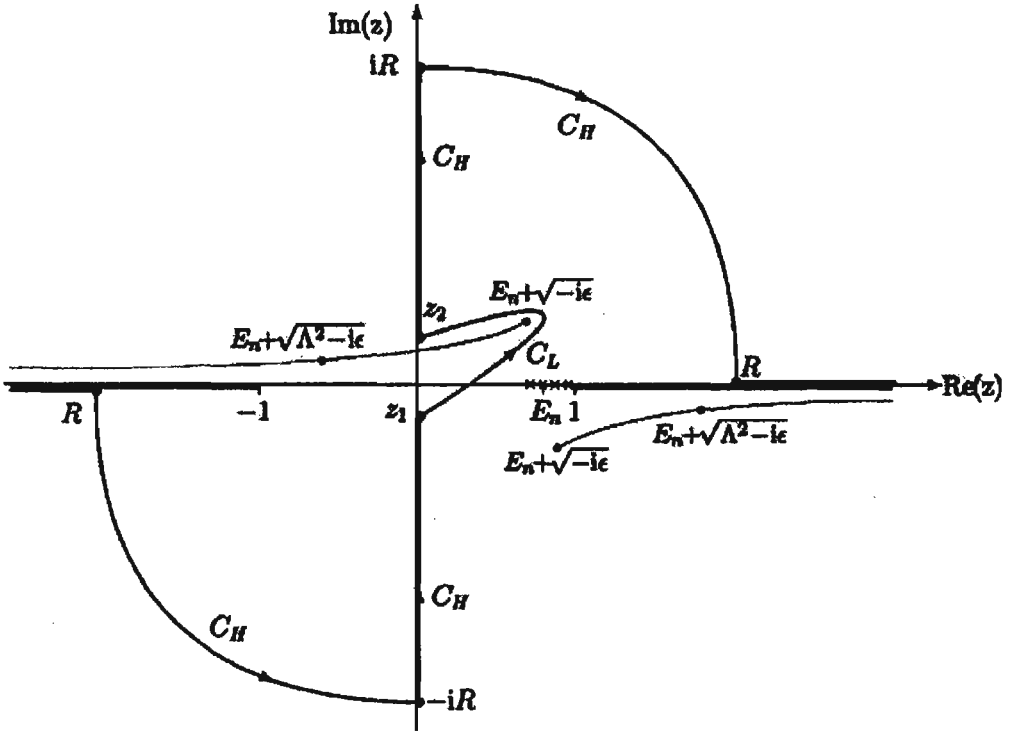

Figure 3.3. New path of the integration contour. The low-energy part of the contour from z_1 to z_2 is denoted as C_L and the high-energy part, which is the rest of the contour, is denoted as C_H.

3.5. LOW-ENERGY PART

In the beginning the low-energy part is considered which is the integration along the contour C_L. The low-energy part is finite without considering the mass renormalization which will be treated together with the high energy part. As it turns out, though, a finite part of the renormalization appears in the result. Form the first calculation of the self-energy contribution to the Lamb shift by Bethe in Ref. [6] it is known that the effect is of order $(Z\alpha)^4 \ln(Z\alpha)^{-2}$. However, terms of lower order than this will appear in the result and can be extracted by an expansion in $Z\alpha$.

The next step is another alteration of the integration contour but this time just for the low-energy contour C_L. For this C_L is considered in the limits $\epsilon \to 0$ and $z_1, z_2 \to 0$. The endpoints of the contour thus meet at 0 and the two branches of b meet at E_n, which is illustrated in Fig. 3.4. The branch cut and the poles of the electron propagator are moved away from the real axis by the addition of a small imaginary part $i\delta$. Thereby, possible ambiguities of the resulting expressions can be avoided. In order to obtain the energy shift the limit $\Lambda \to \infty$ has to be considered, which means $\Lambda > E_n$. Consequently, the part containing Λ has no singularities and is analytic. As now C_L is a closed contour, the part containing Λ vanishes.

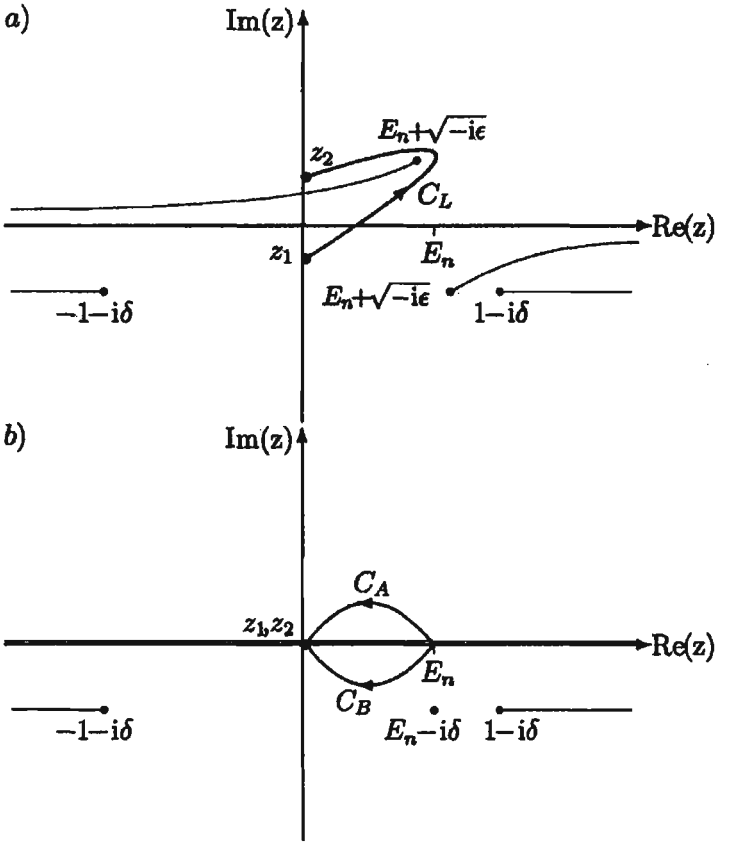

Figure 3.4. Alteration of the low-energy contour C_L in the limits $\epsilon \to 0$ and $z_1, z_2 \to 0$.

Afterwards, the contour C_L for the low-energy part consists of two parts, one part above the real axis denoted as C_A and one below the real axis labeled as C_B.

Recalling the definition of the exponent b, it is found that above and below the real axis b takes the values

$$b = -\mathrm{i}(E_n - z) \quad \text{for } z \text{ on } C_B\,, \tag{130}$$

$$b = +\mathrm{i}(E_n - z) \quad \text{for } z \text{ on } C_A\,. \tag{131}$$

Thus, the integral becomes

$$\begin{aligned}
\Delta E_{n,L}^{(2)\mathrm{SE}} = \frac{\alpha}{\pi} \int d^3x_1 \int d^3x_2 \int_0^{E_n} dz \frac{1}{2\mathrm{i}} \Big(& \exp\left[\mathrm{i}\,|\vec{x}_2 - \vec{x}_1|\,(E_n - z)\right] \\
& - \exp\left[-\mathrm{i}\,|\vec{x}_2 - \vec{x}_1|\,(E_n - z)\right] \Big) \frac{1}{|\vec{x}_2 - \vec{x}_1|} \\
& \times \psi_n^\dagger(\vec{x}_2)\alpha_\mu \frac{1}{H - z(1 - \mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1) \\
= \frac{\alpha}{\pi} \int d^3x_1 \int d^3x_2 \int_0^{E_n} dz & \frac{\sin\left[|\vec{x}_2 - \vec{x}_1|\,(E_n - z)\right]}{|\vec{x}_2 - \vec{x}_1|} \\
& \times \psi_n^\dagger(\vec{x}_2)\alpha_\mu \frac{1}{H - z(1 - \mathrm{i}\delta)} \alpha^\mu \psi_n(\vec{x}_1)\,.
\end{aligned} \tag{132}$$

Remembering and in a sense undoing an integration carried out earlier, it can be seen that

$$\frac{\sin\left[|\vec{x}_2 - \vec{x}_1|\,(E_n - z)\right]}{|\vec{x}_2 - \vec{x}_1|} = \frac{1}{4\pi} \int d\Omega_q \exp\left[\mathrm{i}\vec{q}\cdot(\vec{x}_2 - \vec{x}_1)\right]\,, \tag{133}$$

with $q = |q| = E_n - z$. Furthermore, this is used to transform the variable of integration from $z = E_n - q$ to q with $dz = -dq$. When changing the boundaries of the integral accordingly, the result is

$$\begin{aligned}
\Delta E_{n,L}^{(2)\mathrm{SE}} = \frac{\alpha}{4\pi^2} \int d^3x_1 \int d^3x_2 \int_{q<E_n} d^3q\, \frac{1}{q} & \\
\times \psi_n^\dagger(\vec{x}_2)\alpha_\mu e^{\mathrm{i}\vec{q}\cdot\vec{x}_2} \frac{1}{H - E_n + q - \mathrm{i}\delta} \alpha^\mu e^{-\mathrm{i}\vec{q}\cdot\vec{x}_1} \psi_n(\vec{x}_1) & \\
= P\frac{\alpha}{4\pi^2} \int_{q<E_n} d^3q\, \frac{1}{q} \left\langle \psi_n \left| \alpha_\mu e^{\mathrm{i}\vec{q}\cdot\vec{x}} \frac{1}{H - E_n + q - \mathrm{i}\delta} \alpha^\mu e^{-\mathrm{i}\vec{q}\cdot\vec{x}} \right| \psi_n \right\rangle\,. &
\end{aligned} \tag{134}$$

$\langle\psi_n|\quad|\psi_n\rangle$ denotes the expectation value on the bound state. P is written here to make it clear that this integration procedure leads to a principal value prescription for the integral. Since $\alpha^0 = \mathrm{Id}$ the time-like component can be taken care of right away. For this, a very important relation has to be used which will encountered frequently

$$e^{\mathrm{i}\vec{q}\cdot\vec{x}}\frac{1}{H-E_n+q-\mathrm{i}\delta}e^{-\mathrm{i}\vec{q}\cdot\vec{x}} = \frac{1}{\vec{\alpha}\cdot\vec{p}-\vec{\alpha}\cdot\vec{q}+V+\beta-E_n+q-\mathrm{i}\delta}\,. \tag{135}$$

The denominator is expanded for small $\vec{\alpha}\cdot\vec{q}$ using a common relation for expanding the propagator and get

$$\begin{aligned}
&\frac{1}{\vec{\alpha}\cdot\vec{p}-\vec{\alpha}\cdot\vec{q}+V+\beta-E_n+q-\mathrm{i}\delta} = \frac{1}{\vec{\alpha}\cdot\vec{p}+V+\beta-E_n+q}\\
&+\frac{1}{\vec{\alpha}\cdot\vec{p}+V+\beta-E_n+q}\vec{\alpha}\cdot\vec{q}\frac{1}{\vec{\alpha}\cdot\vec{p}+V+\beta-E_n+q}\\
&+\frac{1}{\vec{\alpha}\cdot\vec{p}+V+\beta-E_n+q}\vec{\alpha}\cdot\vec{q}\frac{1}{\vec{\alpha}\cdot\vec{p}-\vec{\alpha}\cdot\vec{q}+V+\beta-E_n+q-\mathrm{i}\delta}\\
&\times\vec{\alpha}\cdot\vec{q}\frac{1}{\vec{\alpha}\cdot\vec{p}+V+\beta-E_n+q}+\mathcal{O}(\delta)\,.
\end{aligned} \tag{136}$$

For $\mu = 0$, the outer propagators can directly act on the wave functions for which $(\vec{\alpha}\cdot\vec{p}+V+\beta-E_n)\psi_n(x) = 0$ holds. This means

$$\begin{aligned}
q^2\left\langle\psi_n\left|e^{\mathrm{i}\vec{q}\cdot\vec{x}}\frac{1}{H-E_n+q-\mathrm{i}\delta}e^{-\mathrm{i}\vec{q}\cdot\vec{x}}\right|\psi_n\right\rangle &= q\\
+\langle\psi_n|\vec{\alpha}\cdot\vec{q}|\psi_n\rangle+\left\langle\psi_n\left|\vec{\alpha}\cdot\vec{q}\,e^{\mathrm{i}\vec{q}\cdot\vec{x}}\frac{1}{H-E_n+q-\mathrm{i}\delta}\vec{\alpha}\cdot\vec{q}\,e^{-\mathrm{i}\vec{q}\cdot\vec{x}}\right|\psi_n\right\rangle&+\mathcal{O}(\delta)\,.
\end{aligned} \tag{137}$$

Thus Eq. 134 yields

$$\begin{aligned}
\Delta E^{(2)\mathrm{SE}}_{n,L} = \frac{\alpha}{\pi}E_n-\frac{\alpha}{4\pi^2}P\int_{q<E_n}d^3q\,\frac{1}{q}\left(\delta^{ij}-\frac{q^iq^j}{\vec{q}^2}\right)\\
\times\left\langle\psi_n\left|\alpha^i\,e^{\mathrm{i}\vec{q}\cdot\vec{x}}\frac{1}{H-E_n+q-\mathrm{i}\delta}\alpha^j\,e^{-\mathrm{i}\vec{q}\cdot\vec{x}}\right|\psi_n\right\rangle
\end{aligned} \tag{138}$$

because the angular integral over $\vec{\alpha}\cdot\vec{q}$ vanishes. Already from the term E_n it becomes evident that a finite part of the renormalization is carried along, which can be extracted out of the expression by an expansion in $Z\alpha$.

$Z\alpha$ gives the strength of the Coulomb potential and scales the momentum, energy and radial position of the electron. Such a scaling is also typical for bound states of gravity. Thereby, the magnitudes of the relevant parameters can be identified

$$r \sim \frac{1}{Z\alpha}, \quad |p| \sim Z\alpha\,, \tag{139}$$

$$V \sim \frac{Z\alpha}{r} \sim (Z\alpha)^2\,, \tag{140}$$

$$E_n \sim 1 - (Z\alpha)^2\,. \tag{141}$$

Because these quantities are operators, the expansion is carried out by expanding the denominator in Eq. (138) in powers of $\vec{\alpha}\cdot\vec{p}$, V and, finally, in powers of $(1^2 - E_n^2)$. In order to extract the physical part of the low-energy part, which is of order $(Z\alpha)^4 \ln(Z\alpha)^{-2}$, only terms of lower order than this are kept. It will become clear that these lower order terms cancel when added with the high-energy part justifying the procedure. The expansion and the following evaluation of the resulting expression are given in Ref. [37] with the result

$$\begin{aligned}\Delta E_{n,L}^{(2)\mathrm{SE}} &= \frac{\alpha}{\pi}\left[\frac{5}{6}E_n + \frac{2}{3}\langle\psi_n|\beta|\psi_n\rangle + \frac{7}{6}\langle\psi_n|V|\psi_n\rangle + \frac{(Z\alpha)^4}{n^3}f_L(Z\alpha)\right] \\ &= \frac{\alpha}{\pi}\left[\frac{3}{2}E_n + \frac{7}{6}\langle\psi_n|V|\psi_n\rangle + \frac{(Z\alpha)^4}{n^3}f_L(Z\alpha)\right]\,,\end{aligned} \tag{142}$$

where $f_L(Z\alpha)$ is the physical part of the low-energy part in the commonly used scaling. For the evaluation, as described in Refs. [36, 37], Eq. (138) is rewritten in position space as

$$\begin{aligned}\Delta E_{n,L}^{(2)\mathrm{SE}} = \frac{\alpha}{\pi}E_n - P\int_0^{E_n} dz \int d^3x_2 \int d^3x_1 \psi_n^\dagger(\vec{x}_2)\alpha^i G(\vec{x}_2,\vec{x}_1,z)\alpha^j\psi_n(\vec{x}_1) \\ \times\left(\delta_{ij}\vec{\nabla}_2\cdot\vec{\nabla}_1 - \nabla_2^i\nabla_1^j\right)\frac{\sin\left[(E_n-z)r_{21}\right]}{(E_n-z)^2 r_{21}}\,,\end{aligned} \tag{143}$$

with $r_{21} = |\vec{x}_2 - \vec{x}_1|$. The possibility to separate the angular and radial part, allows to carry out the angular integration and a integral over the radial part remains which

can be written as [37]

$$\Delta E_{n,L}^{(2)\mathrm{SE}} = \frac{\alpha}{\pi} E_n - P \int_0^{E_n} dz \int_0^{\infty} dr_2 r_2^2 \int_0^{\infty} dr_1 r_1^2 \times \sum_{\kappa} \sum_{i,j=1}^{2} f_{n,3-i}(r_2) G_{\kappa}^{i,j}(r_2, r_1, z) f_{n,3-j}(r_1) A_{\kappa}^{ij}(r_2, r_1) \,, \tag{144}$$

where $f_{n,1}(r)$ is the radial Dirac eigenfunction $g(r)$ for the reference state n and accordingly $f_{n,2}(r) = f(r)$. The components G_{κ}^{ij} of the radial Coulomb-Dirac Green's function, as well as those from the angular integration of the photon propagator A_{κ}^{ij} are given in Refs. [7,8,36]. The remaining integrations are carried out numerically, the details are given in Ref. [8]. It is important to mention that because of the principal value prescription in Eq. (144), contributions from poles along the integration contour have to be calculated separately. The analytically calculated contributions from the poles have to be subtracted from the expression prior to numerical integration to avoid divergences. The lower-order terms can be subtracted afterwards to determine a value for $f_L(Z\alpha)$.

3.6. HIGH-ENERGY PART

In the high-energy part the integration proceeds along the contour C_H depicted in Fig. 3.4. In it, the regularization of the photon propagator has to be considered as well as the mass renormalization. Therefore, the expression for the high-energy part is

$$\Delta E_{n,H}^{(2)\mathrm{SE}} = \lim_{\Lambda\to\infty} \frac{\alpha}{2\pi \mathrm{i}} \int_{C_H} dz \int d^3x_2 \int d^3x_1 \psi_n^{\dagger}(\vec{x}_2) \alpha_{\mu} G(\vec{x}_2, \vec{x}_1, z) \alpha^{\mu} \psi_n(\vec{x}_1) \times \left(\frac{e^{-br_{21}}}{r_{21}} - \frac{e^{-b'r_{21}}}{r_{21}} \right) - \delta m(\Lambda) \int d^3x \psi_n^{\dagger}(\vec{x}) \beta \psi_n(\vec{x}) \,. \tag{145}$$

As its name implies, the high-energy part treats the photons, which have a energy larger than E_n. Compared to the high energy of the photon here, the potential is just a perturbation. Therefore, the bound electron Green's function G can be expanded in terms of free electron Green's function F without a potential and interactions with the binding potential V in a perturbative expansion. This expansion is graphically

illustrated in Fig. 4.2 using Feynman diagrams [26] and gives

$$\begin{aligned} G(\vec{x}_2,\vec{x}_1,z) &= F(\vec{x}_2,\vec{x}_1,z) - \int d^3x_3 F(\vec{x}_2,\vec{x}_3,z)V(r_3)F(\vec{x}_3,\vec{x}_1,z) \\ &+ \int d^3x_3 \int d^3x_4 F(\vec{x}_2,\vec{x}_4,z)V(r_4)F(\vec{x}_4,\vec{x}_3,z)V(r_3)F(\vec{x}_3,\vec{x}_1,z) + \dots . \end{aligned} \tag{146}$$

For large $|z|$ the expression in Eq. (145) is exponentially damped up to the region where $r_{21} \approx 0$. In turn, this means that for large $|z|$ the major contribution will come from these terms. It has been suggested in Ref. [37] to use an expansion of the wave function at $\vec{x}_1$ around $\vec{x}_2$. This not only allows to extract divergent terms at $r_{21} \approx 0$ but to find the terms of lower order than the physical part of the high-energy part as well. The expansion of the wave function gives

$$\begin{aligned} \psi_n(\vec{x}_1) &= \psi_n(\vec{x}_2) + (\vec{x}_1 - \vec{x}_2)\cdot\vec{\nabla}_2\psi_n(\vec{x}_2) \\ &+ \tfrac{1}{2}(\vec{x}_1 - \vec{x}_2)^i(\vec{x}_1 - \vec{x}_2)^j \frac{\partial}{\partial x_2^i}\frac{\partial}{\partial x_2^j}\psi_n(\vec{x}_2) + \dots . \end{aligned} \tag{147}$$

Finally, an expansion for the potential

$$V(r_3) = V(r_2) + \dots \tag{148}$$

is used as well. The divergent and the lower order terms in Eq. (145) can be extracted as the analytic part ΔE_A which is the sum of four terms

$$\Delta E_A = \lim_{\Lambda\to\infty}\left[\Delta E_H^{0,0} + \Delta E_H^{0,1} + \Delta E_H^{0,2} + \Delta E_H^{1,0} - \delta m(\Lambda)\left\langle\psi_n\left|\beta\right|\psi_n\right\rangle\right] , \tag{149}$$

where the index i in $\Delta E_H^{i,j}$ counts the order in V, while j gives the order in the power series in Eq. (147). The expansions simplifies the integration with respect to x_2 which can be carried out analytically. After that, the integration with respect to z is tackled. As explained in Ref. [7] the structure of the function causes the integrals over the circle parts to vanish and thus z is only integrated from $-\mathrm{i}\infty$ to $\mathrm{i}\infty$, which is depicted in Fig. 3.5. This enables to transform it to $y = -\mathrm{i}z$ above and to $y = \mathrm{i}z$ below the real axis. With the help of the definition of b and b', the resulting integrals over y extend from 0 to ∞ and can be carried out analytically. The calculation is

explained in detail in Ref. [37] and just the results are restated here, they are

$$\Delta E_H^{0,0} = \frac{\alpha}{\pi}\left[\langle\psi_n|\beta|\psi_n\rangle\left(\ln(\Lambda^2) - 1 + \frac{1-E_n^2}{E_n^2}\ln(1+E_n^2)\right)\right. \tag{150a}$$
$$\left. - E_n\left(\frac{1}{4}\ln(\Lambda^2) + \frac{3E_n^2-2}{8E_n^2} + \frac{1-E_n^4}{4E_n^4}\ln(1+E_n^2)\right) + \mathcal{O}(\Lambda^{-1})\right]$$

$$\Delta E_H^{0,1} = \frac{\alpha}{\pi}\langle\psi_n|\vec{\alpha}\cdot\vec{p}|\psi_n\rangle\left(\frac{1}{4}\ln(\Lambda^2) - \frac{6-3E_n^2+7E_n^4}{24E_n^2(1+E_n^2)}\right. \tag{150b}$$
$$\left. + \frac{1-E_n^2}{4E_n^4}\ln(1+E_n^2) + \mathcal{O}(\Lambda^{-1})\right),$$

$$\Delta E_H^{0,2} = \frac{\alpha}{\pi}\left[\langle\psi_n|\beta p^2|\psi_n\rangle\left(-\frac{3+6E_n^2-E_n^4}{3E_n^2(1+E_n^2)^2} + \frac{1}{E_n^4}\ln(1+E_n^2)\right)\right. \tag{150c}$$
$$\left. + \langle\psi_n|E_n p^2|\psi_n\rangle\left(\frac{3+6E_n^2+E_n^4}{12E_n^4(1+E_n^2)} - \frac{1}{2E_n^6}\ln(1+E_n^2)\right) + \mathcal{O}(\Lambda^{-1})\right]$$

$$\Delta E_H^{1,0} = \frac{\alpha}{\pi}\left[\langle\psi_n|V|\psi_n\rangle\left(\frac{1}{4}\ln(\Lambda^2) + \frac{6-E_n^2}{8E_n^2} - \frac{3+E_n^4}{4E_n^4}\ln(1+E_n^2)\right)\right. \tag{150d}$$
$$\left. - \left\langle\psi_n\left|\frac{\beta}{E_n}V\right|\psi_n\right\rangle\left(2 - \frac{2}{E_n^2}\ln(1+E_n^2)\right) + \mathcal{O}(\Lambda^{-1})\right].$$

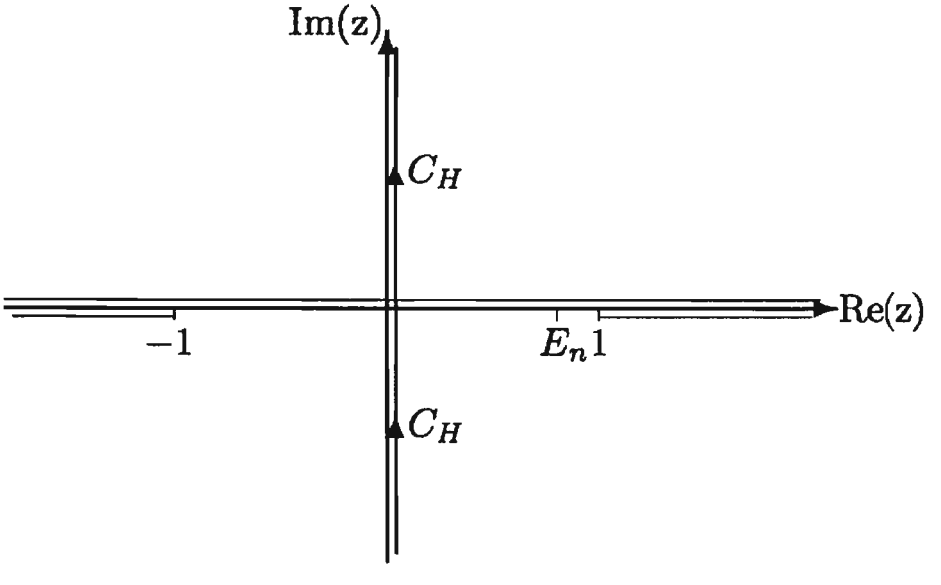

Figure 3.5. Because the integral over the parts of the circle vanish, the high-energy contour C_H takes this form in the limits $\epsilon \to 0$ and $z_1, z_2 \to 0$. The lines below the real axis denote the branch cut of the electron propagator and the line above is the branch cut of b.

As can be seen there, all terms except $\Delta E_H^{0,2}$ contain a term proportional to $\ln(\Lambda^2)$ which is logarithmically divergent in the limit $\Lambda \to \infty$. These terms cancel with the mass renormalization which in these units is [7,26,36,37]

$$\delta m(\Lambda) = \frac{\alpha}{\pi}\left[\frac{3}{4}\ln(\Lambda^2) + \frac{3}{8}\right] . \tag{151}$$

An expansion in powers of $1 - E_n^2$ again allows to extract the terms of order lower than $(Z\alpha)^4 \ln(Z\alpha)^{-2}$ and gives

$$\begin{aligned}\Delta E_A &= \frac{\alpha}{\pi}\left(-\frac{5}{6}E_n - \frac{2}{3}\langle\psi_n|\beta|\psi_n\rangle - \frac{7}{6}\langle\psi_n|V|\psi_n\rangle + \frac{(Z\alpha)^4}{n^3}f_a(Z\alpha)\right) \\ &= \frac{\alpha}{\pi}\left(-\frac{3}{2}E_n - \frac{7}{6}\langle\psi_n|V|\psi_n\rangle + \frac{(Z\alpha)^4}{n^3}f_a(Z\alpha)\right)\end{aligned} \tag{152}$$

with the help of the identity $\langle\psi_n|\beta|\psi_n\rangle = E_n$ for the Coulomb potential. The physical part of ΔE_A is given by the remaining terms in Eq. (150) and is stated in Eq. (48) in Ref. [37].

This analytical calculation is necessary again to extract divergences from the numerical integration. After they have been taken care off, it is possible to define functions which allow a point wise subtraction of these divergences from the numerical integral which has to be calculated. These subtraction functions $K^{i,j}(r_2, r_1, z)$ have been defined in Ref. [37] by

$$\Delta E_H^{i,j} = \frac{\alpha}{2\pi \mathrm{i}}\int_{C_H} dz \int_0^\infty dr_2 r_2^2 \int_0^\infty dr_1 r_1^2 K^{i,j}(r_2, r_1, z) . \tag{153}$$

In this way, the analytically calculated part can be subtracted from the initial integral and the expression which is integrated numerically is then [37]

$$\begin{aligned}\Delta E_B = \frac{\alpha}{2\pi \mathrm{i}}\int_{C_H} dz \int_0^\infty dr_2 r_2^2 \int_0^\infty dr_1 r_1^2 \Bigg(\sum_\kappa \sum_{i,j=1}^{2} \big[f_{n,i}(r_2) G_\kappa^{i,j}(r_2, r_1, z) \\ \times f_{n,j}(r_1) A_\kappa(r_2, r_1) - f_{n,3-i}(r_2) G_\kappa^{i,j}(r_2, r_1, z) f_{n,3-j}(r_1) A_\kappa^{ij}(r_2, r_1)\big] \\ - K_A(r_2, r_1, z)\Bigg) ,\end{aligned} \tag{154}$$

where $K_A(r_2, r_1, z)$ is the sum

$$K_A(r_2, r_1, z) = K^{0,0}(r_2, r_1, z) + K^{0,1}(r_2, r_1, z) + K^{0,2}(r_2, r_1, z) + K^{1,0}(r_2, r_1, z)\,.$$

Note, that the functions $A^{ij}_{\kappa}(r_2, r_1)$ are different from those in Eq. (144) and are given in Refs. [7, 8]. ΔE_B does not contain terms of lower order than $(Z\alpha)^4 \ln(Z\alpha)^{-2}$. Consequently, it is possible to write

$$\Delta E_B = \frac{(Z\alpha)^4}{n^3} f_B(Z\alpha)\,, \tag{155}$$

and, therefore, the total high energy part as

$$\Delta E^{(2),\mathrm{SE}}_{n,H} = \frac{\alpha}{\pi}\left(-\frac{3}{2}E_n - \frac{7}{6}\langle\psi_n|V|\psi_n\rangle + \frac{(Z\alpha)^4}{n^3} f_H(Z\alpha)\right) \tag{156}$$

with $f_H(Z\alpha) = f_A(Z\alpha) + f_B(Z\alpha)$.

Finally, the low-energy and the high-energy part are added in order to obtain a result for the energy shift. As can be seen from a comparison of Eqs. (152) and (142), this will lead to a cancellation of all the lower order terms. The final result, where the electron mass can be reintroduced again, is thus obtained as

$$\Delta E^{(2),\mathrm{SE}}_{n} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3} F(Z\alpha)\,, \tag{157}$$

where

$$F(Z\alpha) = f_L(Z\alpha) + f_H(Z\alpha)\,. \tag{158}$$

4. THEORY: EXPANSION ABOUT NONRELATIVISTIC THEORY

4.1. NONRELATIVISTIC DESCRIPTION OF THE ELECTRON

The fully relativistic formalism provides means to evaluate the QED corrections to the energy levels. These calculations, unfortunately, require a large amount of computer time. In addition, the relativistic formalism often does not allow to identify the physical origin of the investigated corrections. In many cases, though, the nonrelativistic description of the electron provides an accurate enough approximation and greatly simplifies the computations. With the nonrelativistic framework, due to the special character of time, the interaction with the quantized field can be included using time-independent perturbation theory. In this section, it is explained how a nonrelativistic description of the electron QED interaction can be obtained and how the relativistic corrections can be included. These corrections improve the approximation tremendously, while the simplicity of the nonrelativistic calculations can be retained. As will become apparent, the relativistic corrections can be expressed as effective operators, which, interestingly, very clearly show their physical origin.

In the usual description of the quantum mechanics, the bound state of an electron in the potential of a nucleus is given by the Schrödinger equation [1]. For a nucleus with a nuclear charge number Z which is infinitely heavy, the bound states for the electron can be obtained as solutions of the equation

$$H_S\Phi(\vec{x}) = \left(\frac{p^2}{2m_e} - \frac{Z\alpha}{r}\right)\Phi(\vec{x}) = E_S\Phi(\vec{x})\,. \tag{159}$$

The time dependence of the state is thereby given by

$$\Phi(t,\vec{x}) = e^{-\mathrm{i}E_S t}\Phi(\vec{x})\,. \tag{160}$$

The solution of this problem can be found in many books on quantum mechanics. Therefore, it is given here without derivation. It can be obtained by separating the problem into a radial and an angular part. This feature is very important and will be used throughout this work since it allows for many simplifications in our calculations.

The solution is described by three quantum numbers: the principal quantum number n, the orbital angular momentum quantum number ℓ and the magnetic quantum number m. The eigenfunctions are then obtained [24, 38] as

$$\Phi_{n,\ell,m}(\vec{x}) = Y_{\ell,m}(\hat{x}) R_{n\ell}(r)\,, \tag{161}$$

where $Y_{\ell,m}(\hat{x})$ is the spherical harmonic as defined in Ref. [23]. While a solution of the differential equation for the radial part can, in fact, always be found using a power series in r, a normalizable solution can only be obtained for a bound state $E < 0$ with $n \geq \ell + 1$. Under these conditions the power series breaks off and the radial wave function $R_{n\ell}(r)$ is given in terms of the generalized Laguerre polynomials $L_{n+\ell}^{2\ell+1}$ which are finite

$$R_{n\ell}(r) = -\sqrt{\frac{(n-\ell-1)!\left(\frac{2Z}{na_0}\right)^3}{2n((n+\ell)!)^3}}\left(\frac{2Z}{na_0}\right)^{\ell} e^{-\frac{Zr}{na_0}} L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_0}\right)\,, \tag{162}$$

where $a_0 = 1/m_e\alpha$ is the Bohr radius. Alternatively, the power series can be written as a hypergeometric function which reduces to the finite Laguerre polynomials for the above conditions [39]. The respective energies are then

$$E_n = -\frac{m_e(Z\alpha)^2}{2n^2} = -R_\infty \frac{Z^2}{n^2}\,, \tag{163}$$

where $R_\infty = \frac{1}{2}m_e\alpha^2$ is the Rydberg constant. While the predicted energy levels explain the Balmer series, they do not explain the fine-structure of the spectral lines. There are two reasons for this. The first is that the Schrödinger equation does not contain the spin of the electron. The second reason lies in the energy momentum relation used in the Schrödinger equation which is basically $E \sim p^2$. This is the non-relativistic energy momentum relation and therefore relativistic effects are neglected.

It is, however, possible to include both of these effects as perturbations into the Schrödinger equation by using the perturbation Hamiltonian

$$\delta H_S = -\frac{\vec{p}^4}{8m_e^3} + \frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x}) + \frac{Z\alpha}{4m_e^2 r^3}\vec{\sigma}\cdot\vec{\ell}, \tag{164}$$

where $\vec{\sigma}$ are the Pauli matrices. The first term arises from the relativistic kinetic energy and the second from the zitterbewegung of the electron. The last term comes from the interaction of the spin with the magnetic field generated by the core in the rest frame of the electron. This magnetic field is generated because in the rest frame of the electron the core circles it with angular momentum ℓ.

In order to allow a perturbative treatment, it is necessary to include the spin in the wave function of the unperturbed Schrödinger Hamiltonian in Eq. (161). This changes the spherical harmonic $Y_{\ell,m}$ into a Pauli spinor χ^{κ}_{μ}

$$\Phi(\vec{x}) = \chi^{\kappa}_{\mu}(\hat{x}) R_{n\ell}(r)\,. \tag{165}$$

The spinor is defined by

$$\chi^{\kappa}_{\mu}(\hat{x}) = \begin{pmatrix} -d^{\frac{1}{|\kappa|}} \sqrt{\dfrac{\kappa-\mu+\frac{1}{2}}{2\kappa+1}}\, Y_{|\kappa+\frac{1}{2}|-\frac{1}{2},\mu-\frac{1}{2}}(\hat{x}) \\ \sqrt{\dfrac{\kappa+\mu+\frac{1}{2}}{2\kappa+1}}\, Y_{|\kappa+\frac{1}{2}|-\frac{1}{2},\mu+\frac{1}{2}}(\hat{x}) \end{pmatrix}. \tag{166}$$

with the Dirac quantum number $\kappa = (-1)^{j+\ell+\frac{1}{2}}(j+\frac{1}{2})$ and the total angular momentum $\vec{j} = \vec{\ell} + \frac{1}{2}\vec{\sigma}$. The Dirac quantum number is another way of writing the total angular momentum though in terms of integer numbers. For example, the so-called $P_{1/2}$ state with orbital angular momentum $\ell = 1$ and total angular momentum $j = \frac{1}{2}$, has $\kappa = 1$. While the state $S_{1/2}$, which has the same total angular momentum of $j = \frac{1}{2}$ as the $P_{1/2}$ state, has a Dirac quantum number of $\kappa = -1$ because the orbital angular momentum is $\ell = 0$. Hence, the sign allows to differentiate states with the same total angular momentum due to the difference in orbital angular momentum.

Even though the complete Hamiltonian $H_S + \delta H_S$ cannot be solved, the eigenfunction of the unperturbed Hamiltonian H_S with inclusion of the spin can be used to calculate the energy shift due to δH_S in first order of perturbation theory. The result is

$$E_n + \langle \Phi \,|\delta H_S|\, \Phi \rangle = E_{nj} = -\frac{m_e(Z\alpha)^2}{2n^2} + \frac{m_e(Z\alpha)^4}{2n^3}\left(\frac{3}{4n} - \frac{1}{j+\frac{1}{2}}\right). \tag{167}$$

In contrast to E_n, in which the energy only depends on the principal quantum number n, the energy $E_{n,j}$ depends on both the principal quantum number as well as the total angular momentum j. Interestingly, this result agrees with the energy prediction by the Dirac equation expanded in $Z\alpha$ up to and including $\mathcal{O}((Z\alpha)^4)$ [24]. When atoms with a low nuclear charge number Z are considered, these higher order terms are negligible. This means that the electron for such atoms, when some corrections and the spin are included, is very well described by the nonrelativistic Schrödinger equation.

The next step is now to include the effects, which arise because of the quantum nature of the electromagnetic field, as well. But before this can be done, it has to be explained how the electromagnetic field can be quantized, which will be done in the next section.

4.2. QUANTIZED FIELD

After the treatment of the electron, this section will discuss how the electromagnetic field can be transformed from the classical Maxwell theory to a quantum theory. The aim is to quantize the electromagnetic field in order to include the particle nature of the photon as well as its wave nature which is contained in classical electrodynamics. Because the quantum theory has to agree with Maxwell's theory in the classical limit (high energies, many photons), the starting point is to recall Maxwell's equations in covariant formulation which in the unit system in this work are given as [25]

$$\partial_\mu F^{\mu\nu} = j^\nu \,, \tag{168}$$

$$\epsilon_{\mu\nu\rho\sigma}\partial^\rho F^{\mu\nu} = 0 \,, \tag{169}$$

where $F^{\mu\nu}$ is defined by

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu \,. \tag{170}$$

The four-vector potential A^μ is combined of the scalar potential ϕ and the vector potential $\vec{A}$

$$A^\mu = \left(\phi, \vec{A}\right) . \tag{171}$$

Similarly, the four-vector current is

$$j^\mu = \left(\rho, \vec{j}\right) . \tag{172}$$

Using the Hamiltonian principle and the Euler-Lagrange equation similar to classical mechanics the inhomogeneous Maxwell equation (168) can be obtained from the Lagrange density

$$\mathcal{L}_{\text{em}} = -\frac{1}{4} F^{\mu\nu} F_{\mu\nu} - j^\mu A_\mu . \tag{173}$$

The homogeneous Maxwell equation (169) is automatically fulfilled by the use of the four-vector potential. Following the Noether theorem, invariance of the action

$$S = \int d^4x \, \mathcal{L}_{\text{em}} \tag{174}$$

under a transformation leads to a conserved quantity. In this way for example the conservation of the electromagnetic current or the continuity equation

$$\partial_\mu j^\mu = 0 \tag{175}$$

can be shown. As one might recall from electrodynamics the four-vector potentials can be gauge transformed according to

$$A_\mu \rightarrow A'_\mu = A_\mu + \partial_\mu \Lambda , \tag{176}$$

while the electric and magnetic field are invariant under this gauge transformation [25]. Now, this gauge transformation is applied to the Lagrange density in Eq. (173)

to obtain

$$\mathcal{L}' = -\left[\frac{1}{4}F^{\mu\nu}F_{\mu\nu} + j^{\mu}A_{\mu} + j^{\mu}\partial_{\mu}\Lambda\right] . \tag{177}$$

Because the current is conserved and therefore $\partial_{\mu}j^{\mu} = 0$, the term $\partial_{\mu}j^{\mu}\Lambda = 0$ can be added to the Lagrangian which yields

$$\mathcal{L}'_{\text{em}} = -\left[\frac{1}{4}F^{\mu\nu}F_{\mu\nu} + j^{\mu}A_{\mu} + \partial_{\mu}(j^{\mu}\Lambda)\right] . \tag{178}$$

The last term is a total derivative which does not change the action in Eq. (174). This means that the action is invariant under the gauge transformation. Although this gauge freedom can be very useful for the actual calculations, it complicates the quantization of the theory as a specific gauge has to be chosen prior to quantization. Here, in fact, Coulomb gauge will be used

$$\vec{\nabla} \cdot \vec{A} = 0 \tag{179}$$

even though it is not Lorentz-invariant.

For the quantization of the field, it is important to recall that in quantum mechanics momentum and position are elevated to operators. They have to fulfill the commutation relation

$$[x_i, p_j] = \mathrm{i}\delta_{ij} . \tag{180}$$

For the quantization of the electromagnetic field, the vector potential is elevated into an operator. In order to get analogue commutation relations, the conjugate momentum is required. The conjugate momentum is called π and it is obtained in a similar way as in classical mechanics with a derivative of the Lagrangian with respect to the time-derivative of the field

$$\pi^{\mu} = \frac{\partial\mathcal{L}}{\partial(\partial^0 A_{\mu})} . \tag{181}$$

The Lagrangian in Coulomb gauge takes the form

$$\mathcal{L} = \frac{1}{2}\partial^0 A_i \partial_0 A^j - \frac{1}{2}(\partial_j A_i)^2 + j_i A_i + \frac{1}{2}\partial_i A_j \partial_j A_i + \partial^0 A_i \partial_i A^0 + \frac{1}{2}(\partial_i A^0)^2 - j_0 A^0 \,. \quad (182)$$

So for the conjugate momenta this yields

$$\pi^0 = \frac{\partial \mathcal{L}}{\partial(\partial^0 A_0)} = 0 \,, \quad (183)$$

$$\pi^i = \frac{\partial \mathcal{L}}{\partial(\partial^0 A_i)} = -\partial_0 A^i - \partial_i A^0 = E^i \,. \quad (184)$$

Here, the advantage of our choice of gauge can be elucidated. The potential has no dynamics of its own and is given entirely by the charge distribution. This allows to continue to work with the classical Coulomb potential of the electron nucleus interaction and only quantize the vector potential. Thereby, the effects from the bound state potential and the quantized field are separated. Moreover, in this way the unphysical time-like photons are excluded and only the longitudinal photons have to be eliminated in the following. In the Gupta-Bleuler quantization for other gauges [35], at this point both time-like and longitudinal photons have to be extracted as degrees of freedom because the time-like conjugate momentum is non zero. In general, the quantization of a gauge theory is a very intricate subject [26] because all degrees of freedom are required in the calculation but some are unphysical and can therefore not appear in the final results.

With the conjugate momenta a Legendre transformation can be employed to receive the Hamilton density for the free field with $j_\mu = 0$

$$\mathcal{H}_{\text{free}} = \pi^k A_k - \mathcal{L} = \frac{1}{2}\left(\vec{E}^2 + \vec{B}^2\right) . \quad (185)$$

It has the form of a harmonic oscillator but as a density. It is, in fact, a continuous chain of massless harmonic oscillators. Accordingly, the quantization is nearly the same as for the normal harmonic oscillator. Therefore, it is not reiterated here. A detailed derivation can for example be found in Refs. [27, 35]. Here, just the

commutation relations are discussed. They are

$$\left[\hat{A}^i(t,\vec{x}),\hat{A}^j(t,\vec{x}')\right]=0\,, \tag{186}$$

$$\left[\hat{\pi}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=0\,, \tag{187}$$

where the hat is used to make clear that these are operators now. It is important to note here that these relations are always for equal times. Normally, one would expect the commutation relation between A and π to look like

$$\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=\mathrm{i}\delta^{ij}\delta(\vec{x}-\vec{x}')\,. \tag{188}$$

Unfortunately, this is not correct because of the gauge condition, which can be seen by taking the divergence of the commutator

$$\partial_i\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=\left[\partial_i\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=\left[0,\hat{\pi}^j(t,\vec{x}')\right]=0\,, \tag{189}$$

while

$$\partial_i\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=\mathrm{i}\partial_j\delta(\vec{x}-\vec{x}')\neq 0\,. \tag{190}$$

The right idea can be envisioned by looking at a certain choice to fulfill the gauge condition of the vector potential $\partial_i A_i = 0$ which can be imposed by a projection operator

$$A_i(t,\vec{x})\rightarrow\left(\delta_{ij}-\frac{\partial_i\partial_j}{\partial^2}\right)A_j(t,\vec{x})\,. \tag{191}$$

Applying this projection operator to the δ distribution gives

$$\left(\delta_{ij}-\frac{\partial_i\partial_j}{\partial^2}\right)\delta(\vec{x}-\vec{x}')=\int\frac{d^3k}{(2\pi)^3}\left(\delta_{ij}-\frac{k_ik_j}{k^2}\right)e^{\mathrm{i}\vec{k}\cdot(\vec{x}-\vec{x}')}=\delta^{\perp,ij}(\vec{x}-\vec{x}')\,. \tag{192}$$

This transverse δ distribution now leads to the right commutation relation

$$\left[\hat{A}^i(t,\vec{x}),\hat{\pi}^j(t,\vec{x}')\right]=\mathrm{i}\delta^{\perp,ij}(\vec{x}-\vec{x}')\,. \tag{193}$$

The quantized vector potential for a free field in the Schrödinger picture is then [27]

$$\vec{A}(\vec{x}) = \int \frac{d^3k}{(2\pi)^3} \frac{1}{\sqrt{2\omega_{\vec{k}}}} \sum_{\lambda=1}^{2} \left(a^{\lambda}(\vec{k}) \vec{\epsilon}^{\lambda}(\vec{k}) e^{\mathrm{i}\vec{k}\cdot\vec{x}} + a^{\lambda\dagger}(\vec{k}) \vec{\epsilon}^{\lambda}(\vec{k}) e^{-\mathrm{i}\vec{k}\cdot\vec{x}} \right) \tag{194}$$

where the polarization vectors $\vec{\epsilon}^{\lambda}(\vec{k})$ fulfill the relations

$$\vec{\epsilon}^{\lambda}(\vec{k}) \cdot \vec{\epsilon}^{\lambda'}(\vec{k}) = \delta^{\lambda\lambda'} , \tag{195}$$

$$\vec{k} \cdot \vec{\epsilon}^{\lambda}(\vec{k}) = 0 \tag{196}$$

$$\sum_{\lambda=1}^{2} \epsilon_i^{\lambda}(\vec{k}) \epsilon_j^{\lambda}(\vec{k}) = \delta_{ij} - \frac{k_i k_j}{\vec{k}^2} . \tag{197}$$

which accounts for the fact that there are no longitudinal photons i.e. light is a transversal wave. Plugging in the obtained quantized $\vec{A}(x)$ into the Hamiltonian in Eq. (185) leads to a Hamiltonian of the same form as for the harmonic oscillator

$$H_{\text{free}} = \frac{1}{2} \sum_{\lambda=1}^{2} \int d^3k \, \omega_{\vec{k}} \, a^{\lambda,\dagger}(\vec{k}) a^{\lambda}(\vec{k}) , \tag{198}$$

where the δ distributions have been neglected [38].

4.3. COUPLED ELECTRON AND FIELD

After the quantization of the field, it is considered how this field can be coupled to the electron. When atoms with a low nuclear charge number Z like hydrogen are considered, it has become clear that the discussed nonrelativistic description was in fact sufficiently accurate. Therefore, it is now tempting to try and keep the nonrelativistic description of the electron while coupling it to the quantized electromagnetic field because it is much easier to handle. In principle one can just get the effect of the quantized field by using the known Schrödinger Hamiltonian in an electromagnetic field [39]. Because Coulomb gauge was used in the quantization of the field, the electric potential is unaltered by the quantization procedure and only the vector potential $\vec{A}$ has to be treated differently. Moreover, in nonrelativistic quantum mechanics time can be treated differently than space variables, which allows to use the quantized field in the Schrödinger picture where it is time-independent. The coupling term between

the electron and the field can then just be read off from the coupled Hamiltonian H_C

$$\begin{aligned} H_C &= \frac{1}{2m_e}\left(\vec{p} - e\vec{A}(\vec{x})\right)^2 - \frac{Z\alpha}{r} \\ &= \frac{\vec{p}^2}{2m_e} - e\frac{\vec{p}}{2m_e}\cdot\vec{A}(\vec{x}) - e\vec{A}(\vec{x})\cdot\frac{\vec{p}}{2m_e} + \frac{e^2}{2m_e}\vec{A}^2(\vec{x}) - \frac{Z\alpha}{r}\,. \end{aligned} \tag{199}$$

It is possible to simplify the coupling term $-e\frac{\vec{p}}{2m_e}\cdot\vec{A}(\vec{x}) - e\vec{A}(\vec{x})\cdot\frac{\vec{p}}{2m_e}$. In Coulomb gauge the vector potential and the momentum commute because of $\vec{\nabla}\cdot\vec{A}(\vec{x}) = 0$ and thus

$$H_C = \frac{\vec{p}^2}{2m_e} - e\frac{\vec{p}}{m_e}\cdot\vec{A}(\vec{x}) + \frac{e^2}{2m_e}\vec{A}^2(\vec{x}) - \frac{Z\alpha}{r}\,. \tag{200}$$

This also gives a perturbation to the Schrödinger Hamiltonian whose effects can be included using perturbation theory. In contrast to using perturbation theory with a classical field, this interaction does not just couple the electron states but also the photon states. Therefore, for a complete treatment the states have to be constructed as Fock states out of the electron state and the Fock state for the photons. This also means that the energy is given as the sum of the energy of the electron and the photon field. Consequently, the Hamiltonian which gives the energy of the intermediate states also has to give the energy of the electron and of the photon field. Thus, the unperturbed Hamiltonian is the sum of the Schrödinger Hamiltonian for the electron and the free field Hamiltonian for the photon

$$H_0 = H_S + H_{\text{free}} = \frac{p^2}{2m_e} - \frac{Z\alpha}{r} + \frac{1}{2}\sum_{\lambda=1}^{2}\int d^3k\,\omega_{\vec{k}}\,a^{\lambda,\dagger}(\vec{k})a^{\lambda}(\vec{k}) \tag{201}$$

and the interaction Hamiltonian is

$$H_I = -e\frac{\vec{p}}{m_e}\cdot\vec{A}(\vec{x}) + \frac{e^2}{2m_e}\vec{A}^2(\vec{x})\,. \tag{202}$$

Here it is restated again that all quantities are given in the Schrödinger picture, which will be employed in this calculation. A time-independent perturbation series [27, 38] in orders of the electron charge e is used.

The effect of the one-photon self-energy is to be analyzed which is represented graphically in Fig. 4.1 by the corresponding Feynman diagram. That this is the lowest order term can be seen from the fact that the first order term in e vanishes due to symmetry arguments [38]. The second order term $\frac{e^2}{2m_e}\vec{A}^2(\vec{x})$ vanishes for the same reasons. The initial state is a Fock state combined out of the state of the electron and the vacuum for the electromagnetic field, as only the effect from the field of the electron and no outer field is to be investigated. The general second order expression is

$$\Delta E_{\Phi}^{(2)} = \left\langle \Phi, 0 \left| H_I \left(\frac{1}{E_{\Phi,0} - H_0} \right)' H_I \right| \Phi, 0 \right\rangle . \tag{203}$$

Plugging in the appropriate expressions for the self-energy yields

$$\begin{aligned} \Delta E_{\Phi}^{(2)} = e^2 \Bigg\langle \Phi, 0 \Bigg| \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k'}{\sqrt{(2\pi)^3 2\omega_{\vec{k}'}}} \sum_{\lambda'=1}^{2} \Big(a^{\lambda'}(\vec{k}') \vec{\epsilon}^{\lambda'}(\vec{k}') e^{i\vec{k}'\cdot\vec{x}} \\ + a^{\lambda'\dagger}(\vec{k}') \vec{\epsilon}^{\lambda'}(\vec{k}') e^{-i\vec{k}'\cdot\vec{x}} \Big) \Bigg(\frac{1}{E_{\Phi,0} - H_S - \frac{1}{2}\sum_{\lambda'''=1}^{2} \int d^3k''' \, \omega_{\vec{k}'''} a^{\lambda,\dagger'''}(\vec{k}''') a^{\lambda'''}(\vec{k}''')} \Bigg)' \\ \times \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k''}{\sqrt{(2\pi)^3 2\omega_{\vec{k}''}}} \sum_{\lambda''=1}^{2} \Big(a^{\lambda''}(\vec{k}'') \vec{\epsilon}^{\lambda''}(\vec{k}'') e^{i\vec{k}''\cdot\vec{x}} + a^{\lambda''\dagger}(\vec{k}'') \vec{\epsilon}^{\lambda''}(\vec{k}'') e^{-i\vec{k}''\cdot\vec{x}} \Big) \Bigg| \Phi, 0 \Bigg\rangle . \end{aligned} \tag{204}$$

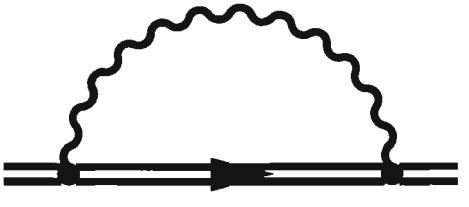

Figure 4.1. One photon self-energy of a bound electron. The double line denotes a bounded electron and the wiggly line the virtual photon.

The energy of the initial state $E_{\Phi,0}$ is just that of the electron in state Φ, E_{Φ}, because the energy of the photon vacuum is zero. Furthermore, it can be inferred that only the creation operator in the last line will give a contribution because the

annihilation operator acting on the vacuum gives zero. Thus, one photon is created out of the vacuum in the intermediate state. This photon is then annihilated again by the annihilation operator in the first line of Eq. (204). There, the creation operator gives no contribution as the photon field has to go back to its vacuum state without photons. Accordingly, the equation simplifies to

$$\begin{aligned}\Delta E_{\Phi}^{(2)} = e^2 \Bigg\langle \Phi, 0 \Bigg| \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k'}{\sqrt{(2\pi)^3 2\omega_{\vec{k}'}}} \sum_{\lambda'=1}^{2} a^{\lambda'}(\vec{k}') \vec{\epsilon}^{\lambda'}(\vec{k}') e^{\mathrm{i}\vec{k}'\cdot\vec{x}} \\ \times \left(\frac{1}{E_{\Phi,0} - H_S - \frac{1}{2}\sum_{\lambda'''=1}^{2} \int d^3k''' \, \omega_{\vec{k}'''} a^{\lambda,\dagger'''}(\vec{k}''') a^{\lambda'''}(\vec{k}''')} \right)' \\ \times \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k''}{\sqrt{(2\pi)^3 2\omega_{\vec{k}''}}} \sum_{\lambda''=1}^{2} a^{\lambda''\dagger}(\vec{k}'') \vec{\epsilon}^{\lambda''}(\vec{k}'') e^{-\mathrm{i}\vec{k}''\cdot\vec{x}} \Bigg| \Phi, 0 \Bigg\rangle .\end{aligned} \tag{205}$$

Since there is only one photon in the intermediate state, a complete basis set of the form

$$\left(\frac{1}{E_{\Phi,0} - H_0} \right)' \Bigg|_{\text{1 photon states}} = \sum_{\xi} \sum_{\lambda=1}^{2} \int d^3k \left| \xi, 1_\lambda(\vec{k}) \right\rangle \frac{1}{E_\Phi - E_\xi - \omega_{\vec{k}}} \left\langle \xi, 1_\lambda(\vec{k}) \right| \tag{206}$$

is introduced. The sum over ξ represents a sum over the complete bound spectrum as well as an integral over the complete unbound spectrum. Here, use has been made out of the earlier discussion because there can only be one photon in the intermediate state. The energy of this photon is then returned by the free field Hamiltonian and added to the energy of the intermediate electron state. The expression, thus, takes the form

$$\begin{aligned}\Delta E_{\Phi}^{(2)} = e^2 \sum_{\xi} \sum_{\lambda=1}^{2} \int d^3k \frac{1}{E_\Phi - E_\xi - \omega_{\vec{k}}} \\ \times \left\langle \Phi, 0 \left| \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k'}{\sqrt{(2\pi)^3 2\omega_{\vec{k}'}}} \sum_{\lambda'=1}^{2} a^{\lambda'}(\vec{k}') \vec{\epsilon}^{\lambda'}(\vec{k}') e^{\mathrm{i}\vec{k}'\cdot\vec{x}} \right| \xi, 1_\lambda(\vec{k}) \right\rangle \\ \times \left\langle \xi, 1_\lambda(\vec{k}) \left| \frac{\vec{p}}{m_e} \cdot \int \frac{d^3k''}{\sqrt{(2\pi)^3 2\omega_{\vec{k}''}}} \sum_{\lambda''=1}^{2} a^{\lambda''\dagger}(\vec{k}'') \vec{\epsilon}^{\lambda''}(\vec{k}'') e^{-\mathrm{i}\vec{k}''\cdot\vec{x}} \right| \Phi, 0 \right\rangle .\end{aligned} \tag{207}$$

With the relation

$$\left\langle \xi, 1_\lambda(\vec{k}) \right| \int \frac{d^3k''}{\sqrt{(2\pi)^3}} \sum_{\lambda''=1}^{2} a^{\lambda''\dagger}(\vec{k}'') \left| \Phi, 0 \right\rangle = \left\langle \xi \right| \int \frac{d^3k''}{\sqrt{(2\pi)^3}} \sum_{\lambda''=1}^{2} \delta(\vec{k} - \vec{k}'') \delta_{\lambda,\lambda''} \left| \Phi \right\rangle \quad (208)$$

this can be simplified with the result

$$\begin{aligned} \Delta E_\Phi^{(2)} = e^2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{2\omega_{\vec{k}}} \sum_{\lambda=1}^{2} \sum_{\xi} \left\langle \Phi \left| \frac{\vec{p}}{m_e} \cdot \vec{\epsilon}^{\,\lambda}(\vec{k}) e^{i\vec{k}\cdot\vec{x}} \right| \xi \right\rangle \\ \times \frac{1}{E_\Phi - E_\xi - \omega_{\vec{k}}} \left\langle \xi \left| \frac{\vec{p}}{m_e} \cdot \vec{\epsilon}^{\,\lambda}(\vec{k}) e^{-i\vec{k}\cdot\vec{x}} \right| \Phi \right\rangle . \end{aligned} \quad (209)$$

Recalling the expression in Eq. (197) for the polarization vectors $\vec{\epsilon}^{\,\lambda}(\vec{k})$ in Coulomb gauge, this can be written as

$$\begin{aligned} \Delta E_\Phi^{(2)} = e^2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{2\omega_{\vec{k}}} \left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2} \right) \sum_{\xi} \left\langle \Phi \left| \frac{p^i}{m_e} e^{i\vec{k}\cdot\vec{x}} \right| \xi \right\rangle \\ \times \frac{1}{E_\Phi - E_\xi - \omega_{\vec{k}}} \left\langle \xi \left| \frac{p^j}{m_e} e^{-i\vec{k}\cdot\vec{x}} \right| \Phi \right\rangle . \end{aligned} \quad (210)$$

Now the question arises how to deal with the exponential in the matrix element. It would be nice if an expansion of the exponential would be possible. But what would be the parameter to expand it in since it is not known whether $\vec{k}$ or $\vec{x}$ are really small. In order to figure that out, it is instructive to analyze the magnitude of momenta and energies in the process as well as the relevant length scale. The length scale is about the size of the atom which is given by the average distance of the electron from the core. This is can be found to be the Bohr radius over the nuclear charge number [38]. In SI units it is

$$\frac{a_0}{Z} = \frac{\hbar}{Z\alpha m_e c} \approx Z^{-1} 0.53 \times 10^{-10}\,\mathrm{m}\,.$$

The momentum scale is given by the momentum of the electron which is just the mass of the electron times the average velocity of the bound electron. The later can be found the easiest by a calculation using the simple Bohr model with the result

$\langle v \rangle = Z\alpha$. The momentum scale is then

$$p \sim m_e \langle v \rangle = m_e(Z\alpha)\,.$$

In SI units this gives $p \sim Z\alpha m_e c = Z \cdot 3.7\,\mathrm{keV}/c$. Following the virial theorem [39] the energy scale for the electron can be expressed in terms of its kinetic energy

$$E = \frac{p^2}{2m_e} \sim \frac{(m_e Z\alpha))^2}{m_e} = m_e(Z\alpha)^2\,.$$

This gives the well known $Z^2 \cdot 27.2\mathrm{eV}$. It is found later that it is necessary to constrain this approach to photon energies where the photon just changes the state of the electron and not its nonrelativistic behavior. Then the photon energy is about the size of the electron energy

$$|\vec{k}| \sim E \sim m_e(Z\alpha)^2\,.$$

In the efforts of finding a sensible expansion parameter, the following magnitudes for the important quantities have been derived

$$|\vec{k}| = \omega \approx E \approx m_e(Z\alpha)^2\,, \tag{211a}$$

$$|\vec{x}| \approx \frac{a_0}{Z} = (m_e Z\alpha)^{-1}\,, \tag{211b}$$

$$|\vec{p}| = m_e v \approx m_e(Z\alpha)\,. \tag{211c}$$

For the magnitude of the exponential one finds accordingly $\vec{k}\cdot\vec{x} \approx Z\alpha$. This parameter now is small, $Z\alpha \ll 1$, for systems where Z is not large. Thus, a parameter in which the exponential can be expanded is found. This expansion in powers of $Z\alpha$ gives

$$e^{-\mathrm{i}\vec{k}\cdot\vec{x}} = 1 - \underbrace{\mathrm{i}\vec{k}\cdot\vec{x}}_{(Z\alpha)} - \frac{1}{2}\underbrace{\left(\vec{k}\cdot\vec{x}\right)^2}_{(Z\alpha)^2} + \ldots\,. \tag{212}$$

This is often called a multipole expansion because in correspondence to the multipole expansion of $1/|\vec{x}-\vec{x}'|$ in classical electrodynamics [25], a scalar function is expanded into terms with increasing tensor dimension [23,25]. This means that a scalar function

is expanded into a series, where the first term transforms like a scalar i.e. 1, the second term like a vector and the third like a tensor of rank 2. In the beginning, only the lowest order term is considered. Furthermore, since the states $|\Phi\rangle$ and $|\xi\rangle$ are both eigenstates of the Schrödinger Hamiltonian, they can be expressed in terms of the quantum numbers n, ℓ, m. With the substitutions $|\Phi\rangle = |n\ell m\rangle$ and $|\xi\rangle = |n'\ell'm'\rangle$ the expression takes the form

$$\begin{aligned}\Delta E^{(2)}_{n\ell m} = e^2 \int \frac{d^3k}{(2\pi)^3}\frac{1}{2\omega_{\vec{k}}}\left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2}\right) \sum_{n'\ell'm'} \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \\ \times \frac{1}{E_n - E_{n'} - \omega_{\vec{k}}} \left\langle n'\ell'm' \left| \frac{p^j}{m_e} \right| n\ell m \right\rangle ,\end{aligned} \tag{213}$$

where E_n is written because the energy in the Schrödinger equation only depends on the principal quantum number n. In the next step the angular integration with respect to $\vec{k}$ can be carried out. For this the relations

$$\int \frac{d\Omega_{\vec{k}}}{4\pi}\delta^{ij} = \delta^{ij} , \tag{214}$$

$$\int \frac{d\Omega_{\vec{k}}}{4\pi}\frac{k^i k^j}{\vec{k}^2} = \frac{1}{3}\delta^{ij} \tag{215}$$

are required. Thus, the integration yields

$$\begin{aligned}\Delta E^{(2)}_{n\ell m} = \frac{2\alpha}{3\pi}\int_0^\infty d\omega_{\vec{k}}\,\omega_{\vec{k}} \sum_{n'\ell'm'} \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \\ \times \frac{1}{E_n - E_{n'} - \omega_{\vec{k}}} \left\langle n'\ell'm' \left| \frac{p^i}{m_e} \right| n\ell m \right\rangle ,\end{aligned} \tag{216}$$

where $|\vec{k}| = \omega_{\vec{k}}$ and $e^2 = 4\pi\alpha$ are used. Unfortunately, the derived expression diverges when the integration with respect to $\omega_{\vec{k}}$ is carried out with the given boundaries. A further investigation reveals that at the vertex where the photon is emitted (see Fig. 4.1) four-momentum is not conserved. The initial state with $p^\mu = (E, \vec{p})$ changes into an intermediate state with $p^{\mu'} = (E - \omega_{\vec{k}}, \vec{p})$. While $|\vec{k}|$ can be neglected against $|\vec{p}|$ in the region where $\omega_{\vec{k}}$ is small because of the discussion in Eq. (211), it is not possible for the region where $\omega_{\vec{k}}$ is large in the integration in Eq. (216). This implies that the procedure used to couple the nonrelativistic electron to the field is valid only

if the quantum field in the nonrelativistic limit is considered i.e. $\omega_{\vec{k}} \ll m_e$. It will be invalid as soon as $\omega_{\vec{k}}$ becomes large. In this region, the considerations which allowed to expand the exponential are also incorrect. The way to deal with this is to introduce a cutoff to the integration over $\omega_{\vec{k}}$ [27,38]. This cutoff is denoted as ϵ, which leads to

$$\begin{aligned}\Delta E^{(2)}_{L,n\ell m} = \frac{2\alpha}{3\pi}\int_0^{\epsilon} d\omega_{\vec{k}}\,\omega_{\vec{k}} \sum_{n'\ell'm'} \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \\ \times \frac{1}{E_n - E_{n'} - \omega_{\vec{k}}} \left\langle n'\ell'm' \left| \frac{p^i}{m_e} \right| n\ell m \right\rangle .\end{aligned} \tag{217}$$

In turn, this implies that Eq. (217) only describes the low-energy part of the energy shift and that the part, where large photon energies are considered, has to be treated differently. Therefore, the subscript L is used to denote that this only describes the low-energy part. With the cutoff the integration with respect to $\omega_{\vec{k}}$ can be carried out with the result

$$\begin{aligned}\Delta E^{(2)}_{L,n\ell m} = \frac{2\alpha}{3\pi} \sum_{n'\ell'm'} \left[-\epsilon + (E_{n'} - E_n) \ln \left| \frac{E_{n'} - E_n + \epsilon}{E_{n'} - E_n} \right| \right] \\ \times \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \left\langle n'\ell'm' \left| \frac{p^i}{m_e} \right| n\ell m \right\rangle .\end{aligned} \tag{218}$$

In the integration a principal value prescription has been used to deal with the poles. The poles arise when $\omega_{\vec{k}} = E_n - E_{n'}$. Using the relation

$$\frac{1}{x + \mathrm{i}\varepsilon} = P\frac{1}{x} - \mathrm{i}\pi\delta(x)\,, \tag{219}$$

where P denotes the principal value, Eq. (218) can be identified as the real part of the self-energy and the imaginary part is found to be

$$\mathrm{Im}\Delta E^{(2)}_{L,n\ell m} = -\frac{2\alpha}{3} \sum_{n'\ell'm'} (E_n - E_{n'}) \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \left\langle n'\ell'm' \left| \frac{p^i}{m_e} \right| n\ell m \right\rangle . \tag{220}$$

In this way, it becomes visible that the self-energy shift is in fact a complex number. The real part gives the energy shift while the imaginary part gives the decay rate Γ.

This is usually expressed as

$$\Delta E = \mathrm{Re}(\Delta E) - \frac{\mathrm{i}}{2}\Gamma\,. \tag{221}$$

Therefore, the one-photon decay rate is given as

$$\Gamma = \frac{4\alpha}{3} \sum_{n'\ell'm',n'<n} (E_n - E_{n'}) \left\langle n\ell m \left| \frac{p^i}{m_e} \right| n'\ell'm' \right\rangle \left\langle n'\ell'm' \left| \frac{p^i}{m_e} \right| n\ell m \right\rangle\,. \tag{222}$$

The sum has to be constraint to states with a lower energy than the initial state. Otherwise, a spontaneous decay is not possible. Using a periodic external classical field, this result can also be obtained with time-dependent perturbation theory. It is, in fact, a classical example for the application of Fermi's Golden Rule [38]. Although talking about the decay rate here may look like a detour, it is important to mention that the subtraction of the poles is a major complication if a numerical integration is used for the photon energy, especially, when highly excited states are treated which have many possible decay channels. Moreover, the two-photon decay rate will be investigated as well.

Coming back to the real part of the self-energy (Eq. (218)), a way has to be found to deal with the terms containing ϵ. There are two main ways to deal with the term linear in ϵ. The first is to subtract the self-energy of a free electron from the expression in Eq. (218). The argument is that the electron cannot be observed without the interaction with its own radiation field and therefore only differences to an electron with the interaction can be observed. This is the method employed in the original calculation by Bethe in Ref. [6]. Here, a method presented in Ref. [40] will be employed. In it ϵ acts as an overlapping parameter between the low- and high-energy part and will cancel when both parts are matched together at the end of the calculation. The real part of low-energy part is expanded in ϵ and terms which have an order higher than ϵ^0 are neglected [41]. Carrying out this expansion in Eq. (218)

yields

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,n\ell m} = \frac{2\alpha}{3\pi}\sum_{n'\ell'm'}\left[(E_{n'}-E_n)\ln\left(\frac{2\epsilon}{m_e(Z\alpha)^2}\right)-(E_{n'}-E_n)\ln\left(\frac{2|E_{n'}-E_n|}{m_e(Z\alpha)^2}\right)\right] \\ \times\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle\left\langle n'\ell'm'\left|\frac{p^i}{m_e}\right|n\ell m\right\rangle .\end{aligned} \tag{223}$$

where a scaling parameter $\frac{1}{2}m_e(Z\alpha)^2 = Z^2R_\infty$ is introduced to split the logarithm with ϵ from the finite logarithm. Dropping the complete basis set for the first expression this can be written as

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,n\ell m} = \frac{2\alpha}{3\pi}\Bigg[\left\langle n\ell m\left|\frac{p^i}{m_e}(H_S-E_n)\frac{p^i}{m_e}\right|n\ell m\right\rangle\ln\left(\frac{2\epsilon}{m_e(Z\alpha)^2}\right) \\ -\sum_{n'\ell'm'}(E_{n'}-E_n)\ln\left(\frac{2|E_{n'}-E_n|}{m_e(Z\alpha)^2}\right) \\ \times\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle\left\langle n'\ell'm'\left|\frac{p^i}{m_e}\right|n\ell m\right\rangle .\end{aligned} \tag{224}$$

The first matrix element can be expressed using a commutator [27]

$$\begin{aligned}\left\langle n\ell m\left|\frac{p^i}{m_e}(H_S-E_n)\frac{p^i}{m_e}\right|n\ell m\right\rangle &= \left\langle n\ell m\left|\left[\frac{p^i}{m_e},\left[(H_S-E_n),\frac{p^i}{m_e}\right]\right]\right|n\ell m\right\rangle \\ &= \frac{2\pi Z\alpha}{m_e^2}\left\langle n\ell m\left|\delta(\vec{x})\right|n\ell m\right\rangle = \frac{2(Z\alpha)^4m_e}{n^3} .\end{aligned} \tag{225}$$

For states with angular momentum $\ell \geq 1$, which are considered in this work, this term vanishes. The second matrix element is defined as the Bethe logarithm $\ln k_0(n,\ell)$ by

$$\begin{aligned}\ln k_0(n,\ell) = \frac{n^3}{2(Z\alpha)^4m_e}\sum_{n'\ell'm'}(E_{n'}-E_n)\ln\left(\frac{2|E_{n'}-E_n|}{m_e(Z\alpha)^2}\right) \\ \times\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle\left\langle n'\ell'm'\left|\frac{p^i}{m_e}\right|n\ell m\right\rangle .\end{aligned} \tag{226}$$

The angular integration in this expression can be carried out by employing the Wigner-Eckhart theorem [23,38]. A detailed calculation can be found in Refs. [27,42]

with the result

$$\begin{aligned}\ln k_0(n,\ell) = \frac{n^3}{2(Z\alpha)^4 m_e^3}\sum_{n'}(E_{n'}-E_n)\,\ln\!\left(\frac{2\,|E_{n'}-E_n|}{(Z\alpha)^2 m}\right)\\ \times\left\{\frac{\ell+1}{2\ell+1}\left(\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r)\right)^2\right.\\ \left.+\frac{\ell}{2\ell+1}\left(\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r)\right)^2\right\}.\end{aligned} \tag{227}$$

The low-energy part of the self-energy is then given for $\ell \geq 1$ as

$$\mathrm{Re}\Delta E^{(2)}_{L,n\ell} = -\frac{4\alpha}{3\pi}\frac{(Z\alpha)^4 m_e}{n^3}\ln k_0(n,\ell)\,, \tag{228}$$

with the Bethe logarithm $\ln k_0(n,\ell)$ which is given in Eq. (227). This expression is already known since 1947 [6] and is of order $\alpha(Z\alpha)^4\ln[(Z\alpha)^{-2}]$. From the multipole expansion of the exponential in Eq. (212) it is known that there are higher order terms in $Z\alpha$, which have not been considered, yet. Unfortunately, these multipole corrections are not the only higher order terms. Similar to the relativistic and spin corrections for the Schrödinger Hamiltonian in Eq. (164) there also are relativistic corrections to the Schrödinger Hamiltonian coupled to the quantized field. Hence, finding all corrections of order $\alpha(Z\alpha)^6\ln[(Z\alpha)^{-2}]$, requires a systematic derivation to make sure all relevant terms are discovered. A theory which provides all these term is nonrelativistic quantum electrodynamics (NRQED) [43].

NRQED is a so-called effective field theory because it is a transformation of a high-energy field theory for lower energy scales which gives the same effects but can allow for some simplifications at these lower energy scales. In the case of QED it basically decreases the resolution of the theory. For illustration let us look at the effect of vacuum polarization. Simply speaking, it means that the vacuum behaves like a dielectric medium and the real charge of the electron is screened by the dielectric vacuum. If one goes down to a very small length scale, the screening effect can be resolved and the real charge observed. At a larger length scale instead only a screened charge can be observed. However, this charge can be used as an effective charge at the length scale one works at and what happens at a smaller length scale can be ignored.

In field theory, this can be achieved by methods of the renormalization group [26]. When these are applied to QED, the renormalization scale, which is basically the resolution of the theory, is reduced down to the electron mass. Fortunately, there is an alternate way of deriving the NRQED Hamiltonian, the Foldy-Wouthuysen transformation [44] of the the full Dirac equation coupled to a fully relativistic field, which will be investigated in the next section.

4.4. FOLDY-WOUTHUYSEN TRANSFORMATION

In the last section the already known result form Bethe [6] has been re-derived for the low-energy part of the self-energy shift for a bound electron. In order to find a better approximation to the fully relativistic description of the electron, necessary for for today's accuracy in spectroscopy, corrections from the fully relativistic description have to be included. Therefore, all the relativistic correction terms to this result of relative order $(Z\alpha)^2$ have to be identified. In the calculation so far multipole corrections to Bethe's result have been found but it is not possible to guess whether these are all terms. As there are relativistic and spin corrections of the Schrödinger Hamiltonian, similar corrections for the coupling are expected as well but there should be a way to deduce these terms systematically. The Foldy-Wouthuysen transformation provides such a systematic derivation and will be able to establish the relativistic corrections to the Schrödinger equation which so far have just been explained by general arguments. Moreover, with the Foldy-Wouthuysen transformation all relevant multipole, relativistic and spin corrections to the interaction current can be deduced and even higher order corrections can be derived. Through this expansion of the relativistic theory about its nonrelativistic limit, which is physical relevant in atomic systems, effects of higher order in $Z\alpha$ can be included. These can be used for calculations in both relativistic atomic physics and nonrelativistic field theory. Although, the Foldy-Wouthuysen transformation is contained in many older textbooks, for example Refs. [35, 38], its usefulness for the derivation of relativistic corrections is rarely explored.

For a systematic derivation it is necessary to start from the fully relativistic treatment for the electron coupled to the quantized field provided by the Dirac Hamiltonian

$$H_D = \vec{\alpha} \cdot \left(\vec{p} - e\vec{A}(\vec{x}) \right) + V + \beta m_e \tag{229}$$

with $V = -Z\alpha/r$. Only in this way can it be ensured that all effects are included. The Hamiltonian is given in terms of 4×4 matrices for which the Dirac representation is used and acts on a four-component Dirac spinor. All this are major complications compared to the Schrödinger equation even when the spin is included. Consequently, the eigenstates are more complicated as well [38]. The question is whether all these complications are really necessary because the Schrödinger Hamiltonian with relativistic and spin corrections already leads to the same energy predictions as the Dirac Hamiltonian, at least for the regime $Z\alpha \ll 1$ which is considered here. An analysis of the solution of the Dirac equation also shows that in the nonrelativistic regime the upper two components are much larger than the lower two components [38]. This means that the state is mainly described by the upper two components. Unfortunately, the α matrix in front of the momentum operator leads to a mixing of the large and small components. When the larger upper components are denoted by ϕ and the smaller, lower components by η, the Dirac equation can be written as

$$H_D \begin{pmatrix} \phi \\ \eta \end{pmatrix} = \begin{pmatrix} V + m_e & \vec{\sigma} \cdot (\vec{p} - e\vec{A}) \\ \vec{\sigma} \cdot (\vec{p} - e\vec{A}) & V - m_e \end{pmatrix} \begin{pmatrix} \phi \\ \eta \end{pmatrix} . \tag{230}$$

The idea would now be to diagonalize this matrix in order to decouple the larger and smaller components of the wave function using a unitary transformation. This is the Foldy-Wouthuysen transformation. Unfortunately, a complete decoupling is not possible [35, 38]. Rather, the decoupling is only possible in orders of the bound-state potential. From the analysis of the corresponding magnitude in Eq. (211) one finds $|V| = (Z\alpha)/r \sim \mathcal{O}(Z\alpha)^2$. Interestingly, this is also the magnitude of the usual nonrelativistic expansion parameter v^2/c^2 for which $v^2/c^2 \sim \mathcal{O}(Z\alpha)^2$ is found. Therefore, the Foldy-Wouthuysen transformation also is an expansion of the Dirac Hamiltonian for nonrelativistic velocities.

For the transformation the part which mixes the components and which should be transformed way has to be found. It can be identified as the part with the α matrix and it is called the odd part $\mathcal{O}$. While terms diagonal in this sense are called the even part and labeled $\mathcal{E}$ accordingly. The β matrix is in that sense not totally classified and therefore kept as a entity. The Dirac equation can then be written in terms of these parts as

$$\begin{aligned} H_D &= \vec{\alpha} \cdot \left(\vec{p} - e\,\vec{A} \right) + V + \beta m_e \\ &= \mathcal{O} + \mathcal{E} + \beta m_e \,, \end{aligned} \tag{231}$$

In the beginning the external vector potential is set to zero, $\vec{A} = 0$. This is not really necessary but is done here for the sake of simplicity and clarity.

The odd part with the α matrix is then given as

$$\mathcal{O} = \vec{\alpha} \cdot \vec{p} \tag{232}$$

while the even part is

$$\mathcal{E} = V \,. \tag{233}$$

Since H is hermitian, so are both the odd part $\mathcal{O}$ and the even part $\mathcal{E}$.

Here, time is taken to recall the Dirac representation and some important relations for the Dirac matrices $\vec{\alpha}$ and β because they make the calculations more apparent. For β these are

$$\beta = \gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \,, \tag{234}$$

$$\beta\,\mathcal{E} = \mathcal{E}\,\beta \,, \tag{235}$$

$$\beta\,\mathcal{O} = -\mathcal{O}\,\beta \tag{236}$$

and for α

$$\vec{\alpha} = \gamma^0 \vec{\gamma} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} , \tag{237}$$

$$\alpha^i \alpha^j = \delta^{ij} + i\epsilon^{ijk}\Sigma^k , \tag{238}$$

$$\alpha^i \alpha^j + \alpha^j \alpha^i = 2\,\delta^{ij} , \tag{239}$$

$$\beta\,\vec{\alpha} = -\vec{\alpha}\,\beta . \tag{240}$$

The generator of the Poincare group is defined by

$$\Sigma^{\mu\nu} = \frac{\mathrm{i}}{2}\left[\gamma^\mu, \gamma^\nu\right] , \tag{241}$$

$$\Sigma^{\mu\nu} = -\epsilon_{\mu\nu\kappa}\Sigma^\kappa . \tag{242}$$

In the Schrödinger picture the operators are time-independent and therefore

$$\frac{\partial H}{\partial t} = 0 . \tag{243}$$

A unitary transformation U is considered which acts on the relativistic wave function

$$|\psi'\rangle = U\,|\psi\rangle . \tag{244}$$

Using this transformation to transform the Dirac equation, yields

$$\mathrm{i}\frac{\partial}{\partial t}U^\dagger\,|\psi'\rangle = H\,|\psi\rangle = HU^\dagger\,|\psi'\rangle = U^\dagger \mathrm{i}\frac{\partial}{\partial t}\,|\psi'\rangle . \tag{245}$$

From which follows

$$\mathrm{i}\frac{\partial}{\partial t}\,|\psi'\rangle = UHU^\dagger\,|\psi'\rangle = H'\,|\psi'\rangle , \tag{246}$$

if U is also time-independent

$$\frac{\partial U}{\partial t} = 0 . \tag{247}$$

The next step is to find the transformation which decouples the upper and lower components of the four spinor. The ansatz is the following [35]

$$U = e^{\mathrm{i}S} \text{ with } S = -\mathrm{i}\frac{\beta}{2m_e}\mathcal{O} \tag{248}$$

For a unitary transformation the operator S has to be hermitian and fulfill

$$U^\dagger U = e^{-\mathrm{i}S^\dagger} e^{\mathrm{i}S} = 1 \tag{249}$$

which follows from

$$S^\dagger = \mathrm{i}\frac{\mathcal{O}^\dagger\beta^\dagger}{2m_e} = \mathrm{i}\frac{\mathcal{O}\beta}{2m_e} = -\mathrm{i}\frac{\beta}{2m_e}\mathcal{O} = S\,, \tag{250}$$

using that the constituting operators are hermitian and employing the commutation relations. The transformation can be applied by employing the Baker-Campbell-Hausdorff identity which can be written as

$$H' = e^{\mathrm{i}S} H e^{-\mathrm{i}S} = \sum_{n=0}^{\infty} \frac{\mathrm{i}^n}{n!}\,{}^n[S,H]\,, \tag{251}$$

where ${}^n[S,H]$ is the n commutator of S and H (${}^0[S,H] = H$). The aim is to transform the odd terms away up to excluding order $(Z\alpha)^6$. Therefore, only terms up to that order are considered while higher order terms are neglected. The relevant terms (commutators) are all given in Ref. [35]. The first commutator is explicitly discussed for illustrative purposes here

$$\mathrm{i}[S,H] = -\mathcal{O} + \frac{\beta}{2m_e}[\mathcal{O},\mathcal{E}] + \frac{1}{m_e}\beta\mathcal{O}^2\,. \tag{252}$$

Evidently from Eq. (252) the odd term in Eq. (231) is canceled. However, new odd terms of higher order arise. The new Hamiltonian after the first transformation up to order $(Z\alpha)^4$ is now given as

$$\begin{aligned} H' &= \beta\left(m_e + \frac{\mathcal{O}^2}{2m_e} - \frac{\mathcal{O}^4}{8m_e^3}\right) + \mathcal{E} - \frac{1}{8m_e^3}[\mathcal{O},[\mathcal{O},\mathcal{E}]] + \frac{\beta}{2m_e}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m_e^2} \\ &= \beta m_e + \mathcal{E}' + \mathcal{O}'\,. \end{aligned} \tag{253}$$

The new odd part

$$\mathcal{O}' = \frac{\beta}{2m_e}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m_e^2} \tag{254}$$

is of order $(Z\alpha)^4$. In order to get rid of this part as well, another transformation is required. The procedure is exactly the same as before and therefore the generator of the transformation is chosen to be

$$S' = -\mathrm{i}\frac{\beta}{2m_e}\mathcal{O}' = -\mathrm{i}\frac{\beta}{2m_e}\left(\frac{\beta}{2m_e}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m_e^2}\right). \tag{255}$$

Again, the first commutator is considered explicitly

$$\begin{aligned}\mathrm{i}[S',H'] = &-\frac{\beta}{2m_e}[\mathcal{O},\mathcal{E}] + \frac{1}{8m_e^3}[[\mathcal{O},\mathcal{E}],\beta\mathcal{O}^2] + \frac{1}{4m_e^2}[[\mathcal{O},\mathcal{E}],\mathcal{E}] - \frac{\beta}{4m_e^3}[\mathcal{O},\mathcal{E}]^2 \\ &+ \frac{\mathcal{O}^3}{3m_e^2} + \frac{\beta}{6m_e^3}[\mathcal{E},\mathcal{O}^3]\,,\end{aligned} \tag{256}$$

where terms of higher order than $(Z\alpha)^4$ are neglected again. For the second transformation only this commutator is required and the transformed Hamiltonian is obtained as

$$H_{\mathrm{FW}} = \beta\left(m_e + \frac{\mathcal{O}^2}{2m_e} - \frac{\mathcal{O}^4}{8m_e^3}\right) + \mathcal{E} - \frac{1}{8m_e^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]]\,. \tag{257}$$

With the definitions in Eqs. (232) and (233) of $\mathcal{O}$ and $\mathcal{E}$ the double commutator can be evaluated and gives

$$\begin{aligned}[\vec{\alpha}\cdot\vec{p},[\vec{\alpha}\cdot\vec{p},V]] &= [\vec{\alpha}\cdot\vec{p},\vec{\alpha}\cdot\vec{p}V - V\vec{\alpha}\cdot\vec{p}] \\ &= [\vec{\alpha}\cdot\vec{p},\alpha^j p^j[V]] = [\vec{\alpha}\cdot\vec{p},-\mathrm{i}\alpha^j\frac{Z\alpha}{r^3}x^j] \\ &= -\mathrm{i}Z\alpha\left(\alpha^i p^i\alpha^j\frac{x^j}{r^3} - \alpha^j\frac{x^j}{r^3}\alpha^i p^i\right) \\ &= -\mathrm{i}Z\alpha\left(\alpha^i\alpha^j p^i\frac{x^j}{r^3} - \alpha^j\alpha^i\frac{x^j}{r^3}p^i\right)\,,\end{aligned} \tag{258}$$

where $p \to -\mathrm{i}\nabla$ has been used. While the α matrices can be combined applying the relations in Eq. (238)

$$\begin{aligned}
[\vec{\alpha}\cdot\vec{p},[\vec{\alpha}\cdot\vec{p},V]] &= -\mathrm{i}Z\alpha\left(\delta^{ij}p^i\frac{x^j}{r^3}+\mathrm{i}\epsilon^{ijk}p^i\frac{x^j}{r^3}\Sigma^k-\delta^{ji}\frac{x^j}{r^3}p^i-\mathrm{i}\epsilon^{jik}\frac{x^j}{r^3}p^i\Sigma^k\right)\\
&= Z\alpha\left(-4\pi\delta(\vec{x})+\epsilon^{ijk}p^i\frac{x^j}{r^3}\Sigma^k-\epsilon^{jik}\frac{x^j}{r^3}p^i\Sigma^k\right)\\
&= Z\alpha\left(-4\pi\delta(\vec{x})-\frac{2}{r^3}\epsilon^{kji}\Sigma^k x^j p^i\right)\\
&= -Z\alpha 4\pi\delta(\vec{x})-\frac{2Z\alpha}{r^3}\left(\vec{\Sigma}\cdot\vec{\ell}\right)
\end{aligned} \tag{259}$$

obtained with the known identities

$$p^iV = p^i[V]+Vp^i, \tag{260}$$

$$\nabla^i\frac{x^i}{r^3} = 4\pi\delta(\vec{x}) \tag{261}$$

and the properties of the ϵ tensor. Finally, the Foldy-Wouthuysen transformation yields the Hamiltonian

$$H_{\mathrm{FW}} = \gamma^0\left(m_e+\frac{\vec{p}^2}{2m_e}-\frac{(\vec{p}^2)^2}{8m_e^3}\right)+V+\frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x})+\frac{Z\alpha}{4m_e^2r^3}\vec{\Sigma}\cdot\vec{\ell}+\mathcal{O}((Z\alpha)^6)\,. \tag{262}$$

For the upper components this gives

$$\begin{aligned}
H^u_{\mathrm{FW}} &= m_e+\underbrace{\frac{\vec{p}^2}{2m_e}+V}_{(Z\alpha)^2m_e}\underbrace{-\frac{(\vec{p}^2)^2}{8m_e^3}+\frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x})+\frac{Z\alpha}{4m_e^2r^3}\vec{\sigma}\cdot\vec{\ell}}_{(Z\alpha)^4m_e}+\mathcal{O}((Z\alpha)^6)\\
&= m_e+H_S+\delta H_S+\mathcal{O}((Z\alpha)^6)\,.
\end{aligned} \tag{263}$$

When the wave function is constraint to the upper components, the relativistic corrections to the Schrödinger Hamiltonian have been derived because the correction terms of order $(Z\alpha)^4m_e$ are found to be identical to δH_S. For the lower components the Foldy-Wouthuysen Hamiltonian has the form

$$H^l_{\mathrm{FW}} = -m_e-\frac{\vec{p}^2}{2m_e}+V+\frac{(\vec{p}^2)^2}{8m_e^3}+\frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x})+\frac{Z\alpha}{4m_e^2r^3}\vec{\sigma}\cdot\vec{\ell}+\mathcal{O}((Z\alpha)^6)\,. \tag{264}$$

It is visible that the potential here is repulsive because it has the opposite sign of m_e and $p^2/2m_e$. The Hamiltonian therefore describes positrons, which cannot arise at low energy. Accordingly, the lower components can be neglected.

The Foldy-Wouthuysen transformation thus is a general approach to deduce relativistic and other corrections. It not only provides a systematic derivation for the relativistic and spin correction terms for a bound electron, it also allows to derive higher order terms if necessary. Even the relativistic, spin and multipole corrections to the nonrelativistic current can be obtained when the same transformation acts on the relativistic current. The transformation of the current will be considered next.

4.4.1. Transformation of the Current. There are in fact two ways to calculate the relativistic corrections to the interaction Hamiltonian. Here, it is discussed how these terms can be obtained by applying the Foldy-Wouthuysen to the relativistic current which couples to the vector potential. In this way relativistic corrections $\delta\vec{j}$ to the nonrelativistic current operator $\vec{j} = \vec{p}/m_e$ are obtained. The relativistic current is [42]

$$\vec{y} = \vec{\alpha} \exp\left[\mathrm{i}\vec{k} \cdot \vec{x}\right] \tag{265}$$

The application of the transformation follows the same steps as for the Hamiltonian. Again, there is no time-dependence. The transformation is then

$$y^j_{\mathrm{FW}} = U y^j U^{-1} = e^{\mathrm{i}S} y^j e^{-\mathrm{i}S}. \tag{266}$$

The Foldy-Wouthuysen transformation of the currents has to use the same transformations as for the Hamiltonian and only terms up to order $(Z\alpha)^4$ are kept. To facilitate this, the current is expanded in $Z\alpha$ first. For the expansion it is important to note the order in $Z\alpha$ of $\vec{k}$ is $\mathcal{O}((Z\alpha)^2)$ and the order of $\vec{r}$ is $\mathcal{O}((Z\alpha)^{-1})$. Therefore, the expansion of the exponential is also an expansion in $Z\alpha$. The terms in each order

are

$$y_0^j = \alpha^j \tag{267}$$

$$y_1^j = \alpha^j (i\vec{k}\cdot\vec{x}) \tag{268}$$

$$y_2^j = \alpha^j \frac{1}{2}(i\vec{k}\cdot\vec{x})^2. \tag{269}$$

In principle, the term y_3^j is of order $(Z\alpha)^4$. Because it is odd, it is neglected as later all odd current terms are neglected. The reason is that because the small component of the wave function, which it couples to, is suppressed by $(Z\alpha)^4$ and, therefore, these term are of a higher order. Let us recall the first Foldy-Wouthuysen transformation

$$S = -\mathrm{i}\beta\frac{\mathcal{O}}{2m_e} = -\mathrm{i}\gamma^0\frac{\vec{\alpha}\cdot\vec{p}}{2m_e}. \tag{270}$$

Here, all commutators are considered as they are rather simple. They are

$$\mathrm{i}[S,\alpha^j] = \frac{\gamma^0}{m_e}p^j \tag{271}$$

$$-\frac{1}{2}[S,[S,\alpha^j]] = -\frac{1}{2m_e^2}(p^j\vec{\alpha}\cdot\vec{p}) \tag{272}$$

$$-\frac{\mathrm{i}}{6}[S,[S,[S,\alpha^j]]] = -\frac{\gamma^0}{6m_e^3}(p^j\vec{p}^2)\,. \tag{273}$$

Accordingly, for the lowest order current operator it is found

$$y_0' = \alpha^j + \frac{\gamma^0}{m_e}p^j - \frac{1}{2m_e^2}p^j(\vec{\alpha}\cdot\vec{p}) - \frac{\gamma^0}{6m_e^3}(p^j\vec{p}^2)\,. \tag{274}$$

The second transformation is

$$S' = -\mathrm{i}\frac{\gamma^0}{2m_e}\left(\frac{\gamma^0}{2m_e}[\vec{\alpha}\cdot\vec{p},V] \neg \frac{(\vec{\alpha}\cdot\vec{p})^3}{3m_e^2}\right) \tag{275}$$

and again only the first commutator is relevant up to the considered order

$$y'' = y' + \mathrm{i}[S',y'] + \text{higher order}\,. \tag{276}$$

Actually of the first commutator only the α^j term is relevant for y_0' since all other terms would be of higher order. The commutator is then

$$\begin{aligned} \mathrm{i}[S', y_0'] = \mathrm{i}[S', \alpha^j] &= [\left(\frac{1}{4m_e^2}[\vec{\alpha}\cdot\vec{p}, V] - \frac{\gamma^0(\vec{\alpha}\cdot\vec{p})^3}{6m_e^3}\right), \alpha^j] \\ &= \frac{1}{2m_e^2}\left([p^j, V] - \alpha^j[\vec{\alpha}\cdot\vec{p}, V]\right) - \frac{1}{3m_e^3}(p^j\vec{p}^2). \end{aligned} \tag{277}$$

Plugging in Eqs. (277) and (274) into Eq. (276) yields

$$\begin{aligned} y^j_{0,\mathrm{FW}} = \alpha^j &+ \gamma^0\left(\frac{p^j}{m_e} - \frac{1}{2m_e^3}(p^j\vec{p}^2)\right) - \frac{1}{2m_e^2}p^j(\vec{\alpha}\cdot\vec{p}) \\ &- \frac{1}{2m_e^2}\alpha^j[\vec{\alpha}\cdot\vec{p}, V] + \frac{1}{2m_e^2}[p^j, V]. \end{aligned} \tag{278}$$

For the terms y_1^j and y_2^j only the commutator with S has to be considered. All other contributions are of a higher order. Consequently, in the second transformation in Eq. (276) only the y' term is relevant and no commutator has to be calculated. At first y_1^j is calculated which is given as

$$\begin{aligned} y^j_{1,\mathrm{FW}} = y_1^j + \mathrm{i}[S, y_1^j] &= \alpha^j(i\vec{k}\cdot\vec{x}) + \mathrm{i}[-\mathrm{i}\frac{\beta}{2m_e}\vec{\alpha}\cdot\vec{p}, \alpha^j(i\vec{k}\cdot\vec{x})] \\ &= \alpha^j(\mathrm{i}\vec{k}\cdot\vec{x}) + \frac{\beta}{2m_e}\vec{\alpha}\cdot\vec{p}\,\alpha^j(\mathrm{i}\vec{k}\cdot\vec{x}) - \alpha^j(\mathrm{i}\vec{k}\cdot\vec{x})\frac{\beta}{2m_e}\vec{\alpha}\cdot\vec{p} \\ &= \alpha^j(\mathrm{i}\vec{k}\cdot\vec{x}) + \frac{\mathrm{i}\beta}{2m_e}\left(\vec{\alpha}\cdot\vec{p}\,\alpha^j(\vec{k}\cdot\vec{x}) + \alpha^j(\vec{k}\cdot\vec{x})\vec{\alpha}\cdot\vec{p}\right). \end{aligned} \tag{279}$$

From Eq. (239) one can derive $\alpha^i\alpha^j = 2\delta^{ij} - \alpha^j\alpha^i$, which simplifies Eq. (279) to

$$\begin{aligned} y^j_{1,\mathrm{FW}} &= \alpha^j(\mathrm{i}\vec{k}\cdot\vec{x}) + \frac{\mathrm{i}\beta}{2m_e}\left(2\delta^{ij}p^i(\vec{k}\cdot\vec{x}) - \alpha^j\alpha^i\,p^i(\vec{k}\cdot\vec{x}) + \alpha^j(\vec{k}\cdot\vec{x})(\alpha^i\,p^i)\right) \\ &= \alpha^j(\mathrm{i}\vec{k}\cdot\vec{x}) + \frac{\mathrm{i}\beta}{2m_e}\left(-\alpha^j[\vec{\alpha}\cdot\vec{p}, \vec{k}\cdot\vec{x}] + 2p^j(\vec{k}\cdot\vec{x})\right). \end{aligned} \tag{280}$$

Again, substituting the momentum operator $p \longrightarrow -\mathrm{i}\nabla$, yields the expression

$$y^j_{1,\mathrm{FW}} = \alpha^j(i\vec{k}\cdot\vec{x}) + \frac{\mathrm{i}\beta}{2m_e}\left(-\alpha^j[\vec{\alpha}\cdot\vec{p}, \vec{k}\cdot\vec{x}] + 2(\vec{k}\cdot\vec{x})p^j - 2\mathrm{i}\,k^j\right). \tag{281}$$

An analogue calculation for y_2^j leads to

$$\begin{aligned} y_{2,\mathrm{FW}}^j &= -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 + \mathrm{i}[S, y_2^j] \\ &= -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 - \frac{1}{4m_e}\left(\beta\vec{\alpha}\cdot\vec{p}\,\alpha^j(\vec{k}\cdot\vec{x})^2 - \alpha^j(\vec{k}\cdot\vec{x})^2\beta\vec{\alpha}\cdot\vec{p}\right) \\ &= -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 - \frac{\beta}{4m_e}\left(\alpha^i\,p^i\alpha^j(\vec{k}\cdot\vec{x})^2 + \alpha^j(\vec{k}\cdot\vec{x})^2\alpha^i\,p^i\right) \\ &= -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 - \frac{\beta}{4m_e}\left(2\delta^{ij}p^i(\vec{k}\cdot\vec{x})^2 - \alpha^j\vec{\alpha}\cdot\vec{p}(\vec{k}\cdot\vec{x})^2 + \alpha^j(\vec{k}\cdot\vec{x})^2\vec{\alpha}\cdot\vec{p}\right) \\ &= -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 - \frac{\beta}{4m_e}\left(2p^j(\vec{k}\cdot\vec{x})^2 - \alpha^j[\vec{\alpha}\cdot\vec{p}, (\vec{k}\cdot\vec{x})^2]\right). \end{aligned} \tag{282}$$

This is rewritten to

$$y_{2,\mathrm{FW}}^j = -\frac{\alpha^j}{2}(\vec{k}\cdot\vec{x})^2 - \frac{\beta}{4m_e}\left(2(\vec{k}\cdot\vec{x})^2p^j + 2[p^j, (\vec{k}\cdot\vec{x})^2] - \alpha^j[\vec{\alpha}\cdot\vec{p}, (\vec{k}\cdot\vec{x})^2]\right). \tag{283}$$

In the following, the odd terms in these expressions will be neglected. For the final expression of the y_{FW}, the remaining products and commutators containing α matrices will be evaluated with the result

$$\begin{aligned} \alpha^j[\vec{\alpha}\cdot\vec{p}, V] &= \alpha^j\alpha^ip^iV - \alpha^jV\alpha^ip^i \\ &= p^i\delta^{ji}V + \mathrm{i}\epsilon^{jik}p^iV\Sigma^k - Vp^i\delta^{ji} - \mathrm{i}\epsilon^{jik}Vp^i\Sigma^k \\ &= [p^j, V] + \mathrm{i}\epsilon^{jik}p^i[V]\Sigma^k, \end{aligned} \tag{284}$$

where in the second step Eq. (238) and in the following step Eq. (260) have been used. The known relation

$$p^i[V] = -\mathrm{i}\nabla^i\left[-\frac{Z\alpha}{r}\right] = -\mathrm{i}\frac{Z\alpha}{r^3}x^i \tag{285}$$

is recalled, which is applied together with the definition of the cross product using the ϵ tensor, to yield

$$\alpha^j[\vec{\alpha}\cdot\vec{p}, V] = [p^j, V] + \frac{Z\alpha}{r^3}\left(\vec{x}\times\vec{\Sigma}\right)^j. \tag{286}$$

The other commutators give analogous

$$\begin{aligned}\alpha^j[\vec{\alpha}\cdot\vec{p},\vec{k}\cdot\vec{x}] &= \alpha^j\alpha^i p^i(\vec{k}\cdot\vec{x}) - \alpha^j(\vec{k}\cdot\vec{x})\alpha^i p^i \\ &= \delta^{ji}p^i[\vec{k}\cdot\vec{x}] + \mathrm{i}\epsilon^{jik}p^i[\vec{k}\cdot\vec{x}]\Sigma^k \\ &= -\mathrm{i}k^j + \epsilon^{jik}k^i\Sigma^k = -\mathrm{i}k^j + \left(\vec{k}\times\vec{\Sigma}\right)^j\end{aligned} \tag{287}$$

and

$$\begin{aligned}\alpha^j[\vec{\alpha}\cdot\vec{p},(\vec{k}\cdot\vec{x})^2] &= \alpha^j\alpha^i p^i(\vec{k}\cdot\vec{x})^2 - \alpha^j(\vec{k}\cdot\vec{x})^2\alpha^i p^i \\ &= \delta^{ji}p^i(\vec{k}\cdot\vec{x})^2 + \mathrm{i}\epsilon^{jik}p^i[(\vec{k}\cdot\vec{x})^2]\Sigma^k - (\vec{k}\cdot\vec{x})^2\delta^{ji}p^i \\ &= [p^j,(\vec{k}\cdot\vec{x})^2] + 2\epsilon^{jik}(\vec{k}\cdot\vec{x})k^i\Sigma^k \\ &= [p^j,(\vec{k}\cdot\vec{x})^2] + 2(\vec{k}\cdot\vec{x})\left(\vec{k}\times\vec{\Sigma}\right)^j .\end{aligned} \tag{288}$$

After the transformation the lower components are suppressed by $(Z\alpha)^4$ and therefore the odd terms which couple to the lower components can be neglected. Thus, the Hamiltonian can be constrained to the upper components and, therefore, only the upper components of all matrices i. e. $\gamma^0 \to 1$ and $\vec{\Sigma} \to \vec{\sigma}$ are considered. The final result for the currents $y^j_{i,FW}$ is then

$$y^j_{0,\mathrm{FW}} = \frac{p^j}{m_e} - \frac{1}{2m_e^3}p^j\vec{p}^2 - \frac{1}{2m_e^2}\frac{Z\alpha}{r^3}\left(\vec{x}\times\vec{\sigma}\right)^j , \tag{289a}$$

$$y^j_{1,\mathrm{FW}} = -\frac{\mathrm{i}}{2m_e}\left(\vec{k}\times\vec{\sigma}\right)^j + \frac{\mathrm{i}}{m_e}\left(\vec{k}\cdot\vec{x}\right)p^j + \frac{k^j}{2m_e}, \tag{289b}$$

$$y^j_{2,\mathrm{FW}} = -\frac{1}{2m_e}\left(\vec{k}\cdot\vec{x}\right)^2 p^j + \frac{1}{2m_e}\left(\vec{k}\cdot\vec{x}\right)\left(\vec{k}\times\vec{\sigma}\right)^j + \frac{1}{2m_e}[p^j,(\vec{k}\cdot\vec{x})^2] . \tag{289c}$$

Through the Foldy-Wouthuysen transformation the corrections to the nonrelativistic current p^j/m_e have been derived. The second term in Eq. (289a) gives the correction due to the relativistic momentum and the third is the correction due to the physical momentum $\vec{p} - e\vec{A}$ coupling to the spin. The first term in Eq. (289b) gives the coupling of the spin to the magnetic field of the quantized field and the second one is the dipole correction to the coupling. The first term of Eq. (289c) is an octupole correction, while the second is a quadrupole correction to the magnetic coupling. The last terms of both Eq. (289b) and Eq. (289c) are terms arising from commutators of

p and multipole corrections and vanish when contracted with $\delta^{ij} - k^i k^j/\vec{k}^2$. These current corrections are relevant for the correction of the interaction current for both the coupling to virtual photons, which give rise to the QED corrections, as well as for the coupling to real photons, which lead to relativistic corrections in atomic physics.

4.4.2. Alternative Derivation. For simplicities sake, only the separate transformations of the Hamiltonian without a quantized radiation field and the relativistic current coupling to this quantized field have been considered. It is nevertheless possible to transform the complete Hamiltonian of a bound electron coupled to the quantized field. It is however better to start from a modified Hamiltonian which includes not only the coupling of the electron to the quantized radiation field but also contains the major QED radiative corrections [26]. In fact for some applications it is even necessary to use the transformation of the complete Hamiltonian because only in this way certain terms can be obtained, namely the seagull terms. The details of the calculation can be found in Ref. [45] or in Eq. (2.9b) of Ref. [46]. Following the analogue procedure, one obtains the Foldy-Wouthuysen Hamiltonian up to order including order of $(Z\alpha)^4$ which is

$$\begin{aligned} H_{\mathrm{FW}}^{m} = & \frac{(\vec{p}-e\vec{A})^2}{2m_e} + V - \frac{e}{2m_e}\vec{\sigma}\cdot\vec{B} - \frac{(\vec{p}-e\vec{A})^4}{8m_e^3} + \frac{1}{8m_e^2}\vec{\nabla}^2 V \\ & + \frac{e}{8m_e^2}\frac{\partial}{\partial t}\vec{\nabla}\cdot\vec{A} + \frac{e}{8m_e^2}\left[\vec{\sigma}\cdot(\vec{\nabla}V\times\vec{p}) - \vec{\sigma}\cdot(\vec{p}\times\vec{\nabla}V)\right] \\ & + \frac{e}{4m_e^2}\vec{\sigma}\cdot\left(\frac{\partial}{\partial t}\vec{A}\times\vec{p}\right) - \frac{e}{4m_e^2}\vec{\sigma}\cdot\left(\vec{\nabla}V\times\vec{A}\right) + \mathcal{O}((Z\alpha)^6)\,. \end{aligned} \tag{290}$$

For $\vec{A} = 0$, this again yields Eq. (262). It is important to note that in the nonrelativistic Schrödinger equation in an electromagnetic field the interaction parts are the ones related to the vector potential $\vec{A}$. Alternatively, this can be seen from the normal coupling interaction Hamiltonian to the radiation field which is given as $H_{\mathrm{int}} = -e\vec{j}\cdot\vec{A}$. In fact, it is basically derived form the above. In the same way the relativistic corrections to this interaction Hamiltonian can be obtained by taking the terms linear

in $\vec{A}$ which yields

$$\begin{aligned} H_{\text{int}} &= -\frac{e\vec{A}\cdot\vec{p}}{m_e} - \frac{e}{2m_e}\vec{\sigma}\cdot\left(\vec{\nabla}\times\vec{A}\right) - \frac{e\vec{A}\cdot\vec{p}\vec{p}^2}{2m_e^3} + \frac{e}{4m_e^2}\vec{\sigma}\cdot\left(\frac{\partial}{\partial t}\vec{A}\times\vec{p}\right) - \frac{e}{4m_e^2}\vec{\sigma}\cdot\left(\vec{\nabla}V\times\vec{A}\right) \\ &= -\frac{e\vec{A}\cdot\vec{p}}{m_e} - \frac{e}{2m_e}\left(\vec{\sigma}\times\vec{\nabla}\right)\cdot\vec{A} - e\frac{\vec{A}\cdot\vec{p}\vec{p}^2}{2m_e^3} - \frac{e}{4m_e^2}(\vec{\sigma}\times\vec{p})\cdot\frac{\partial}{\partial t}\vec{A} - \frac{e}{4m_e^2}\left(\vec{\sigma}\times\vec{\nabla}V\right)\cdot\vec{A} \\ &= -e\vec{j}\cdot\vec{A}. \end{aligned} \tag{291}$$

Note that because Coulomb gauge is used, one has $\vec{\nabla}\cdot\vec{A} = 0$. For the action of the ∇ operator the expression for the quantized radiation field in Eq. (194) is considered.

For the annihilation part, this means $\vec{\nabla}\exp(\mathrm{i}\vec{k}\cdot\vec{x}) = i\vec{k}\exp(\mathrm{i}\vec{k}\cdot\vec{x})$. Furthermore the exponentials are again expanded in their argument as mentioned before this corresponds to a $Z\alpha$-expansion. So up to and including order $(Z\alpha)^4$ the following current is obtained

$$\begin{aligned} j^j = &\frac{p^j}{m_e}\left(1 + \mathrm{i}\vec{k}\cdot\vec{x} - \tfrac{1}{2}(\vec{k}\cdot\vec{x})^2\right) + \frac{\mathrm{i}}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^j\left(1 + \mathrm{i}\vec{k}\cdot\vec{x}\right) \\ &- \frac{p^j\vec{p}^2}{2m_e^3} - \frac{\mathrm{i}\omega}{4m_e^2}(\vec{\sigma}\times\vec{p})^j - \frac{1}{4m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})^j\ . \end{aligned} \tag{292}$$

While the result in the last section was

$$\begin{aligned} j^j = &\frac{p^j}{m}\left(1 + \mathrm{i}\vec{k}\cdot\vec{x} - \tfrac{1}{2}(\vec{k}\cdot\vec{x})^2\right) + \frac{\mathrm{i}}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^j\left(1 + \mathrm{i}\vec{k}\cdot\vec{x}\right) \\ &- \frac{p^j\vec{p}^2}{2m_e^3} - \frac{1}{2m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})^j \end{aligned} \tag{293}$$

On the first glance these are different, but it can be shown that they are equivalent using the relation

$$\langle\phi| - \frac{\mathrm{i}}{4m_e^2}(\vec{\sigma}\times\vec{p})\,\omega = \langle\phi| - \frac{\mathrm{i}}{4m_e^2}(\vec{\sigma}\times\vec{p})\,[(H_S - E_S + \omega) - (H_S - E_S)]. \tag{294}$$

Now the term with $(H_S - E_S + \omega)$ does not give a finite contribution to the low-energy part of the self-energy. So one has

$$\begin{aligned}\langle\phi|\frac{\mathrm{i}}{4m_e^2}(\vec{\sigma}\times\vec{p})(H_S-E_S) &= \langle\phi|\frac{\mathrm{i}}{4m_e^2}(\vec{\sigma}\times[\vec{p},(H_S-E_S)]) \\ &= \langle\phi|\frac{1}{4m_e^2}\left(\vec{\sigma}\times\vec{\nabla}V\right) \\ &= \langle\phi|\frac{Z\alpha}{4m_e^2 r^3}(\vec{\sigma}\times\vec{x})\ . \end{aligned} \tag{295}$$

The term can then be combined with the last term in Eq. (292). With a few more transformations described in Ref. [42], finally the two results coincide and can be further simplified with the result

$$j^j = \frac{p^j}{m_e}\left(1+\mathrm{i}\vec{k}\cdot\vec{x}-\tfrac{1}{2}(\vec{k}\cdot\vec{x})^2\right) - \frac{p^j\vec{p}^2}{2m_e^3} - \frac{1}{4m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})^j\ , \tag{296}$$

with the current correction

$$\delta j^j = \frac{p^j}{m_e}\left(\mathrm{i}\vec{k}\cdot\vec{x}-\tfrac{1}{2}(\vec{k}\cdot\vec{x})^2\right) - \frac{p^j\vec{p}^2}{2m_e^3} - \frac{1}{4m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})^j\ . \tag{297}$$

The terms proportional to $\vec{A}^2$ in Eq. (290) give the seagull terms which describe the simultaneous emission of two-photons. They are proportional to $e^2 = 4\pi\alpha$ and two-loop effects, thus they appear in a different order in perturbation theory.

4.5. LOW-ENERGY PART

So far the low-energy part of the self-energy is found to be

$$\mathrm{Re}\Delta E^{(2)}_{L,n\ell} = -\frac{4\alpha}{3\pi}\frac{(Z\alpha)^4 m_e}{n^3}\ln k_0(n,\ell)\,, \tag{298}$$

which was derived from the expression

$$\mathrm{Re}\Delta E^{(2)}_{L,\Phi} = \int_{\omega_{\vec{k}}<\epsilon}\frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\tilde{P}^{ij}\,. \tag{299}$$

$\tilde{P}^{ij}$ has been used therein to denote the matrix element

$$\tilde{P}^{ij} = \langle\Phi| \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} |\Phi\rangle \ . \tag{300}$$

The expression is of order $\alpha(Z\alpha)^4 \ln[(Z\alpha)^{-2}]$. In this section the aim is to obtain the self-energy shift up to order $\alpha(Z\alpha)^6 \ln[(Z\alpha)^{-2}]$ by including correction terms to Bethe's result. In the last section the Foldy-Wouthuysen transformation yielded a complete expression for the multipole, spin and relativistic corrections up to relative order $(Z\alpha)^2$ to the current. This correction has to be added in the matrix element by changing the current operator from p^i/m_e to $p^i/m_e + \delta j^i$ with

$$\delta j^j = \frac{p^j}{m_e} \left(\mathrm{i}\vec{k} \cdot \vec{x} - \tfrac{1}{2}(\vec{k} \cdot \vec{x})^2 \right) - \frac{p^j \vec{p}^2}{2m_e^3} - \frac{1}{4m_e^2} \frac{Z\alpha}{r^3} (\vec{x} \times \vec{\sigma})^j \ . \tag{301}$$

The Foldy-Wouthuysen transformation not only allowed to find the correction to the current but also the correction to the Schrödinger Hamiltonian. This correction is also of relative order $(Z\alpha)^2$ with respect to the Schrödinger Hamiltonian and therefore also has to be included in all corrections of relative order $(Z\alpha)^2$ to Eq. (300) and changes the Hamiltonian from H_S to $H_S + \delta H_S$ with

$$\delta H_S = -\frac{(\vec{p}^2)^2}{8m_e^3} + \frac{\pi Z\alpha}{2m_e^2} \delta(\vec{x}) + \frac{Z\alpha}{4m_e^2 r^3} \vec{\sigma} \cdot \vec{\ell} . \tag{302}$$

This correction to the Hamiltonian also leads to a correction of the energy of the initial state of the same order which has to be altered from E_Φ to $E_\Phi + \delta E$ with $\delta E = \langle\Phi|\delta H|\Phi\rangle$ in first order of perturbation theory. Another effect of relative order $(Z\alpha)^2$ of δH_S to Eq. (300) is a correction to the wave function. The first order perturbation to the wave function can be obtained by [38]

$$|\delta\Phi\rangle = \left(\frac{1}{E_\Phi - H_S} \right)' \delta H_S |\Phi\rangle \ . \tag{303}$$

Including all the corrections Eq. (300) takes the form

$$\begin{aligned}\tilde{P}^{ij} = \langle \Phi + \delta\Phi | \left\{ \frac{p^i}{m_e} + \delta j^i \right\} \frac{1}{E_\Phi + \delta E - H_S - \delta H_S - \omega_{\vec{k}}} \\ \times \left\{ \frac{p^j}{m_e} + \delta j^j \right\} | \Phi + \delta\Phi \rangle \ .\end{aligned} \tag{304}$$

In order to find the right expression for the corrections to Bethe's result [6] in order $\alpha(Z\alpha)^6 \ln[(Z\alpha)^{-2}]$, the matrix element above has to be expanded such that only one correction term of relative order $(Z\alpha)^2$ appears in the resulting matrix elements. A term containing two such correction terms would be of relative order $(Z\alpha)^4$ which is a too high order for our analysis here. This can be achieved by writing

$$\begin{aligned}\tilde{P}^{ij} = & \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} | \Phi \rangle \\ & + 2 \cdot \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \delta j^j | \Phi \rangle \\ & - \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \delta E \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} | \Phi \rangle \\ & + \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \delta H_S \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} | \Phi \rangle \\ & + 2 \cdot \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} | \delta\Phi \rangle + \mathcal{O}((Z\alpha)^4) \, .\end{aligned} \tag{305}$$

The first term is the leading term and leads to the discussed result by Bethe

$$\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nd} = \int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3} \frac{2\pi\alpha}{\omega_{\vec{k}}} \left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2} \right) \langle \Phi | \frac{p^i}{m_e} \frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \frac{p^j}{m_e} | \Phi \rangle \, . \tag{306}$$

All the other terms are now all corrections to this result of relative order $(Z\alpha)^2$. Due to the Foldy-Wouthuysen transformation one can be sure that no term has been forgotten. In the following all these correction term will be listed. The first term

comes from the formerly neglected higher multipoles which gives

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\left\{\langle\Phi|\frac{p^i}{m_e}\left(\mathrm{i}\vec{k}\cdot\vec{x}\right)\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}\left(-\mathrm{i}\vec{k}\cdot\vec{x}\right)|\Phi\rangle\right.\\ &\left.-\langle\Phi|\frac{p^i}{m_e}\left(\vec{k}\cdot\vec{x}\right)^2\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\right\}.\end{aligned} \tag{307}$$

Then there are the relativistic momentum correction, the spin coupling to the physical momentum and the quadrupole correction to the magnetic coupling to the interaction current which give rise to the terms

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,p^ip^2} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{-p^jp^2}{m_e^3}|\Phi\rangle\ ,\end{aligned} \tag{308}$$

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,r\times\sigma} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\left(\frac{-Z\alpha\left(\vec{x}\times\vec{\sigma}\right)^j}{m_e^2r^3}\right)|\Phi\rangle\ ,\end{aligned} \tag{309}$$

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\left(\frac{\left(\vec{k}\cdot\vec{x}\right)\left(\vec{k}\times\vec{\sigma}\right)^j}{m_e}\right)|\Phi\rangle\ .\end{aligned} \tag{310}$$

The shift of the energy because of the relativistic corrections δH_S gives the term

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta E} = -&\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\delta E\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\ .\end{aligned} \tag{311}$$

δH_S leads to the contribution

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta H_S} = &-\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\langle\Phi|\,\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\\ &\times\left(\frac{\vec{p}^{\,4}}{8m_e^3}-\frac{Z\alpha}{4m_e^2r^3}\vec{\ell}\cdot\vec{\sigma}\right)\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}\,|\Phi\rangle\,.\end{aligned} \tag{312}$$

In δH_S, the Darwin term is neglected because in this work only states with angular momentum $\ell \geq 2$ are considered for which this term vanishes. Finally, the relativistic corrections to the wave function yield the term

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta\Phi} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}\left(\frac{1}{E_\Phi - H_S}\right)'\delta H_S\,|\Phi\rangle\,.\end{aligned} \tag{313}$$

The details of the calculation are not shown here because they follow the basic principles outlined for the leading term. It is just mentioned that a logarithmic term with ϵ arises, which is commonly called A_{61}, as well as a logarithmic part without ϵ, which leads to a term similar to the Bethe logarithm. In it, only the relativistic corrections are contained. Therefore, it is called the relativistic Bethe logarithm β_{SE}.

The total low-energy part for states with $\ell \geq 2$ is then given by

$$\mathrm{Re}\Delta E^{(2)}_{L,\Phi} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3}F_L(\epsilon)\,, \tag{314}$$

with

$$F_L(\epsilon) = -\frac{4}{3}\ln k_0 + (Z\alpha)^2\left\{A_{61}\left[\ln\left(\frac{\epsilon}{(Z\alpha)^2 m}\right)+\frac{1}{\epsilon}\right]+\beta_{\mathrm{SE}}\right\}\,. \tag{315}$$

This expression does still contain the parameter ϵ which was introduced to regularize divergences. The final self-energy shift cannot depend on it. This is why the effect from highly energetic photons have to be considered, which will be done in the following section.

4.6. HIGH-ENERGY PART

In the calculation of the low-energy part using NRQED it became clear that the theory is only valid at low photon energy. This made it necessary to cut off the integrals over the photon momentum at a photon energy $(Z\alpha)^2 m_e \ll \epsilon \ll m_e$. The results obtained for the low-energy part are then dependent on this cutoff. If there is a real physical, observable energy shift due to the self-energy, the final result cannot contain this parameter ϵ. Moreover, there has to be a different treatment which allows to evaluate the effect on a bound electron from high photon energies. Adding both results for the different parts should then cancel the cutoff and allow to obtain a result independent of ϵ.

This is indeed the case. At high photon energies the photon energy becomes much larger than the binding energy. This enables to treat the Coulomb potential as a perturbation in the high-energy part. The second approximation is to assume that the electron is on the mass shell $E_n \approx m_e$. In the arising expressions some terms will depend on ϵ and cancel the terms containing ϵ coming form the low-energy part when both are added.

The high-energy part is discussed in a graphical way by considering the expansion depicted in Fig. 4.2. In the zeroth order diagram the electron has no interaction with the core while the photon is "underway". This means the electron is basically free. The term therefore cancels with the self-energy of free electron which has to be subtracted because the electron cannot be observed without this radiative effect and to keep the expression finite.

The first order diagram in Fig. 4.2 has the form of the so-called vertex correction [26]. Its effect is that it alters the way the electron interacts with the electromagnetic field. For example, the vertex correction causes the electron magnetic moment anomaly i.e. the difference between the observed magnetic moment of the electron from the value 2 predicted by Dirac theory. Formally, it changes the coupling of the four-vector potential in the Dirac equation [38]

$$\gamma^\mu A_\mu(x) \Rightarrow \Gamma^\mu(p, p') A_\mu(x)\,, \tag{316}$$

where $\Gamma^{\mu}(p,p')$ is given as [26]

$$\Gamma^{\mu}(p,p') = \gamma^{\mu}F_1(-q^2) + \frac{\mathrm{i}\Sigma^{\mu\nu}q_{\nu}}{2m_e}F_2(-q^2)\,. \tag{317}$$

with $q = p - p'$ and $\Sigma^{\mu\nu} = \frac{\mathrm{i}}{2}[\gamma^{\mu},\gamma^{\nu}]$ as well as the form factors F_1 and F_2. Consequently, the vertex correction alters the Dirac Hamiltonian to

$$\begin{aligned} H_D^{(m)} = \gamma^0 \Big[\vec{\gamma}\left(\vec{p} - eF_1(-\vec{q}^2)\vec{A}\right) + m_e + e\gamma^0 F_1(-\vec{q}^2)\phi \\ + eF_2(-\vec{q}^2)\frac{\mathrm{i}\Sigma^{\mu\nu}q_{\nu}}{2m_e}\left(\gamma^0\phi - \vec{\gamma}\cdot\vec{A}\right)\Big]\,. \end{aligned} \tag{318}$$

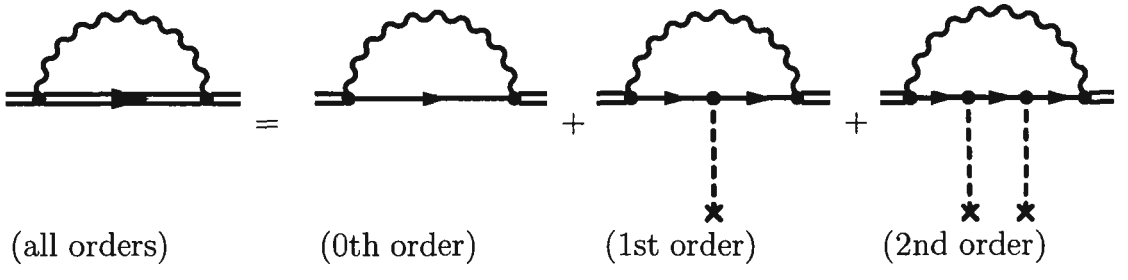

Figure 4.2. Expansion of the full bound propagator in terms of the binding Coulomb potential. The double line denotes a bounded electron, a single line a free electron, the dashed line represents the instantaneous Coulomb interactions and the wiggly line the virtual photon.

The momentum operator q can also be written as a derivative. With the use of the equation for the electric field [25]

$$E_a = -\partial_a\phi - \partial_0 A_a$$

this allows to simplify the term with F_2 to

$$\frac{\Sigma^{0a}\partial_a}{2m_e}\gamma^0\phi + \frac{\Sigma^{a0}\partial_0}{2m_e}\gamma^a A_a = \frac{\mathrm{i}}{2m_e}\gamma^0\gamma^a\left(-\partial_a\phi - \partial_0 A_a\right) = \gamma^0\frac{\mathrm{i}}{2m_e}\vec{\gamma}\vec{E}\,. \tag{319}$$

Moreover, with the definition of the magnetic field

$$B_a = \epsilon_{aij}\partial_i A_j$$

and $\Sigma^{\mu\nu} = -\epsilon_{\mu\nu\kappa}\Sigma^{\kappa}$

$$-\frac{\Sigma^{ab}\partial_b}{2m_e}\gamma^a A_a = -\frac{1}{2m_e}\epsilon_{cba}\Sigma^c\partial_b A_a = -\frac{1}{2m_e}\vec{\Sigma}\cdot\vec{B} \tag{320}$$

can be obtained. This modified Dirac Hamiltonian which includes the vertex correction thus takes the form

$$H_D^{(m)} = \vec{\alpha}\left[\vec{p} - eF_1(\nabla^2)\vec{A}\right] + \beta m_e + eF_1(\nabla^2)\phi + F_2(\nabla^2)\frac{e}{2m_e}\left(i\vec{\gamma}\cdot\vec{E} - \beta\vec{\Sigma}\cdot\vec{B}\right) . \tag{321}$$

Without an external magnetic field, $\vec{B}$ and $\vec{A}$ can in fact be set to 0, ϕ is given by $e\phi = V(r) = -Z\alpha/r$. The energy shift from the additional terms compared to the unmodified Dirac equation [38] can then be obtained by first order of perturbation theory with the relativistic wave function. The first term which is different from the unmodified Dirac Hamiltonian is

$$V_1 = eF_1(\nabla^2)\phi = F_1(\nabla^2)\left(-\frac{Z\alpha}{r}\right) . \tag{322}$$

For an electron on mass shell $q \approx 0$, the expressions can be expanded in ∇^2

$$\begin{aligned} V_1 &= F_1'(0)(\nabla^2)\left(-\frac{Z\alpha}{r}\right) \\ &= F_1'(0)4\pi Z\alpha\delta(\vec{x}) . \end{aligned} \tag{323}$$

The corresponding matrix element can be calculated with the non relativistic wave function and $F_1'(0) = \frac{\alpha}{3\pi m_e^2}[\ln\frac{m_e}{2\epsilon} + \frac{11}{24}]$ [27] gives

$$\Delta E_H^1(n\ell_j) = \langle n\ell m\,|V_1|\,n\ell m\rangle = \frac{4\alpha}{3\pi}\frac{(Z\alpha)^4 m_e}{n^3}\left[\ln\left(\frac{m_e}{2\epsilon}\right) + \frac{11}{24}\right]\delta_{\ell 0} . \tag{324}$$

This is correction therefore is only non zero for states with $\ell = 0$ and vanishes for the states with $\ell \geq 2$ which are considered here. The second relevant matrix element

is given by the term, where the magnetic form factor F_2 couples to the electric field $e\vec{E} = \vec{\nabla} Z\alpha/r$ in Eq. (321). It is

$$\Delta E_H^2(n\ell_j) = \langle \psi^+ | \, F_2(\nabla^2) \frac{e}{2m_e} \mathrm{i}\vec{\gamma} \cdot \vec{E} \, | \psi \rangle \; . \tag{325}$$

Here, the matrix element has to be evaluated with the fully relativistic wave function expanded in powers of $Z\alpha$. In this way divergences when using the unexpanded wave function can be avoided and it is easier to match the respective orders in $Z\alpha$ with the low-energy part. An expansion around $q \approx 0$ is carried out once more. For the magnetic form factor F_2 the known Schwinger value $F_2 = \frac{\alpha}{2\pi}$ [26] is used. The resulting integral has been evaluated in Ref. [47] with the help of generalized virial theorems and integrals in Ref. [48] with the result

$$\begin{aligned} \frac{n^3}{(Z\alpha)^4} \left\langle \psi^+ \left| \mathrm{i} \frac{\vec{\gamma} \cdot \vec{E}}{4m_e^2} \right| \psi \right\rangle &= -\frac{1}{2\kappa\,(2\ell+1)} \\ &+ (Z\alpha)^2 \left(-\frac{12\kappa^2 - 1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2} - \frac{1}{n} \frac{3}{4\kappa^2\,(2\kappa+1)} \right. \\ &\left. + \frac{1}{n^2} \frac{8\kappa - 3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)} \right) \\ &\equiv -\frac{1}{2\kappa\,(2\ell+1)} + (Z\alpha)^2 \, \Xi \, , \end{aligned} \tag{326}$$

where the contribution of relative order $(Z\alpha)^2$ is denoted here as Ξ. Here, again the Dirac quantum number is $\kappa = (-1)^{j-\ell+1/2}(j+\frac{1}{2})$ and $\vec{j} = \vec{\ell} + \vec{s}$ is the total angular momentum.

The last contribution to the high-energy part comes from the last diagram in Fig. 4.2, where two interactions between the core and the electron take place between the emission and absorption of the photon. The effect from the two vertex interaction can be expressed as a further Hamiltonian. Similar to the term $\Delta E^1_{H,n\ell m}$ it also exhibits an infrared divergence. Regularizing this divergence with the overlapping parameter ϵ, allows to match it with the low-energy part and cancel the divergence for large photon energy there. It has been derived in a different regularization scheme

in Ref. [46]. In the regularization used in this work it can be written as [47]

$$H_{2v}(\epsilon) = \frac{\alpha}{\pi}\left[\frac{2}{3}\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{2}{3\epsilon} + \frac{34}{45}\right]\frac{(\vec{\nabla}V)^2}{m_e^3}\,. \tag{327}$$

The energy shift from this correction can be calculated with the non relativistic wave function. The corresponding matrix element is commonly called the A_{61} coefficient and given by

$$\begin{aligned} A_{61} &= \frac{2}{3}\frac{n^3}{(Z\alpha)^4}\left\langle n\ell m\left|\frac{1}{(m_e r)^4}\right|n\ell m\right\rangle \\ &= \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\,. \end{aligned} \tag{328}$$

For states with $\ell \geq 2$ considered in this work, the result can be obtained by the identity

$$(k+1)\frac{(Z\alpha)^2}{n^2}\left\langle r^k\right\rangle_{n\ell} - (2k+1)Z\alpha\left\langle r^{k-1}\right\rangle_{n\ell} + \frac{k}{4}[(2\ell+1)^2-k^2]\left\langle r^{k-2}\right\rangle_{n\ell} = 0$$

and the known results for $\langle r^{-2}\rangle_{n\ell}$ and $\langle r^{-3}\rangle_{n\ell}$.

The total high-energy part is then given by

$$\mathrm{Re}\Delta E^{(2)}_{H,\Phi} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3}F_H(\epsilon)\,, \tag{329}$$

with

$$F_H(\epsilon) = \Xi + (Z\alpha)^2 A_{61}\left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right]\,, \tag{330}$$

Adding the high- and low-energy part, the terms containing ϵ cancel exactly and $(Z\alpha)^2$ arises as the natural scale for the logarithms. The final result for the self-energy of a bound electron is then given as

$$\mathrm{Re}\Delta E^{(2)}_{\Phi} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3}F\,, \tag{331}$$

with

$$F = F_L(\epsilon) + F_H(\epsilon) = -\frac{4}{3}\ln k_0 + (Z\alpha)^2\left\{A_{61}\left[\ln\left(\frac{\epsilon}{(Z\alpha)^2 m_e}\right) + \frac{1}{\epsilon}\right] + \beta_{\rm SE}\right\}$$
$$- \frac{1}{2\kappa\,(2\ell+1)} + (Z\alpha)^2\left\{A_{61}\left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right] + \Xi\right\} \qquad (332)$$
$$= -\frac{1}{2\kappa\,(2\ell+1)} - \frac{4}{3}\ln k_0 + (Z\alpha)^2\left\{A_{61}\left[\ln\left(\frac{1}{2(Z\alpha)^2}\right) + \frac{17}{15}\right] + \Xi + \beta_{\rm SE}\right\}.$$

5. THEORY: OVERLAPPING PARAMETER

5.1. MODEL EXAMPLE

In the previous section, two approaches to calculate the one-photon self-energy effect on a bound electron have been presented. Since both basically evaluate the same quantity just in different ways, they should give the same result. Otherwise, one or both of them contain errors.

Before comparing actual results of calculations with both methods, it seems worthwhile to take the time and consider, why mathematically both ways of evaluation are possible and why the apparent differences arise. To elucidate the point, a model problem is studied, which is given by the integral

$$I = \int_0^1 d\omega\, \omega \frac{\sqrt{\omega^2 + (Z\alpha)^2}}{\sqrt{1-\omega^2}} \left(-8\omega + \frac{256}{3\pi}\omega^2 - 20\omega^3 \right) . \tag{333}$$

As explained in Refs. [42, 49], the factor $\sqrt{\omega^2 + (Z\alpha)^2}$ corresponds to the full Coulomb-Dirac propagator, while the factor $(1-\omega^2)^{-\frac{1}{2}}$ basically arises from transforming the boundaries of the integrals from 0 to ∞ to 0 to 1. Another important point this example shall illustrate is that while with a concrete cutoff spurious lower order terms can arise, they can be avoided if an infinitesimal overlapping parameter is used.

Before this integral is investigated using both presented methods, a look is taken at the final result for this integral. In contrast to the bound electron self-energy, this model problem can be treated without a separation, which provides a check of the calculation. For all numerical integrations in this section, the parameter Z is set to 1 and for α the value $\alpha^{-1} = 137.036$ is used. With these values a numerical integration of Eq. (333) yields

$$I = 9.213 \times 10^{-9} \tag{334}$$

Additionally, I can also be expressed in terms of elliptical integrals, which can be expanded in a semi-analytic series in $Z\alpha$ with the result

$$I = \frac{(Z\alpha)^4}{2}\left[\ln\left(\frac{8}{(Z\alpha)^2}\right) - \frac{37}{6}\right] + (Z\alpha)^5\frac{512}{45\pi} + \frac{3(Z\alpha)^6}{4}\left[1 - \ln\left(\frac{8}{(Z\alpha)^2}\right)\right] + \mathcal{O}((Z\alpha)^7)\,. \tag{335}$$

In the above series $(Z\alpha)$ can be replaced by its numerical value which gives the result in Eq. (334) as well.

In the following, this integral will be treated by both methods discussed so far. Finally, both results will be compared in the end. Even though it might seem weird to start from the solution, and then look into both discussed methods in solving the integral, knowing the order of the physical part of the integral helps to extract terms up to the right order in the numerical method. In fact, in case of the self-energy shift the magnitude of the physical part was also known before the numerical method was developed.

5.1.1. Numerical Method. In the beginning the methods of Sec. 3 are investigated. As in both methods, the integral is split into a high- and a low-energy part. For the numerical integration, a numerical overlapping parameter is required, for which the value $\frac{1}{10}$ is chosen. Therefore, in the low-energy part the integral

$$I_{\mathrm{lep},n} = \int_0^{1/10} d\omega\, \frac{\sqrt{\omega^2+\beta^2}}{\sqrt{1-\omega^2}}\omega\left(-8\omega + \frac{256}{3\pi}\omega^2 - 20\omega^3\right)\,, \tag{336}$$

where lep denotes the low-energy part and n denotes that the numerical method is used, has to be evaluated. This is done numerically with the result

$$I_{\mathrm{lep},n} = -1.503\,355\,67 \times 10^{-4}\,. \tag{337}$$

the obtained result is much larger in magnitude than the final numerical result. This means that in the numerical integral terms of order lower than the physical part of the low-energy part are contained as well. In accordance with the method explained in Sec. 3, therefore, an expansion in $Z\alpha$ is carried out in order to extract these terms of lower order. From the complete expansion it is known that the physical part is

of order $(Z\alpha)^4 \ln(Z\alpha)^{-2}$. The expansion is carried out by expressing the integral in Eq. (336) in terms of elliptical integrals and logarithms which can be expanded in $Z\alpha$. This yields

$$I_{\mathrm{lep},n} = \frac{120603\sqrt{11}}{25000} - \frac{604\sqrt{11}}{625\pi} + \frac{\sqrt{11}}{25}(Z\alpha)^2\left(\frac{321}{4} - \frac{16}{\pi}\right) + \mathcal{O}((Z\alpha)^4 \ln(Z\alpha)^{-2})\,. \quad (338)$$

The physical part can then be extracted by subtracting the lower order terms form the numerical result. Therefore, the definition

$$I_{\mathrm{lep},n} = N_{\mathrm{lep},n} + P_{\mathrm{lep},n} \quad (339)$$

is used with the nonphysical lower order part of the integral of the low-energy part

$$N_{\mathrm{lep},n} = \frac{120603\sqrt{11}}{25000} - \frac{604\sqrt{11}}{625\pi} + \frac{\sqrt{11}}{25}(Z\alpha)^2\left(\frac{321}{4} - \frac{16}{\pi}\right) \quad (340)$$

and the physical part

$$P_{\mathrm{lep},n} = I_{\mathrm{lep},n} - N_{\mathrm{lep},n} = 7.833 \times 10^{-9}\,. \quad (341)$$

Consequently, in the high-energy part the integral

$$I_{\mathrm{hep},n} = \int_{1/10}^{1} d\omega\, \frac{\sqrt{\omega^2+\beta^2}}{\sqrt{1-\omega^2}}\omega\left(-8\omega + \frac{256}{3\pi}\omega^2 - 20\omega^3\right)\,, \quad (342)$$

is evaluated numerically with the result

$$I_{\mathrm{hep},n} = 1.503\,369\,47 \times 10^{-4}\,. \quad (343)$$

Here, hep is used to denote the high-energy part. Again, the lower order contributions are extracted by expanding the integral in $Z\alpha$, which gives

$$\begin{aligned} I_{\mathrm{hep},n} = &-\frac{120603\sqrt{11}}{25000} + \frac{604\sqrt{11}}{625\pi} - \frac{\sqrt{11}}{25}(Z\alpha)^2\left(\frac{321}{4} - \frac{16}{\pi}\right) \\ &+ \mathcal{O}((Z\alpha)^4 \ln(Z\alpha)^{-2})\,. \end{aligned} \quad (344)$$

Analogue to the low-energy part the physical and nonphysical lower order part is defined again by

$$I_{\mathrm{hep},n} = N_{\mathrm{hep},n} + P_{\mathrm{hep},n} \tag{345}$$

with the nonphysical part

$$N_{\mathrm{hep},n} = -\frac{120603\sqrt{11}}{25000} + \frac{604\sqrt{11}}{625\pi} - \frac{\sqrt{11}}{25}(Z\alpha)^2\left(\frac{321}{4} - \frac{16}{\pi}\right) \tag{346}$$

and the physical part

$$P_{\mathrm{hep},n} = I_{\mathrm{hep},n} - N_{\mathrm{hep},n} = 1.380 \times 10^{-9}\,. \tag{347}$$

When the nonphysical part of the low- and the high-energy part are added, the terms cancel exactly i.e.

$$N_{\mathrm{lep},n} + N_{\mathrm{hep},n} = 0\,. \tag{348}$$

The total value for the integral can thus be obtained by adding both physical parts with the result

$$I_n = P_{\mathrm{lep},n} + P_{\mathrm{hep},n} = 9.213 \times 10^{-9} \tag{349}$$

in agreement with Eq. (334).

5.1.2. Analytical Method. In this section, the analytic method will be applied to the integral in Eq. (333). Initially, the low-energy part of the integral, in which ω is integrated from 0 to ε, is considered. In this region ω is small and it is possible to use the expansion

$$\frac{1}{\sqrt{1-\omega^2}} = 1 + \frac{\omega^2}{2} + \frac{3\omega^4}{8} + \ldots \tag{350}$$

for the denominator in Eq. (333). Similar to the application of the analytic method to the bound electron self-energy, the analogue to the propagator $\sqrt{\omega^2 + (Z\alpha)^2}$ is left

intact. Therefore, the integral, which has to be evaluated for the low-energy part, is

$$I_{\mathrm{lep},a} = \int_0^{\varepsilon} d\omega\, \omega \sqrt{\omega^2 + (Z\alpha)^2} \left(-8\omega + \frac{256}{3\pi}\omega^2 - 20\omega^3\right) \times \left(1 + \frac{\omega^2}{2} + \frac{3\omega^4}{8} + \ldots\right), \tag{351}$$

where a denotes that the analytic method and lep once more that this is the low-energy part. The integration is carried out analytically. The result is then expanded in $Z\alpha$ followed by an expansion in ε. As the final result for the low-energy part

$$I_{\mathrm{lep},a} = (Z\alpha)^4 \left[\ln\left(\frac{2\varepsilon}{Z\alpha}\right) - \frac{1}{4}\right] + \frac{512(Z\alpha)^5}{45\pi} + \frac{3(Z\alpha)^6}{2}\left[\frac{5}{12} + \frac{1}{6\varepsilon^2} - \frac{32}{9\pi\varepsilon} - \ln\left(\frac{2\varepsilon}{Z\alpha}\right)\right] + \ldots . \tag{352}$$

is obtained.

The integral for the high-energy part extends from ε to 1. In Sec. 4 the Coulomb-Dirac propagator was expanded in terms of the external potential which represents an expansion in $Z\alpha$. The corresponding procedure here is to expand $\sqrt{\omega^2 + (Z\alpha)^2}$ in powers of $Z\alpha$ which gives

$$\sqrt{\omega^2 + (Z\alpha)^2} = \omega\left(1 + \frac{1}{2}\frac{(Z\alpha)^2}{\omega^2} - \frac{1}{8}\frac{(Z\alpha)^4}{\omega^4} + \frac{1}{16}\frac{(Z\alpha)^6}{\omega^6} + \ldots\right). \tag{353}$$

Consequently, the integral for the high-energy part is

$$I_{\mathrm{hep},a} = \int_{\varepsilon}^{1} d\omega\, \omega \sqrt{\frac{\omega^2}{1-\omega^2}} \left(-8\omega + \frac{256}{3\pi}\omega^2 - 20\omega^3\right) \times \left(1 + \frac{1}{2}\frac{(Z\alpha)^2}{\omega^2} - \frac{1}{8}\frac{(Z\alpha)^4}{\omega^4} + \frac{1}{16}\frac{(Z\alpha)^6}{\omega^6} + \ldots\right). \tag{354}$$

This integral also illustrates an interesting point. Because in order $(Z\alpha)^4$ the integral is divergent at $\omega = 0$, the overlapping parameter ε acts as a so-called infrared regulator. As a consequence terms $\sim \ln\varepsilon$ arise in the integration.

The result of integration is expanded in ε to obtain

$$I_{\mathrm{hep},a} = (Z\alpha)^4 \left[\ln\left(\frac{2}{\varepsilon}\right) - \frac{17}{6}\right] + \frac{3(Z\alpha)^6}{2}\left[\frac{1}{12} - \frac{1}{6\varepsilon^2} + \frac{32}{9\pi\varepsilon} - \ln\left(\frac{2}{\varepsilon}\right)\right] + \dots . \quad (355)$$

When the low- and the high-energy parts are added, the terms containing ε cancel. Up to order $(Z\alpha)^6$ the integral is found to be

$$\begin{aligned} I_a = I_{\mathrm{lep},a} + I_{\mathrm{hep},a} = \frac{(Z\alpha)^4}{2}\left[\ln\left(\frac{16}{(Z\alpha)^2}\right) - \frac{37}{6}\right] + (Z\alpha)^5 \frac{512}{45\pi} \\ + \frac{3(Z\alpha)^6}{4}\left[1 - \ln\left(\frac{16}{(Z\alpha)^2}\right)\right] + \dots , \end{aligned} \quad (356)$$

which agrees with the expansion of the elliptical integrals for the whole integral in Eq. (335). For the numerical values considered here, this gives

$$I_a = 9.213 \times 10^{-9} \quad (357)$$

which agrees with the result from the numerical method as well as the result from the numerical integration of the whole integral.

The analysis of this model very nicely illustrates, for which region of nuclear charge number Z the two presented methods to treat self-energy corrections for a bound electron are suited best.

For low nuclear charge number Z the parameter $Z\alpha$ is small. This means that the numerical calculation is dominated by the terms of lower order than the physical part. As the result is obtained by subtracting two about equally large numbers, one usually loses a few significant figures (in this model example here about 5) of numerical precision. In the analytic approach no such lower order terms arise and therefore no such problem is present. Moreover, because the parameter $Z\alpha$ is small, the error introduced due to missing higher order terms is small.

For large nuclear charge number Z, $Z\alpha$ becomes close to unity. In turn, the magnitude of the physical part due to the scaling with Z becomes large, whereas the magnitude of the nonphysical does not change as much. Therefore, less significant figures are lost by the subtraction of the lower order terms. In the analytic method, on the other hand, the higher-order terms are no longer negligible if $Z\alpha$ is close to 1.

It is not possible to reach an arbitrary high precision in the numerical calculation as well as to go up to arbitrary high orders in the expansion in the analytic method for practical reasons. As a consequence, the analytic method is generally more suited for lower Z, while the numerical method is more suited for higher Z.

5.2. APPLICATION TO VACUUM POLARIZATION

It is the aim of this section to show that the separation of an integral using an overlapping parameter is not only interesting to illustrate this procedure in bound self-energy calculation but can, in fact, be very useful for many integrals. For this a physical example is considered which is also very important for the study of quantum electrodynamics in bound systems, the vacuum polarization. Vacuum polarization is the second very important effect of the quantum nature of the photon field and, as seen in Sec. 3, it contributes to the energy shift. The effect of vacuum polarization in first loop order is to give a correction potential to the Coulomb potential. This additional potential is the Uehling potential [50]. Here, the method is applied to find the leading asymptotic behavior of this potential for $r \longrightarrow 0$.

The question may arise, why the energy shift due to this potential has not appeared in the presented calculation of the energy shift due to the quantum nature of the photon field. The reason is that in one-electron ions the Uehling potential can be approximated by [26]

$$V_{\mathrm{vp}}(\vec{x}) = -\frac{\alpha}{\pi}\frac{4\pi Z\alpha}{15m_e^2}\delta(\vec{x})\,. \tag{358}$$

Therefore, only the energy levels of states with $\ell = 0$ are shifted and the effect can be neglected for the highly excited states which are considered in this work. Interestingly, the energy shift due to vacuum polarization has the opposite sign of the self-energy level shift.

When the electron is exchanged with a muon, this approximation is no longer valid and it becomes necessary to calculate the effect in more depth. In general, the potential is calculated by a Fourier transform of the photon propagator, which was already encountered in Secs. 3 and 4. There, the photon propagator without vacuum polarization was used. Its Fourier transform gives the Coulomb potential.

The inclusion of vacuum polarization alters the photon propagator and leads to the following expression for the Uehling Potential [26]

$$V_{\rm vp}(r) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\frac{2}{3}\int_{2m_e}^{\infty} dq\,\frac{e^{-qr}}{q}\sqrt{1-\frac{4m_e^2}{q^2}}\left(1+\frac{2m_e^2}{q^2}\right). \tag{359}$$

When r is larger than the Compton wavelength of the electron $1/m_e$, this leads to the known screening effects of vacuum polarization due to virtual pairs of electrons and positrons. Here, the asymptotic behavior for $r \to 0$ is investigated which will be calculated using the analytical method with an overlapping parameter. In order to obtain a similar structure as in our model example, the substitution $q = 2m_e u$ is used. In turn, the integral takes the form

$$V_{\rm vp}(r) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_{1}^{\infty} du\,\exp[-2m_e u r]\,\frac{\sqrt{u^2-1}\,(2u^2+1)}{3u^4}. \tag{360}$$

This is the integral, which was evaluated in Ref. [51]. Here, another substitution, which is $u = (1-v^2)^{1/2}$, is employed in order to arrive at the integral in Ref. [52]

$$V_{\rm vp}(r) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_{0}^{1} dv\,\exp\left[-\frac{2m_e r}{\sqrt{1-v^2}}\right]\,\frac{v^2\left(1-\frac{v^2}{3}\right)}{1-v^2}. \tag{361}$$

Consequently, the integral has the same boundaries as the model problem discussed so far in this section. However, the problematic region now is where $v \approx 1$. Hence, the integral is split into a low-energy part from 0 to $1-\epsilon$ and into a high-energy part from $1-\epsilon$ to 1. In fact the naming is correct here because the region where $v \approx 1$ corresponds to large photon momentum q in the original integral in Eq. (359). In the model problem the first expansion parameter was $Z\alpha$. As the asymptotic behavior of the Uehling potential for $r \to 0$ is to be investigated, the corresponding expansion parameter here is r instead. The second expansion is still carried out in ϵ.

Again, the analysis starts with the low-energy part of the integral which is

$$V_{\rm vp,lep}(r,\epsilon) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_{0}^{1-\epsilon} dv\,\exp\left[-\frac{2m_e r}{\sqrt{1-v^2}}\right]\,\frac{v^2\left(1-\frac{v^2}{3}\right)}{1-v^2}. \tag{362}$$

In contrast to the model problem, the low-energy part does not contain the problematic region for an expansion in the first expansion parameter r. Thus, the exponential is expanded in r before the integration. The integral for the low-energy part is then

$$V_{\mathrm{vp,lep}}(r,\epsilon) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_0^{1-\epsilon} dv\, \frac{v^2\left(1-\frac{v^2}{3}\right)}{1-v^2}\left[1-\frac{2m_e r}{\sqrt{1-v^2}}+\mathcal{O}(r)\right]. \tag{363}$$

Carrying out the integration and expanding the obtained result in ϵ yields

$$V_{\mathrm{vp,lep}}(r,\epsilon) = \frac{\alpha}{\pi}\left[\frac{2\sqrt{2}Z\alpha m_e}{3\sqrt{\epsilon}} - \frac{\pi}{2}Z\alpha m_e + \frac{5}{9}\frac{Z\alpha}{r} + \frac{Z\alpha}{3r}\ln\left(\frac{\epsilon}{2}\right)+\mathcal{O}(r)\right]. \tag{364}$$

For the high-energy part the integral

$$V_{\mathrm{vp,hep}}(r,\epsilon) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_{1-\epsilon}^{1} dv\, \exp\left[-\frac{2m_e r}{\sqrt{1-v^2}}\right]\frac{v^2\left(1-\frac{v^2}{3}\right)}{1-v^2}. \tag{365}$$

has to be considered. Because in the region considered for the high-energy part, the integral is divergent if an expansion in r is carried out, a similar expansion to the low-energy part in the model problem has to be found. There, $(1-\omega^2)^{-1/2}$ was expanded for $\omega \approx 0$. In fact, this leads to the right idea for the integral here but in contrast to the model the expansion is carried out around $v \approx 1$. This procedure is greatly facilitated by transforming the integral first, using $v^2 = 1-h$, which yields the integral

$$V_{\mathrm{vp,hep}}(r,\epsilon) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]\int_0^{2\epsilon-\epsilon^2} dh\, \exp\left[-\frac{2m_e r}{\sqrt{h}}\right]\frac{2-h-h^2}{6h\sqrt{1-h}}. \tag{366}$$

Expanding this integral around $h=0$ gives

$$\begin{aligned} V_{\mathrm{vp,hep}}(r,\epsilon) = \frac{\alpha}{\pi}\left[-\frac{Z\alpha}{r}\right]&\int_0^{2\epsilon-\epsilon^2} dh\, \exp\left[-\frac{2m_e r}{\sqrt{h}}\right] \\ &\times\left(\frac{1}{3h}-\frac{h}{8}-\frac{h^2}{24}-\frac{3h^3}{128}-\mathcal{O}(h^4)\right). \end{aligned} \tag{367}$$

The resulting expression is expanded in r before the expansion in ϵ is carried out. The high-energy part of the integral is then obtained as

$$V_{\mathrm{vp,hep}}(r,\epsilon) = \frac{\alpha}{\pi}\left\{-\frac{2\sqrt{2}Z\alpha m_e}{3\sqrt{\epsilon}} + \frac{Z\alpha}{3r}\left[2\gamma_E + \ln\left(\frac{2m_e r}{\epsilon}\right)\right] + \mathcal{O}(r)\right\}, \tag{368}$$

where γ_E is the Euler gamma. Once more, matching both the high- and the low-energy part together the overlapping parameter cancels and the result is independent of ϵ. In agreement with Ref. [53] it is found

$$V_{\mathrm{vp}}(r) = \frac{\alpha}{\pi}\frac{Z\alpha}{r}\left[\frac{2}{3}\left(\gamma_E + \ln(m_e r)\right) - \frac{\pi}{2}m_e r + \frac{5}{9}\right] + \mathcal{O}(r)\,. \tag{369}$$

It is important to mention that the argument of the logarithm is, in fact, unitless as in Heavyside-Lorentz units the mass is given in inverse length units. Moreover, the leading term $\sim \ln(m_e r)/r$ constitutes an attractive potential for distances $r < 1/m_e$ since the logarithm is negative if the argument is smaller than 1.

6. CALCULATION: RELATIVISTIC CORRECTIONS IN ATOMS

6.1. ORIENTATION

The first problem that is investigated here with the nonrelativistic expansion of the fully relativistic theory, is a problem of atomic physics, namely the two-photon decay. In it an initial state decays via the emission of two real photons into a final state. With the formalism developed in Sec. 4, relativistic corrections to the Hamiltonian but also to the interaction current, which is relevant for the emission of real as well as virtual photons, are deduced. Applying it to the two-photon decay allows to obtain the relativistic corrections in order $(Z\alpha)^2$ to the two-photon decay rate which is a problem of relativistic atomic physics. Before coming to that, two different formulation of the problem are discussed. The coupling of the electron to the photon can be expressed in Coulomb or velocity gauge which was used in Sec. 4 but also in Yennie or length gauge. This is done in the next section.

6.2. VELOCITY VS LENGTH GAUGE

While some time was spent in the derivation of the quantized field on the gauge freedom, so far only Coulomb gauge was used in the calculations. However, all the calculations can also be carried in a different gauge and the same results should be obtained. Actually, in some cases the calculation can be simplified when a different gauge is used. Fried and Yennie in Ref. [29] discovered that a specific choice for the gauge allowed to avoid problems in QED calculation, which were encountered in a different gauge. Because the results obtained so far in Coulomb gauge should be independent of the choice of gauge, gauge invariance provides a highly nontrivial check of the calculation.

The choice of gauge from Fried and Yennie in Ref. [29] is indeed very useful for many problems in QED. It corresponds to setting $\xi = 3$ in the photon propagator in Eq. (46). As described in Ref. [45] the corresponding Hamiltonian for NRQED

can be obtained by two consecutive Power-Zienau transformations [54] of the Foldy-Wouthuysen Hamiltonian for the upper components coupled to a quantized field

$$\begin{aligned} H_{\mathrm{FW}} = & \frac{\vec{\pi}^2}{2m_e} - \frac{Z\alpha}{r} + eA^0 - \frac{e}{2m_e}\vec{\sigma}\cdot\vec{B} - \frac{\vec{\pi}^4}{8m_e^3} \\ & + \frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x}) + \frac{Z\alpha}{4m_e^2}\vec{\sigma}\cdot\frac{\vec{x}}{r^3}\times\vec{\pi} \\ & - \frac{e}{8m_e^2}\left[\vec{\nabla}\cdot\vec{E} + \vec{\sigma}\left(\vec{E}\times\vec{\pi} - \vec{\pi}\times\vec{E}\right)\right] \\ & + \frac{e}{8m_e^3}\left\{\vec{\sigma}\cdot\vec{B}\vec{\pi}^2 + \vec{\pi}^2\vec{\sigma}\cdot\vec{B} + \kappa\left[\vec{\pi}\cdot\vec{B}\vec{\pi}\cdot\vec{\sigma} + \vec{\pi}\cdot\vec{\sigma}\vec{\pi}\cdot\vec{B}\right]\right\}, \end{aligned} \tag{370}$$

where $\vec{\pi} = \vec{p} - e\vec{A}$ denotes the physical momentum in presence of the quantized field. This Hamiltonian is now transformed with the first of the Power-Zienau transformations. The transformed Hamiltonian is obtained from the equation

$$H' = e^{-\mathrm{i}\phi}He^{\mathrm{i}\phi} + \partial_t\phi \tag{371}$$

with ϕ given by

$$\phi = e\int_0^1 du\ \vec{x}\cdot\vec{A}(u\vec{x})\,. \tag{372}$$

Here, the so-called long wavelength approximation is made, i.e. the field $\vec{A}$ varies only slowly over a short distance. This allows to perform an expansion of $\vec{A}$ around $\vec{x}\approx 0$

$$A^\mu(\vec{x},t) = A^\mu(0,t) + x^i A^\mu_{,i}(0,t) + \frac{1}{2!}x^i x^j A^\mu_{,ij}(0,t) + \frac{1}{3!}x^i x^j x^k A^\mu_{,ijk}(0,t) + \ldots\,. \tag{373}$$

With this, also ϕ can be expanded to give

$$\phi = e\left[x^i A^i + \frac{1}{2!}x^i x^j A^i_{,j} + \frac{1}{3!}x^i x^j x^k A^i_{,jk} + \frac{1}{4!}x^i x^j x^k x^l A^i_{,jkl} + \ldots\right], \tag{374}$$

Here, the subscript separated by commas denotes the spatial derivatives with respect to the indicated Cartesian coordinates, evaluated at the origin [45], which is defined to be the location of the ionic nucleus. The $(0,t)$ which goes with every field will be suppressed in the following. Applying this first transformation, the transformed

Hamiltonian is, thus found, to be [45]

$$
\begin{aligned}
H' = & \frac{\vec{p}^2}{2m_e} - \frac{Z\alpha}{r} - \frac{\vec{p}^4}{8m_e^3} + \frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x}) + \frac{Z\alpha}{4m_e^2}\frac{\vec{\sigma}\cdot\vec{L}}{r^3} - e\,\vec{x}\cdot\vec{E} \\
& - \frac{e}{2m_e}\left[\vec{L}+\vec{\sigma}\right]\cdot\vec{B} - \frac{e}{2}x^i x^j E^i_{,j} + \frac{e^2}{8m_e}\left(\vec{x}\times\vec{B}\right)^2 - \frac{e}{6m_e}\left(L^i x^j + x^j L^i\right)B^i_{,j} \\
& - \frac{e}{2m_e}\sigma^i x^j B^i_{,j} - \frac{e}{4m_e^2}\vec{\sigma}\cdot\vec{E}\times\vec{p} + \frac{e}{4m_e^3}\vec{p}^2\left(\vec{L}+\vec{\sigma}\right)\cdot\vec{B} \\
& + \frac{e\kappa}{4m_e^3}(\vec{p}\cdot\vec{\sigma})(\vec{p}\cdot\vec{B}) - \frac{e}{8m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})(\vec{x}\times\vec{B}) - \frac{e^2}{8m_e^2}(\vec{\sigma}\times\vec{E})(\vec{x}\times\vec{B}) \\
& - \frac{e}{6}x^i x^j x^k E^i_{,jk} - \frac{e}{16m_e}(L^k x^i x^j + x^i x^j L^k)B^k_{,ij} - \frac{e}{4m_e}\sigma^k x^i x^j B^k_{,ij} \\
& + \frac{e}{8m_e^2}[x^i(\vec{\sigma}\times\vec{p})^j + (\vec{\sigma}\times\vec{p})^j x^i]E^j_{,i} - \frac{e}{4!}x^i x^j x^k x^l E^i_{,jkl}\,.
\end{aligned}
\tag{375}
$$

It is important to note that the electric field $\vec{E}$ in this Hamiltonian is the electric field of the quantized field

$$
\begin{aligned}
\vec{E}(0,t) &= -\vec{\nabla}A^0(0,t) - \partial_t\vec{A}(0,t) \\
&= \sum_{\lambda=1}^{2}\int \frac{d^3k}{\sqrt{2\omega_{\vec{k}}(2\pi)^3}}\,\mathrm{i}\omega_{\vec{k}}\,\vec{\epsilon}_\lambda(\vec{k})\left(a_\lambda(\vec{k})e^{-\mathrm{i}\omega_{\vec{k}}t} - a^\dagger_\lambda(\vec{k})e^{\mathrm{i}\omega_{\vec{k}}t}\right),
\end{aligned}
\tag{376}
$$

because of the different gauge used. Equally, the magnetic field $\vec{B}$ is the magnetic field of the quantized field

$$
\begin{aligned}
\vec{B}(0,t) &= \vec{\nabla}\times\vec{A}(0,t) \\
&= \sum_{\lambda=1}^{2}\int \frac{d^3k}{\sqrt{2\omega_{\vec{k}}(2\pi)^3}}[\mathrm{i}\vec{k}\times\vec{\epsilon}_\lambda(\vec{k})]\left(a_\lambda(\vec{k})e^{-\mathrm{i}\omega_{\vec{k}}t} - a^\dagger_\lambda(\vec{k})e^{\mathrm{i}\omega_{\vec{k}}t}\right).
\end{aligned}
\tag{377}
$$

and not an external field.

For the second Power-Zienau transformation ϕ is chosen to be [45]

$$
\phi = \frac{e}{4m_e}\int_0^1 du\,\vec{\sigma}\cdot\vec{E}(u\,\vec{x})\times\vec{x} = \frac{e}{4m_e}\vec{\sigma}\left(\vec{E}\times\vec{x} + \frac{x^i}{2}\vec{E}\times\vec{x} + \ldots\right). \tag{378}
$$

The resulting Hamiltonian thus has the form [45]

$$\begin{aligned} H_{LW} = & \frac{\vec{p}^2}{2m_e} - \frac{Z\alpha}{r} - \frac{\vec{p}^4}{8m_e^3} + \frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x}) + \frac{Z\alpha}{4m_e^2}\frac{\vec{\sigma}\cdot\vec{\ell}}{r^3} \\ & - e\,\vec{x}\cdot\vec{E} - \frac{e}{2m_e}\left(\vec{\ell}+\vec{\sigma}\right)\cdot\vec{B} - \frac{e}{2}\,x^i x^j E^i_{,j} + \frac{e^2}{8m_e}(\vec{x}\times\vec{B})^2 \\ & - \frac{e}{6m_e}(\ell^i x^j + x^j\ell^i)B^i_{,j} - \frac{e}{2m_e}\sigma^i x^j B^i_{,j} + \frac{e^2}{8m_e^2}(\vec{\sigma}\times\vec{E})\cdot(\vec{x}\times\vec{B}) \\ & - \frac{e}{6}\,x^i x^j x^k E^i_{,jk} + \frac{e}{4m_e}\vec{\sigma}\cdot\left(\dot{\vec{E}}\times\vec{x}\right). \end{aligned} \tag{379}$$

This is the NRQED Hamiltonian of Yennie gauge. Due to the long wavelength approximation used to obtain it, this Hamiltonian is often referred to as the long-wavelength Hamiltonian. A comparison to the Foldy-Wouthuysen Hamiltonian reveals that, while the noninteracting terms of the Hamiltonian did not change, the part coupled to the quantized field has changed. Because in lowest order now $\vec{x}$ couples to the quantized electric field, this choice of gauge is called length gauge. In Coulomb gauge, p/m_e, i.e the velocity couples to the quantized vector potential in lowest order. For this reason it is called velocity gauge. Extracting the terms coupled to the electric and magnetic field of the quantized field up to including order $(Z\alpha)^4$, yields the interaction Hamiltonian in length gauge

$$\begin{aligned} H_{\text{int}} = & -e\,\vec{x}\cdot\vec{E} - \frac{e}{2m_e}\left(\vec{\ell}+\vec{\sigma}\right)\cdot\vec{B} - \frac{e}{2}\,x^i x^j E^i_{,j} + \frac{e^2}{8m_e}(\vec{x}\times\vec{B})^2 \\ & - \frac{e}{6m_e}(\ell^i x^j + x^j\ell^i)B^i_{,j} - \frac{e}{2m_e}\sigma^i x^j B^i_{,j} + \frac{e^2}{8m_e^2}(\vec{\sigma}\times\vec{E})\cdot(\vec{x}\times\vec{B}) \\ & - \frac{e}{6}\,x^i x^j x^k E^i_{,jk} + \frac{e}{4m_e}\vec{\sigma}\cdot\left(\dot{\vec{E}}\times\vec{x}\right). \end{aligned} \tag{380}$$

It has a very different form from the interaction Hamiltonian in Coulomb gauge, still the result obtained with either should be the same. In Yennie or length gauge, the Hamiltonian is expressed exclusively in terms of observable field strength, whereas in Coulomb or velocity gauge the effects from the quantized field are contained in the vector potential alone.

However, the highly non trivial dependence on the coordinates of the nonrelativistic gauge transformation given by the Power-Zienau transformation and problems related to the physical interpretation of non-gauge invariant quantities [55–57], lead

to a few subtleties in the study of gauge invariance. In general, gauge transformation in bound-state problems always have to be considered very carefully.

In the case of the one-photon self-energy the method of the overlapping parameter provides the advantage that the remainder terms which arise in the gauge transformation are of order $\mathcal{O}(\epsilon)$ and therefore do not contribute to the finite part of the low-energy part [45]. Here, the problem of gauge invariance is discussed in a purely nonrelativistic problem with a definite cutoff, the two-photon decay rate. For the radiative corrections to the two-photon decay rate for example it has been shown in Ref. [58] that the results are invariant under a "hybrid" gauge transformation [56]. In it only the interaction Hamiltonian is gauge transformed, while the gauge transformation of the wave function is neglected. In general, properties of atomic states, which can be expressed using the formalism of adiabatic S-matrix theory discussed in Sec. 3, are invariant under this kind of hybrid gauge transformation. In genuinely time-dependent problems, even more care has to be taken in the choice of gauge and gauge transformations [55–57].

In the next section, the gauge invariance of the relativistic corrections to the two-photon decay rate under this kind of hybrid gauge transformation will be shown. This result has been published in Ref. [59] and adds to the leading logarithmic QED corrections, which have been calculated and proven to be gauge invariant in Ref. [58].

6.3. TWO-PHOTON DECAY

The decay processes in one-electron ions proceeding through the emission of two real photons are of special interest for many reason. The transition frequency, which has been measured with the highest accuracy in Ref. [9], is the two-photon transition between the $2S$ and the $1S$ level in hydrogen. One of the reasons lies in the very small line width of this transition, which is based on the metastability of the $2S$ level. This level decays predominantly through a two-photon transition, which has a much smaller transition rate compared to single photon dipole transitions. A further point, which has sparked much interest lately, is the discussion of two-photon transition through a cascade [60–69] i.e. a transition which can take place through a two-photon transition or by a cascade through two one-photon transition over an intermediate state.

The first study of the two-photon decay was carried out by Göppert-Mayer already in 1931 [70], where the decay rate Γ for the two-photon decay of the $2S$ was calculated nonrelativistically. The obtained result

$$\tau^{-1} = \Gamma_0 = 8.229\,352\,Z^6 s^{-1} = 1.309\,742\,Z^6\,\mathrm{Hz} \tag{381}$$

could also be verified experimentally [71–73].

Again, for the determination of the corrections to this result in this work the non-recoil limit will be used. In it the nucleus is assumed to be infinitely heavy. Then, the leading correction is given by the relativistic corrections of relative order $(Z\alpha)^2$. The leading QED radiative corrections of relative order $\alpha(Z\alpha)^2 \ln[(Z\alpha)^{-2}]$ can also be obtained. In NRQED the corrections are usually included by writing the two-photon decay rate in form of an expansion for small $Z\alpha$ which is

$$\Gamma = \Gamma_0 \left[1 + \gamma_2 (Z\alpha)^2 + \gamma_3 \frac{\alpha}{\pi} (Z\alpha)^2 \ln[(Z\alpha)^{-2}] + \dots\right] . \tag{382}$$

Here, the coefficient γ_2 for the relativistic corrections will be determined which has not be computed so far. The coefficient γ_3 for the leading QED correction is only known for the $2S$-$1S$ transition [58, 74] and results for more transitions will be given in this section. In contrast to Sec. 4, a multiplicative expansion is used where the corrections are normalized by the nonrelativistic result. The next higher-order term is expected to be a nonlogarithmic radiative correction of relative order $\alpha(Z\alpha)^2$ so the treatment is complete up to order $\alpha^3 \ln(\alpha)$.

6.3.1. Deriving the Formal Expression. As the one-photon decay rate is the imaginary part of the one-photon self-energy, the two-photon decay rate is the imaginary part of the two-photon self-energy. Similar to the discussion in Sec. 4, initially only the leading term of the interaction current in Coulomb gauge, p/m_e, is considered and the corrections are included later. The energy of the first photon will be denoted as ω_1 and the energy of the second as ω_2 respectively. In contrast to Sec. 4, the denominators will written in the from $H_S - E_\Phi + \omega$ which is the notation used in Ref. [58]. The relevant terms of the leading NRQED expression for the two-loop

self-energy for our considerations here are [58, 75]

$$\Delta E_\Phi^{(4)} = -\left(\frac{2\alpha}{3\pi}\right)^2 \int_0^{\epsilon_1} d\omega_1\, \omega_1 \int_0^{\epsilon_2} d\omega_2\, \omega_2 \tag{383}$$
$$\times \left\{ \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_1 + \omega_2} \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^j}{m_e} \right| \Phi \right\rangle \right.$$
$$+ \frac{1}{2} \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_1 + \omega_2} \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^i}{m_e} \right| \Phi \right\rangle$$
$$+ \frac{1}{2} \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_1 + \omega_2} \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^i}{m_e} \right| \Phi \right\rangle$$
$$\left. + \ldots \right\}.$$

This correction arises in fourth order of perturbation theory, hence the superscript (4). The other terms given in Refs. [58,75] do not contribute to the two-photon decay width, which is obtained from the above expression by introducing a complete set of bases for the propagator

$$\frac{1}{H_S - E_\Phi + \omega_1 + \omega_2} = \sum_\xi \frac{|\xi\rangle\langle\xi|}{E_\xi - E_\Phi + \omega_1 + \omega_2}. \tag{384}$$

The sum over ξ again represents the sum over all discrete as well as the integral over all continuum states. In order to extract the imaginary part this propagator introduces when integrated with respect to ω_2, the identity from Eq.(219) is used to write

$$\sum_\xi \frac{|\xi\rangle\langle\xi|}{E_\xi - E_\Phi + \omega_1 + \omega_2} = \sum_\xi P \frac{|\xi\rangle\langle\xi|}{E_\xi - E_\Phi + \omega_1 + \omega_2} - i\pi \sum_\xi |\xi\rangle\langle\xi|\, \delta(E_\xi - E_\Phi + \omega_1 + \omega_2). \tag{385}$$

Since the decay rate is the imaginary part of this expression, the Dirac δ can be used to carry out the integration with respect to ω_2, which gives the condition for $\omega_2 = E_\Phi - E_\xi - \omega_1$. In turn, this constrains the range of integration of ω_1 because it also implies $E_\Phi - E_\xi = \omega_1 + \omega_2$. Therefore, ω_1 can only go up to the maximum energy $\omega_{\mathrm{max}} = E_\Phi - E_\xi$ for $\omega_2 = 0$. This corresponds to a natural cutoff of the photon-energy integral, where the upper boundary is of the order $(Z\alpha)^2$ at least if only transition between bound states are considered. For these, the decay rate in leading order can

thus be written as

$$\begin{aligned}\Gamma_0 = 2\pi \left(\frac{2\alpha}{3\pi}\right)^2 \int_0^{\omega_{\max}} d\omega_1\, \omega_1\, \omega_2 \sum_{\xi} \\ \times \Bigg\{ \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^j}{m_e} \right| \xi \right\rangle \left\langle \xi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^j}{m_e} \right| \Phi \right\rangle \\ + \frac{1}{2} \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^j}{m_e} \right| \xi \right\rangle \left\langle \xi \left| \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^i}{m_e} \right| \Phi \right\rangle \\ + \frac{1}{2} \left\langle \Phi \left| \frac{p^i}{m_e} \frac{1}{H_S - E_\Phi + \omega_2} \frac{p^j}{m_e} \right| \xi \right\rangle \left\langle \xi \left| \frac{p^j}{m_e} \frac{1}{H_S - E_\Phi + \omega_1} \frac{p^i}{m_e} \right| \Phi \right\rangle \Bigg\}.\end{aligned} \tag{386}$$

Instead of calculating the complete decay rate of the reference state Φ, the rate of decay from the reference state to one definite final state, which is denoted as Φ_f, is determined. Accordingly, the reference state is the initial state of the decay and is denoted as Φ_i in the following. For the decay rate of the state Φ_i to the final state Φ_f using the binomial theorem then the expression

$$\begin{aligned}\Gamma = \frac{4}{9}\pi \left(\frac{\alpha}{\pi}\right)^2 \mathrm{Re} \int_0^{\omega_{\max}} d\omega_1\, \omega_1\, \omega_2 \Bigg[\left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_2 + \mathrm{i}\epsilon} \frac{p^j}{m_e} \right| \Phi_i \right\rangle \\ + \left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1 + \mathrm{i}\epsilon} \frac{p^j}{m_e} \right| \Phi_i \right\rangle \Bigg]^2.\end{aligned} \tag{387}$$

is found. Following the discussion in Refs. [65–67], a $\mathrm{i}\epsilon$ prescription is used and the real part of the resulting expression is considered. This allows to deal with the problematic poles if cascade transitions are possible. This expression was derived from the interaction Hamiltonian with the quantized field in velocity (Coulomb) gauge, which is

$$H_I = -\frac{e}{m_e} \vec{p} \cdot \vec{A} + \frac{e^2 \vec{A}^2}{2m}. \tag{388}$$

It already contains the leading term proportional to $\vec{A}^2$, called seagull term, whose effects will be discussed later. Here, the superscript ξ for the decay rate in velocity gauge is introduced and the denominators are expressed in Eq. (387) in terms of ω_1

exclusively, which yields for the nonrelativistic two-photon decay rate

$$\Gamma^{\xi} = \frac{4\alpha^2}{9\pi}\mathrm{Re}\int_0^{\omega_{\max}} d\omega_1\, \omega_1\, \omega_2 \left[\left\langle \Phi_f \left| \frac{p^i}{m_e}\frac{1}{H_S - E_{\Phi_f} - \omega_1 + \mathrm{i}\epsilon}\frac{p^j}{m_e}\right| \Phi_i\right\rangle + \left\langle \Phi_f \left| \frac{p^i}{m_e}\frac{1}{H_S - E_{\Phi_i} + \omega_1 + \mathrm{i}\epsilon}\frac{p^j}{m_e}\right| \Phi_i\right\rangle\right]^2, \tag{389}$$

where $\omega_2 = E_{\Phi_i} - E_{\Phi_f} - \omega_1$ and $\omega_{\max} = E_{\Phi_i} - E_{\Phi_f}$.

In the beginning of this section, the interaction Hamiltonian in length (Yennie) gauge is derived, whose leading term is

$$H_I = -e\vec{E}\cdot\vec{x}\,. \tag{390}$$

This Hamiltonian can also be used to derive an expression for the two-photon decay rate from an initial state Φ_i to a final state Φ_f. An analogue derivation to the one presented leads to the expression in length gauge

$$\Gamma^{\zeta} = \frac{4\alpha^2}{9\pi}\mathrm{Re}\int_0^{\omega_{\max}} d\omega_1\, \omega_1^3\, \omega_2^3 \left[\left\langle \Phi_f \left| x^i\frac{1}{H_S - E_{\Phi_f} - \omega_1 + \mathrm{i}\epsilon}x^j\right| \Phi_i\right\rangle + \left\langle \Phi_f \left| x^i\frac{1}{H_S - E_{\Phi_i} + \omega_1 + \mathrm{i}\epsilon}x^j\right| \Phi_i\right\rangle\right]^2, \tag{391}$$

where the superscript ζ was introduced to differentiate this expression from the one in velocity gauge. The gauge invariance of the nonrelativistic result for the two-photon decay rate under the gauge transformation carried out in Sec. 6.2 can now be proven if it can be shown that the above expressions are equivalent. That this is indeed the case follows form the relation [55, 76]

$$\begin{aligned}&\left\langle \Phi_f \left| p^i\frac{1}{H_S - E_{\Phi_f} - \omega_1}p^j\right| \Phi_i\right\rangle + \left\langle \Phi_f \left| p^i\frac{1}{H_S - E_{\Phi_i} + \omega_1}p^j\right| \Phi_i\right\rangle \\ &= -m_e^2\omega_1\omega_2\left[\left\langle \Phi_f \left| x^i\frac{1}{H_S - E_{\Phi_f} - \omega_1}x^j\right| \Phi_i\right\rangle + \left\langle \Phi_f \left| x^i\frac{1}{H_S - E_{\Phi_i} + \omega_1}x^j\right| \Phi_i\right\rangle\right].\end{aligned} \tag{392}$$

If a set of bases is used for the representation of the intermediate propagator, special care has to be taken to make sure the set is complete because otherwise this relation is not valid.

Relativistic corrections to this result of relative order $(Z\alpha)^2$ are now included in the same way as in Sec. 4.5. In both gauges the relativistic corrections to non-interacting part of the Hamiltonian i.e. the Schrödinger Hamiltonian H_S are the same. Likewise, they can be included by

$$\begin{aligned} H_S &\to H_S + \delta H_S\,, \\ H_S &= \frac{p^2}{2m_e} - \frac{Z\alpha}{r}\,, \\ \delta H_S &= -\frac{(\vec{p}^{\,2})^2}{8m_e^3} + \frac{\pi Z\alpha}{2m_e^2}\delta(\vec{x}) + \frac{Z\alpha}{4m_e^2 r^3}\vec{\sigma}\cdot\vec{\ell}\,. \end{aligned} \tag{393}$$

Because the analysis now also includes S states, the Darwin term, which describes the zitterbewegung of the electron, has to be included additionally to the correction due to relativistic kinetic energy and the spin-orbit coupling term. Consequently, the relativistic corrections of the Hamiltonian also cause relativistic corrections of the energy and the wave function, which read as follows

$$E_\Phi \to E_\Phi + \delta E_\Phi = E_\Phi + \langle\Phi\,|\delta H_S|\,\Phi\rangle\ , \tag{394}$$

$$|\Phi\rangle \to |\Phi\rangle + |\delta\Phi\rangle = |\Phi\rangle + \left(\frac{1}{E_\Phi - H_S}\right)' \delta H_S\,|\Phi\rangle\ . \tag{395}$$

This correction is the same for both gauges, whereas the differences arise in the inclusion of the relativistic corrections to the interaction current. In velocity (Coulomb) gauge, the interaction part of the Foldy-Wouthuysen Hamiltonian is given by

$$\begin{aligned} H_{\rm int} = &-\frac{e\vec{A}\cdot\vec{p}}{m_e} - \frac{e}{2m_e}\left(\vec{\sigma}\times\vec{\nabla}\right)\cdot\vec{A} + \frac{e}{2m_e^3}\left(\vec{A}\cdot\vec{p}\right)\vec{p}^{\,2} \\ &- \frac{e}{4m_e^2}\left(\vec{\sigma}\times\vec{p}\right)\cdot\frac{\partial\vec{A}}{\partial t} - \frac{e}{4m_e^2}\left(\vec{\sigma}\times\vec{\nabla}V\right)\cdot\vec{A} \equiv -e\vec{J}\cdot\vec{A}\,. \end{aligned} \tag{396}$$

The photon degrees of freedom contained in the vector potential can be traced out as in Sec. 4.3 and in Eq. (296). The interaction current $\vec{J}$ is thus

$$\begin{aligned} J^i \equiv \frac{p^i}{m_e} + \delta J^i = &\frac{p^i}{m_e}\left(1 - \mathrm{i}\,\vec{k}\cdot\vec{x} - \tfrac{1}{2}(\vec{k}\cdot\vec{x})^2\right) - \frac{p^i\vec{p}^{\,2}}{2m_e^3} \\ &- \frac{1}{2m_e^2}\frac{Z\alpha}{r^3}(\vec{x}\times\vec{\sigma})^i - \frac{\mathrm{i}}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^i\left(1 - \mathrm{i}\,\vec{k}\cdot\vec{x}\right)\,. \end{aligned} \tag{397}$$

As mentioned earlier, in contrast to the one-photon self-energy the contribution from the terms proportional to $\vec{A}^2$ also have to be taken into account because they represent the emission of two photons from the same vertex. They are contained in the so-called seagull Hamiltonian which is given by combining all terms proportional to $\vec{A}^2$ in the Foldy-Wouthuysen Hamiltonian. It is given by

$$H_{\text{sea}} = \frac{e^2\vec{A}^2}{2m_e} - \frac{e^2}{2m_e^3}\left(\vec{A}\cdot\vec{p}\right)^2 - \frac{e^2}{4m_e^3}\vec{A}^2\vec{p}^2\,. \tag{398}$$

All its terms are of a different order in α compared to the normal interaction Hamiltonian and therefore appear in a different order of perturbation theory. The photon degrees of freedom are traced out once again. This is achieved here by only considering the creation part of the photon operators and expanding the associated exponential $\exp(-\mathrm{i}\,\vec{k}\cdot\vec{r})$ up to lowest order for the last two terms, which already carry a power $(Z\alpha)^2$ from the momentum operators but up to order $(Z\alpha)^2$ for the first term. Because the expansion has to be carried out for each of the two photons emitted through the seagull term separately, the corresponding correction after this process is

$$\delta S^{ij} = -\frac{1}{2m_e}(\vec{k}_1\cdot\vec{x})^2\delta^{ij} - \frac{1}{2m_e}(\vec{k}_2\cdot\vec{x})^2\delta^{ij} - \frac{p^ip^j}{m_e^3} - \frac{p^2}{2m_e^3}\delta^{ij}\,. \tag{399}$$

Interestingly, the matrix element of the leading seagull term $-\frac{1}{2m_e}\delta^{ij}$ vanishes and it does therefore not contribute to the two-photon decay rate. There is, however, a correction term with this leading seagull acting on the perturbed wave function but the total correction introduced by this term can be shown to vanish as well.

The interaction Hamiltonian in length gauge was already extracted out of the long-wavelength Hamiltonian in Eq. (380). For our purposes here, the relevant terms are

$$\begin{aligned} H_{\text{int}} = {} & -e\,\vec{x}\cdot\vec{E} - \frac{e}{2m_e}\left(\vec{\ell}+\vec{\sigma}\right)\cdot\vec{B} - \frac{e}{2}\,x^ix^jE^i_{,j} - \frac{e}{6m_e}\left(\ell^ix^j + x^j\ell^i\right)B^i_{,j} \\ & - \frac{e}{2m_e}\sigma^ix^jB^i_{,j} - \frac{e}{6}\,x^ix^jx^kE^i_{,jk} + \frac{e}{4m_e}\vec{\sigma}\cdot\left(\dot{\vec{E}}\times\vec{x}\right)\,. \end{aligned} \tag{400}$$

The corresponding interaction current, which for length gauge will be denoted as $\vec{I}$, can be extracted in the same way as before to give

$$I^i \equiv x^i + \delta I^i = x^i \left(1 - \tfrac{\mathrm{i}}{2}\vec{k}\cdot\vec{x} - \tfrac{1}{6}(\vec{k}\cdot\vec{x})^2\right) + \frac{\mathrm{i}\omega}{4m_e}(\vec{\sigma}\times\vec{x})^i + \frac{1}{2m_e\omega}(\vec{\ell}\times\vec{k})^i + \frac{1}{2m_e\omega}\left(\vec{\sigma}\times\vec{k}\right)^i\left(1 - \mathrm{i}\vec{k}\cdot\vec{x}\right) - \frac{\mathrm{i}}{6m_e\omega}\left\{(\vec{\ell}\times\vec{k})^i, \vec{k}\cdot\vec{x}\right\}, \tag{401}$$

where $\{A, B\} = AB + BA$ is the anticommutator. After the discussion of the relativistic corrections arising in both gauges, it is now possible to turn to how these terms correct the nonrelativistic result and how the resulting matrix elements can be derived in the different gauges, starting with the velocity gauge.

6.3.2. Velocity Gauge. In accordance with the notation used in Refs. [58,59] the nonrelativistic two-photon decay rate in velocity gauge given in Eq. (389) is written in the shortened form

$$\Gamma^{\xi} = \frac{4\alpha^2}{9\pi}\int_0^{\omega_{\max}} d\omega_1\,\omega_1\,\omega_2\,\xi^2, \tag{402}$$

where ξ denotes the sum of the matrix elements in velocity gauge

$$\xi = \xi_1 + \xi_2 \tag{403a}$$

with

$$\xi_1 = \left\langle \Phi_f \left| \frac{p^i}{m_e}\frac{1}{H_S - E_{\Phi_i} + \omega_1}\frac{p^j}{m_e}\right| \Phi_i \right\rangle, \tag{403b}$$

$$\xi_2 = \left\langle \Phi_f \left| \frac{p^i}{m_e}\frac{1}{H_S - E_{\Phi_f} - \omega_1}\frac{p^j}{m_e}\right| \Phi_i \right\rangle. \tag{403c}$$

In order to keep the notation compact, the tensor indices ij of the tensor ξ are suppressed but it is implied that $\xi^2 \equiv \xi^{ij}\,\xi^{ij}$, where the indices i and j are summed over, and that $\xi\delta\xi \equiv \xi^{ij}\,\delta\xi^{ij}$. $\delta\xi$ therein is defined as the sum of all the correction terms due to the relativistic corrections. In the way described in Ref. [58], the first order relativistic correction $\delta\Gamma^{\xi}$ to the decay rate in velocity gauge can thus be written

as

$$\delta\Gamma^{\xi} = 2\,\frac{4\alpha^2}{9\pi}\int_0^{\omega_{\max}} d\omega_1\,\omega_1\,\omega_2\,\xi\,\delta\xi + \frac{4\alpha^2}{9\pi}\delta\omega_2\int_0^{\omega_{\max}} d\omega_1\,\omega_1\,\xi^2\,. \tag{404}$$

Compared to the self-energy corrections in Sec. 4.5, an additional correction of the photon energy arises. It is necessary to ensure that after the inclusion of the relativistic energy corrections, energy conservation is still fulfilled. Therefore, one has

$$\omega_1 + \omega_2 = E_{\Phi_i} - E_{\Phi_f} + \delta\omega_2\,, \tag{405a}$$

$$\delta\omega_2 = \delta E_{\Phi_i} - \delta E_{\Phi_f} = \langle\Phi_i|\delta H_S|\Phi_i\rangle - \langle\Phi_f|\delta H_S|\Phi_f\rangle\,. \tag{405b}$$

The correction $\delta\xi$ is now obtained in a similar manner as in Sec. 4.5, where the relativistic corrections to the self-energy are deduced. However, because here one has a final and initial state as well as two different matrix elements, the number of terms is much greater. For the correction to the wave function for example corrections for both the initial and the final wave function have to be considered for each of the two matrix elements ξ_1 and ξ_2. This gives rise to four correction terms from the wave function alone, compared to just one in the case of the self-energy. In total the correction $\delta\xi$ is given as the sum of 15 such correction matrix elements

$$\delta\xi = \sum_{k=1}^{15}\delta\xi_k\,. \tag{406}$$

The first two corrections arise due to the relativistic correction to the energy of the initial and final state

$$\delta\xi_1 = \left\langle\Phi_f\left|\frac{p^i}{m_e}\left(\frac{1}{H_S - E_{\Phi_i} + \omega_1}\right)^2\frac{p^j}{m_e}\right|\Phi_i\right\rangle\langle\Phi_i\,|\delta H_S|\,\Phi_i\rangle\,, \tag{407a}$$

$$\delta\xi_2 = \langle\Phi_f\,|\delta H_S|\,\Phi_f\rangle\left\langle\Phi_f\left|\frac{p^i}{m_e}\left(\frac{1}{H_S - E_{\Phi_f} - \omega_1}\right)^2\frac{p^j}{m_e}\right|\Phi_i\right\rangle. \tag{407b}$$

Then the mentioned four correction matrix elements for the initial and final wave function are

$$\delta\xi_3 = \left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \left(\frac{1}{E_{\Phi_i} - H} \right)' \delta H_S \middle| \Phi_i \right\rangle , \tag{407c}$$

$$\delta\xi_4 = \left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \middle| \Phi_i \right\rangle , \tag{407d}$$

$$\delta\xi_5 = \left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle , \tag{407e}$$

$$\delta\xi_6 = \left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle . \tag{407f}$$

The correction of the Hamiltonian in ξ_1 and ξ_2 leads to the two terms

$$\delta\xi_7 = -\left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle , \tag{407g}$$

$$\delta\xi_8 = -\left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle . \tag{407h}$$

The corrections to the interaction current now leads to four terms because acting the correction on the initial or the final state gives rise to different corrections, so one has

$$\delta\xi_9 = \left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta J^j \middle| \Phi_i \right\rangle , \tag{407i}$$

$$\delta\xi_{10} = \left\langle \Phi_f \middle| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta J^j \middle| \Phi_i \right\rangle , \tag{407j}$$

$$\delta\xi_{11} = \left\langle \Phi_f \middle| \delta J^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle , \tag{407k}$$

$$\delta\xi_{12} = \left\langle \Phi_f \middle| \delta J^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle . \tag{407l}$$

The relativistic corrections to the seagull term lead to the term

$$\delta\xi_{13} = -\left\langle \Phi_f \middle| \delta S^{ij} \middle| \Phi_i \right\rangle . \tag{407m}$$

The seagull term represents the emission of two photons from the same vertex and is therefore of a different order in perturbation theory than the one-photon emission. To obtain its second-order perturbation, it has to be applied in first order perturbation

theory. The minus sign arises because in this section the perturbation series is written in the "$1/(H-E)$" form. The matrix element of the leading order seagull term $e^2\vec{A}^2/(2m_e)$ vanishes when applied to the unperturbed wave function. In relative order $(Z\alpha)^2$ it can be applied to the perturbed wave function. The resulting matrix elements found in Ref. [58] are then

$$\delta\xi_{14} = -\frac{1}{m_e}\left\langle\Phi_f\left|\left(\frac{1}{E_{\Phi_i}-H_S}\right)'\delta H_S\right|\Phi_i\right\rangle\delta^{ij}\,, \tag{407n}$$

$$\delta\xi_{15} = -\frac{1}{m_e}\left\langle\Phi_f\left|\delta H_S\left(\frac{1}{E_{\Phi_f}-H_S}\right)'\right|\Phi_i\right\rangle\delta^{ij}\,. \tag{407o}$$

These terms can be simplified by introducing a complete basis set of hydrogen eigenfunctions and writing the initial and final state in terms of the usual quantum number $|\Phi_i\rangle = |n_i\ell_i j_i m_i\rangle$ which gives

$$\begin{aligned}
-m_e(\delta\xi_{14}+\delta\xi_{15}) &= \left\langle n_f\ell_f j_f m_f\left|\left(\frac{1}{E_{n_i}-H_S}\right)'\delta H_S\right|n_i\ell_i j_i m_i\right\rangle \\
&\quad+\left\langle n_f\ell_f j_f m_f\left|\delta H_S\left(\frac{1}{E_{n_f}-H_S}\right)'\right|n_i\ell_i j_i m_i\right\rangle \\
&= \sum_{n'\ell'j'm'\neq n_i\ell_i j_i m_i}\frac{\langle n_f\ell_f j_f m_f|n'\ell'j'm'\rangle}{E_{n_i}-E_{n'}}\langle n'\ell'j'm'\,|\delta H_S|\,n_i\ell_i j_i m_i\rangle \\
&\quad+\sum_{n'\ell'j'm'\neq n_f\ell_f j_f m_f}\langle n_f\ell_f j_f m_f\,|\delta H_S|\,n'\ell'j'm'\rangle\frac{\langle n'\ell'j'm'|n_i\ell_i j_i m_i\rangle}{E_{n_f}-E_{n'}}\,.
\end{aligned} \tag{408}$$

Because there is no operator in between one of the matrix elements, it can only take a nonvanishing value if both states are identical due to the orthonormality of hydrogen eigenfunctions. This leads to

$$\begin{aligned}
-m_e(\delta\xi_{14}+\delta\xi_{15}) &= \frac{\langle n_f\ell_f j_f m_f|n_f\ell_f j_f m_f\rangle}{E_{n_i}-E_{n_f}}\langle n_f\ell_f j_f m_f\,|\delta H_S|\,n_i\ell_i j_i m_i\rangle \\
&\quad+\langle n_f\ell_f j_f m_f\,|\delta H_S|\,n_i\ell_i j_i m_i\rangle\frac{\langle n_i\ell_i j_i m_i|n_i\ell_i j_i m_i\rangle}{E_{n_f}-E_{n_i}} \\
&= \frac{\langle n_f\ell_f j_f m_f\,|\delta H_S|\,n_i\ell_i j_i m_i\rangle}{E_{n_i}-E_{n_f}}-\frac{\langle n_f\ell_f j_f m_f\,|\delta H_S|\,n_i\ell_i j_i m_i\rangle}{E_{n_i}-E_{n_f}}=0
\end{aligned} \tag{409}$$

and, thus, the sum $\delta\xi_{14}+\delta\xi_{15}$ vanishes.

6.3.3. Length Gauge. With the same shortened notation used for the velocity gauge the corresponding length gauge expression in Eq. (391) is written as

$$\Gamma^{\zeta} = \frac{4\alpha^2}{9\pi} \int_0^{\omega_{\max}} d\omega_1 \, \omega_1^3 \, \omega_2^3 \, \zeta^2 \,, \tag{410}$$

where the superscript ζ denotes the length-gauge expression. Here, ω_2 is defined as in Eq. (402), and the length-gauge matrix elements are

$$\zeta = \zeta_1 + \zeta_2 \,, \tag{411a}$$

$$\zeta_1 = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \,, \tag{411b}$$

$$\zeta_2 = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle \,. \tag{411c}$$

The corrections to this result are obtained in the same manner as for the velocity gauge and the first-order correction to the two-photon decay rate in length gauge thus is

$$\delta\Gamma^{\zeta} = 2\frac{4\alpha^2}{9\pi} \int_0^{\omega_{\max}} d\omega_1 \, \omega_1^3 \, \omega_2^3 \, \zeta \, \delta\zeta + 3\frac{4\alpha^2}{9\pi} \delta\omega_2 \int_0^{\omega_{\max}} d\omega_1 \, \omega_1^3 \, \omega_2^2 \, \zeta^2 \,. \tag{412}$$

The sum of all the different correction matrix elements due to the different relativistic corrections in length gauge is denoted as $\delta\zeta$. In contrast to the velocity gauge, it only consists of twelve terms due to the absence of seagull terms

$$\delta\zeta = \sum_{k=1}^{12} \delta\zeta_k \,. \tag{413}$$

In the following, all the different corrections will be given, starting with the relativistic corrections of the initial and final state energy

$$\delta\zeta_1 = \left\langle \Phi_f \left| x^i \left(\frac{1}{H_S - E_{\Phi_i} + \omega_1} \right)^2 x^j \right| \Phi_i \right\rangle \langle \Phi_i \left| \delta H_S \right| \Phi_i \rangle \,, \tag{414a}$$

$$\delta\zeta_2 = \langle \Phi_f \left| \delta H_S \right| \Phi_f \rangle \left\langle \Phi_f \left| x^i \left(\frac{1}{H_S - E_{\Phi_f} - \omega_1} \right)^2 x^j \right| \Phi_i \right\rangle \,. \tag{414b}$$

The next terms are due to the perturbations of the initial and final state wave functions

$$\delta\zeta_3 = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle , \tag{414c}$$

$$\delta\zeta_4 = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle , \tag{414d}$$

$$\delta\zeta_5 = \left\langle \Phi_f \left| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle , \tag{414e}$$

$$\delta\zeta_6 = \left\langle \Phi_f \left| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle . \tag{414f}$$

The correction to the Hamiltonian is accounted for by the two terms

$$\delta\zeta_7 = -\left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle , \tag{414g}$$

$$\delta\zeta_8 = -\left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle . \tag{414h}$$

Finally, the relativistic corrections to the interaction current gives rise to the last four terms

$$\delta\zeta_9 = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta I^j \right| \Phi_i \right\rangle , \tag{414i}$$

$$\delta\zeta_{10} = \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta I^j \right| \Phi_i \right\rangle , \tag{414j}$$

$$\delta\zeta_{11} = \left\langle \Phi_f \left| \delta I^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle , \tag{414k}$$

$$\delta\zeta_{12} = \left\langle \Phi_f \left| \delta I^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle . \tag{414l}$$

6.4. PROOF OF GAUGE INVARIANCE

In this section, the equivalence of the length and velocity gauge expression is proven. Thereby, the gauge invariance of the two-photon decay rate under a hybrid gauge transformation, where the gauge transformation of the wave function is ignored, is shown. In order to ease the understanding and illustrate the interlinking of the different corrections, the calculation is divided into three parts. In the first part, the

generalized corrections because of the relativistic Hamiltonian are considered. In this correction, current and seagull terms will arise, which would not be linked to the relativistic Hamiltonian *a priori*, hence the term generalized. The second part deals with the quadrupole corrections to the electron's interaction current. In the third part it will be shown that the remaining terms, which mainly are due to the magnetic interactions, vanish separately.

6.4.1. Correction to the Hamiltonian. For the proof of gauge invariance for the corrections to the Hamiltonian, the expression in velocity gauge will be transformed into the corresponding length-gauge expression. In the shortened notation, where the velocity-gauge form is denoted as ξ and the length-gauge form as ζ, the gauge invariance of the leading nonrelativistic result can be traced to the formula in Eq. (392), which is written as

$$\xi = -\omega_1 \omega_2 \zeta \,, \tag{415}$$

where the tensor indices ij are suppressed as explained previously. The first terms, which are due to the relativistic correction of the Hamiltonian, are the correction terms $\delta\xi_1$ and $\delta\xi_2$ of the initial and final state energy in velocity gauge. They can be brought into length with the relations

$$p^i = \mathrm{i} m_e \left[H_S - E + \omega, x^i\right], \tag{416}$$

$$\omega_2 = E_{\Phi_i} - E_{\Phi_f} - \omega_1 \,. \tag{417}$$

The transformation of $\delta\xi_1$ leads to

$$\begin{aligned}
\delta\xi_1 &= \left\langle \Phi_f \left| \frac{p^i}{m_e} \left(\frac{1}{H_S - E_{\Phi_i} + \omega_1} \right)^2 \frac{p^j}{m_e} \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle \\
&= -\omega_1 \omega_2 \left\langle \Phi_f \left| x^i \left(\frac{1}{H_S - E_{\Phi_i} + \omega_1} \right)^2 x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle \\
&\quad + (\omega_2 - \omega_1) \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle \\
&\quad + \left\langle \Phi_f \left| x^i x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle \,.
\end{aligned} \tag{418}$$

An analogous relation also holds for $\delta\xi_2$,

$$\begin{aligned}
\delta\xi_2 &= \left\langle \Phi_f \left| \frac{p^i}{m_e} \left(\frac{1}{H_S - E_{\Phi_f} - \omega_1} \right)^2 \frac{p^j}{m_e} \right| \Phi_i \right\rangle \langle \Phi_f | \delta H_S | \Phi_f \rangle \\
&= -\omega_1\omega_2 \left\langle \Phi_f \left| x^i \left(\frac{1}{H_S - E_{\Phi_f} - \omega_1} \right)^2 x^j \right| \Phi_i \right\rangle \langle \Phi_f | \delta H_S | \Phi_f \rangle \\
&\quad + (\omega_1 - \omega_2) \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle \langle \Phi_f | \delta H_S | \Phi_f \rangle \\
&\quad + \left\langle \Phi_f \left| x^i x^j \right| \Phi_i \right\rangle \langle \Phi_f | \delta H_S | \Phi_f \rangle .
\end{aligned} \tag{419}$$

The relations from Ref. [58] for a radiative corrections potential are generalized to the relativistic corrections of the Hamiltonian. While this does not alter the relation for the energy, the transformation of the correction to the wave function takes a new form. For the following corrections it is useful to recall the relation

$$\begin{aligned}
&(H_S - E_\phi + \omega) \left(\frac{1}{E_\phi - H_S} \right)' \delta H_S \left| \phi \right\rangle \\
&= \left[(H_S - E_\phi) \left(\frac{1}{E_\phi - H_S} \right)' + \omega \left(\frac{1}{E_\phi - H_S} \right)' \right] \delta H_S \left| \phi \right\rangle \\
&= \left[(H_S - E_\phi) \left\{ \left(\frac{1}{E_\phi - H_S} \right) - \frac{\left| \phi \right\rangle \left\langle \phi \right|}{E_\phi - \left\langle \phi \right| H_S \left| \phi \right\rangle} \right\} + \omega \left(\frac{1}{E_\phi - H_S} \right)' \right] \delta H_S \left| \phi \right\rangle \\
&= \left[-1 + \left| \phi \right\rangle \left\langle \phi \right| + \omega \left(\frac{1}{E_\phi - H_S} \right)' \right] \delta H_S \left| \phi \right\rangle .
\end{aligned} \tag{420}$$

Thus, $\delta\xi_3$ gives

$$\begin{aligned}
\delta\xi_3 &= \left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \left(\frac{1}{E_{\Phi_i} - H} \right)' \delta H_S \right| \Phi_i \right\rangle \\
&= -\omega_1\omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle \\
&\quad - \omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle + \left\langle \Phi_f \left| x^i x^j \delta H_S \right| \Phi_i \right\rangle \\
&\quad + \underbrace{\left\langle \Phi_f \left| x^i (H_S - E_{\Phi_i} + \omega_2) x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle}_{\equiv T_1} \\
&\quad - \left\langle \Phi_f \left| x^i x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle + \omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \delta H_S \right| \Phi_i \right\rangle .
\end{aligned} \tag{421}$$

For $\delta\xi_4$ this yields

$$\begin{aligned}
\delta\xi_4 &= \left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle \\
&= -\omega_1\omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle \\
&\quad - \omega_1 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle + \langle \Phi_f | x^i x^j \delta H_S | \Phi_i \rangle \\
&\quad + \underbrace{\left\langle \Phi_f \left| x^i (H_S - E_{\Phi_f} - \omega_2) x^j \left(\frac{1}{E_{\Phi_i} - H_S} \right)' \delta H_S \right| \Phi_i \right\rangle}_{\equiv T_2} \\
&\quad - \langle \Phi_f | x^i x^j | \Phi_i \rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle + \omega_1 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \delta H_S \right| \Phi_i \right\rangle .
\end{aligned} \tag{422}$$

For the correction $\delta\xi_5$ to the final-state wave function

$$\begin{aligned}
\delta\xi_5 &= \left\langle \Phi_f \left| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \right| \Phi_i \right\rangle \\
&= -\omega_1\omega_2 \left\langle \Phi_f \left| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \\
&\quad + \omega_1 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \langle \Phi_f | \delta H_S | \Phi_f \rangle + \langle \Phi_f | \delta H_S x^i x^j | \Phi_i \rangle \\
&\quad + \underbrace{\left\langle \Phi_f \left| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S} \right)' x^i (H_S - E_{\Phi_f} - \omega_1) x^j \right| \Phi_i \right\rangle}_{\equiv T_3} \\
&\quad - \langle \Phi_f | \delta H_S | \Phi_f \rangle \langle \Phi_f | x^i x^j | \Phi_i \rangle - \omega_1 \left\langle \Phi_f \left| \delta H_S x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle ,
\end{aligned} \tag{423}$$

and for $\delta\xi_6$

$$\begin{aligned}
\delta\xi_6 &= \left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S}\right)' \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \middle| \Phi_i \right\rangle \\
&= -\omega_1\omega_2 \left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S}\right)' x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \middle| \Phi_i \right\rangle \\
&\quad + \omega_2 \langle \Phi_f | \delta H_S | \Phi_f \rangle \left\langle \Phi_f \middle| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \middle| \Phi_i \right\rangle + \left\langle \Phi_f \middle| \delta H_S x^i x^j \middle| \Phi_i \right\rangle \\
&\quad + \underbrace{\left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S}\right)' x^i (H_S - E_{\Phi_i} + \omega_1) x^j \middle| \Phi_i \right\rangle}_{\equiv T_4} \\
&\quad - \langle \Phi_f | \delta H_S | \Phi_f \rangle \langle \Phi_f | x^i x^j | \Phi_i \rangle - \omega_2 \left\langle \Phi_f \middle| \delta H_S x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \middle| \Phi_i \right\rangle
\end{aligned} \tag{424}$$

are obtained. In the transformation of the corrections to the wave function remainder terms, which have been denoted as T_1 to T_4 arise. They can be further simplified by combining them and carrying out another transformation, which leads to

$$\begin{aligned}
T_1 + T_2 &= \frac{1}{m_e} \left\langle \Phi_f \middle| \left(\frac{1}{E_{\Phi_i} - H_S}\right)' \delta H_S \middle| \Phi_i \right\rangle \delta^{ij} \\
&\quad + \langle \Phi_f | x^i x^j | \Phi_i \rangle \langle \Phi_i | \delta H_S | \Phi_i \rangle - \langle \Phi_f | x^i x^j \delta H | \Phi_i \rangle \ ,
\end{aligned} \tag{425}$$

$$\begin{aligned}
T_3 + T_4 &= \frac{1}{m_e} \left\langle \Phi_f \middle| \delta H_S \left(\frac{1}{E_{\Phi_f} - H_S}\right)' \middle| \Phi_i \right\rangle \delta^{ij} \\
&\quad + \langle \Phi_f | \delta H_S | \Phi_f \rangle \langle \Phi_f | x^i x^j | \Phi_i \rangle - \langle \Phi_f | \delta H_S x^i x^j | \Phi_i \rangle \ .
\end{aligned} \tag{426}$$

The first term of Eq. (425) is the negative of the seagull corrections $\delta\xi_{14}$ and the first term of Eq. (426) is the negative of $\delta\xi_{15}$. So, these terms cancel the seagull terms in the transition from velocity to length gauge as it is expected because the length-gauge expression does not contain seagull terms. This makes it apparent that in the transition from velocity to length gauge of the Hamiltonian corrections terms are generated, which cancel correction present in velocity gauge but not in length gauge. The other terms on the right-hand side will be treated separately, later.

The final Hamiltonian corrections are those of the Hamiltonian itself, which can be brought into length gauge form in the following way:

$$\begin{aligned}
\delta\xi_7 &= -\left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_i} + \omega_1} \frac{p^j}{m_e} \right| \Phi_i \right\rangle \\
&= \omega_1\omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle . \\
&\quad - \omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} \delta H_S x^j \right| \Phi_i \right\rangle \\
&\quad + \omega_1 \left\langle \Phi_f \left| x^i \delta H_S \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle - \left\langle \Phi_f \left| x^i \delta H_S x^j \right| \Phi_i \right\rangle .
\end{aligned} \tag{427}$$

For the second correction to the Hamiltonian $\delta\xi_8$ the analogue transformation gives

$$\begin{aligned}
\delta\xi_8 &= -\left\langle \Phi_f \left| \frac{p^i}{m_e} \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_f} - \omega_1} \frac{p^j}{m_e} \right| \Phi_i \right\rangle \\
&= \omega_1\omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta H_S \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle \\
&\quad - \omega_1 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} \delta H_S x^j \right| \Phi_i \right\rangle \\
&\quad + \omega_2 \left\langle \Phi_f \left| x^i \delta H_S \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle - \left\langle \Phi_f \left| x^i \delta H_S x^j \right| \Phi_i \right\rangle .
\end{aligned} \tag{428}$$

Combining all the discussed corrections the result reads as follows,

$$\begin{aligned}
\sum_{i=1}^{8} \delta\xi_i &= -\omega_1\omega_2 \sum_{i=1}^{8} \delta\zeta_i - \delta\omega_2\,\omega_1\zeta + \omega_2 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_i} + \omega_1} [x^j, \delta H_S] \right| \Phi_i \right\rangle \\
&\quad - \delta\xi_{14} - \delta\xi_{15} + \omega_1 \left\langle \Phi_f \left| x^i \frac{1}{H_S - E_{\Phi_f} - \omega_1} [x^j, \delta H_S] \right| \Phi_i \right\rangle \\
&\quad + \omega_2 \left\langle \Phi_f \left| [x^i, \delta H_S] \frac{1}{H_S - E_{\Phi_i} + \omega_1} x^j \right| \Phi_i \right\rangle \\
&\quad + \omega_1 \left\langle \Phi_f \left| [x^i, \delta H_S] \frac{1}{H_S - E_{\Phi_f} - \omega_1} x^j \right| \Phi_i \right\rangle - \left\langle \Phi_f \left| [[x^i, \delta H_S], x^j] \right| \Phi_i \right\rangle .
\end{aligned} \tag{429}$$

where $\delta\omega_{\max}$ is defined in Eq. (405b). Evaluating the commutator $[x^j, \delta H_S]$ gives

$$[x^i, \delta H_S] = \left[x^i, -\frac{\vec{p}^{\,4}}{8m_e^3} \right] + \left[x^i, \frac{Z\alpha}{4m_e^2 r^3} \vec{\sigma} \cdot \vec{\ell} \right] = -\mathrm{i} \frac{p^i \vec{p}^{\,2}}{2m_e^3} - \frac{\mathrm{i}}{4m_e^2} \frac{Z\alpha}{r^3} (\vec{x} \times \vec{\sigma})^i , \tag{430}$$

with which the terms containing this commutator can be further simplified yielding

$$\begin{aligned}
&\omega_1\left\langle\Phi_f\left|[x^i,\delta H_S]\frac{1}{H_S-E_{\Phi_i}+\omega_1}x^j\right|\Phi_i\right\rangle+\omega_2\left\langle\Phi_f\left|[x^i,\delta H_S]\frac{1}{H_S-E_{\Phi_f}-\omega_1}x^j\right|\Phi_i\right\rangle\\
&+\omega_2\left\langle\Phi_f\left|x^i\frac{1}{H_S-E_{\Phi_i}+\omega_1}[x^j,\delta H_S]\right|\Phi_i\right\rangle\\
&+\omega_1\left\langle\Phi_f\left|x^i\frac{1}{H_S-E_{\Phi_f}-\omega_1}[x^j,\delta H_S]\right|\Phi_i\right\rangle\\
=&-\left\langle\Phi_f\left|\delta J_H^i\frac{1}{H_S-E_{\Phi_i}+\omega_1}\frac{p^j}{m_e}\right|\Phi_i\right\rangle-\left\langle\Phi_f\left|\delta J_H^i\frac{1}{H_S-E_{\Phi_f}-\omega_1}\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&-\left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{H_S-E_{\Phi_i}+\omega_1}\delta J_H^j\right|\Phi_i\right\rangle-\left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{H_S-E_{\Phi_f}-\omega_1}\delta J_H^j\right|\Phi_i\right\rangle\\
&+2\left\langle\Phi_f\left|[[x^i,\delta H_S],x^j]\right|\Phi_i\right\rangle\,.
\end{aligned}\tag{431}$$

In it the current correction of the Hamiltonian δJ_H^i is given by the current corrections due to the relativistic correction of the momentum and due to the coupling of the physical momentum to the spin. So, it is defined as

$$\delta J_H^i=-\frac{p^i\,\vec{p}^{\,2}}{2m_e^3}-\frac{1}{4m_e^2}\frac{Z\alpha}{r^3}\left(\vec{x}\times\vec{\sigma}\right)^i\,.\tag{432}$$

It can be seen that these corrections are very closely related to the Hamiltonian and are canceled in the transition from velocity to length gauge by terms arising form the Hamiltonian corrections. The interesting implication of this is that these corrections in velocity gauge are included in the Hamiltonian corrections in length gauge.

Incorporating this result into Eq. (429) yields

$$\begin{aligned}
&\sum_{i=1}^{8}\delta\xi_i+\sum_{i=9}^{12}\delta\xi_i\Big|_{\delta J=\delta J_H}\\
&\qquad=-\omega_1\omega_2\sum_{i=1}^{8}\delta\zeta_i-\delta\omega_2\,\omega_1\,\zeta-\delta\xi_{14}-\delta\xi_{15}+\left\langle\Phi_f\left|[[x^i,\delta H_S],x^j]\right|\Phi_i\right\rangle\,.
\end{aligned}\tag{433}$$

The remaining double commutator can be evaluated to give

$$[[x^i,\delta H_S],x^j]=\left[\left[x^i,-\frac{\vec{p}^{\,4}}{8m_e^3}\right],x^j\right]=\left[-\mathrm{i}\,\frac{p^ip^2}{2m_e^3},x^j\right]=-\delta^{ij}\,\frac{p^2}{2m_e^3}-\frac{p^jp^i}{m_e^3}=\delta S_H^{ij}\,,\tag{434}$$

which is defined as the seagull correction due to the Hamiltonian. The transformation of the Hamiltonian corrections in velocity gauge can thus be written as

$$\sum_{i=1}^{8}\delta\xi_i+\sum_{i=9}^{12}\delta\xi_i\Big|_{\delta J=\delta J_H}=-\omega_1\omega_2\sum_{i=1}^{8}\delta\zeta_i-\delta\omega_2\,\omega_1\,\zeta-\delta\xi_{13}\Big|_{\delta S=\delta S_H}-\delta\xi_{14}-\delta\xi_{15}\,. \quad (435)$$

When the Hamiltonian corrections in velocity gauge are defined as

$$\delta\xi_H=\sum_{i=1}^{8}\delta\xi_i+\sum_{i=9}^{12}\delta\xi_i\Big|_{\delta J=\delta J_H}+\delta\xi_{13}\Big|_{\delta S=\delta S_H}+\delta\xi_{14}+\delta\xi_{15} \quad (436)$$

and the Hamiltonian corrections in length gauge as

$$\delta\zeta_H=\sum_{i=1}^{8}\delta\zeta_i\,, \quad (437)$$

then the gauge invariance relation takes the simple form

$$\delta\xi_H=-\omega_1\,\omega_2\,\delta\zeta_H-\delta\omega_2\,\omega_1\,\zeta\,. \quad (438)$$

This relation used in Eq. (404) allows to prove the gauge invariance of the corrections to the two-photon decay rate $\delta\xi_H$ due to the relativistic Hamiltonian with the addition of current and seagull terms, which are seen to be generated in the transition,

$$\begin{aligned}\delta\Gamma_H^{\xi}&=2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{\max}}d\omega_1\,\omega_1\,\omega_2\,\xi\delta\xi_H+\frac{4\alpha^2}{9\pi}\,\delta\omega_2\int_0^{\omega_{\max}}d\omega_1\,\omega_1\,\xi^2\\&=2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{\max}}d\omega_1\,\omega_1\,\omega_2\,(-\omega_1\omega_2\zeta)\,[-\omega_1\omega_2\delta\zeta_H-\delta\omega_2\,\omega_1\zeta]\\&\quad+\frac{4\alpha^2}{9\pi}\,\delta\omega_2\int_0^{\omega_{\max}}d\omega_1\,\omega_1^3\,\omega_2^2\,\zeta^2\\&=2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{\max}}d\omega_1\,\omega_1^3\,\omega_2^3\,\zeta\delta\zeta_H+3\frac{4\alpha^2}{9\pi}\,\delta\omega_2\int_0^{\omega_{\max}}d\omega_1\,\omega_1^3\,\omega_2^2\,\zeta^2=\delta\Gamma_H^{\zeta}\,.\end{aligned} \quad (439)$$

Here, again, the superscript ξ denotes the velocity gauge, whereas ζ denotes the length gauge.

6.4.2. Quadrupole Corrections. The quadrupole correction is a pure correction of the interaction current. In the discussion of the one-photon self-energy it was explained, how the quadrupole correction in velocity gauge arises due to the expansion of the exponential associated with the vector potential. For the quadrupole correction of the two-photon decay rate only the multipole corrections to the nonrelativistic interaction current are considered. Multipole corrections to the magnetic interactions are treated separately in the next section.

$$\begin{aligned}\delta J_Q^i &= \frac{p^i}{m_e}\left(-\mathrm{i}\vec{k}\cdot\vec{x}\right) - \frac{1}{2}\frac{p^i}{m_e}(\vec{k}\cdot\vec{x})^2 \\ &\to -\frac{1}{2}\frac{p^i}{m_e}(\vec{k}\cdot\vec{x})^2 .\end{aligned} \tag{440}$$

In the case of the two-photon decay, the first term does actually not contribute because it vanishes after angular integration. Similar to the Hamiltonian correction, the quadrupole correction in velocity gauge also includes the multipole correction to the seagull term in relative order $(Z\alpha)^2$, which is

$$\delta S_Q^{ij} = -\frac{1}{2m_e}(\vec{k}_1\cdot\vec{x})^2\delta^{ij} - \frac{1}{2m_e}(\vec{k}_2\cdot\vec{x})^2\delta^{ij} . \tag{441}$$

Now, the sum of δS_Q^{ij} and δS_H^{ij} is the full higher-order seagull term δS^{ij} given in Eq. (399).

In length gauge, the quadrupole correction to the interaction is given by the multipole correction to the nonrelativistic interaction current but here, also the magnetic coupling to the angular momentum of the electron has to be included. Actually, the quadrupole corrections in both gauges are the multipole corrections to those terms of the interaction currents, which do not contain the electron's spin. The spin-dependent terms will be treated in the next section and can be shown to vanish entirely [59].

The quadrupole correction to the interaction current in length gauge is then

$$\begin{aligned}\delta I_Q^i &= x^i\left(-\frac{\mathrm{i}}{2}\vec{k}\cdot\vec{x}-\frac{1}{6}(\vec{k}\cdot\vec{x})^2\right)+\frac{1}{2m_e\omega}(\vec{\ell}\times\vec{k})^i \\ &\quad -\frac{\mathrm{i}}{6m_e\omega}\left[(\vec{\ell}\times\vec{k})^i(\vec{k}\cdot\vec{x})+(\vec{k}\cdot\vec{x})(\vec{\ell}\times\vec{k})^i\right] \\ &\to x^i\left(-\frac{1}{6}(\vec{k}\cdot\vec{x})^2\right) \\ &\quad -\frac{\mathrm{i}}{6m_e\omega}\left[(\vec{\ell}\times\vec{k})^i(\vec{k}\cdot\vec{x})+(\vec{k}\cdot\vec{x})(\vec{\ell}\times\vec{k})^i\right], \end{aligned} \tag{442}$$

where in the last step again the terms that vanish after angular integration have been taken out. For the following calculations, it is practical to rewrite the last part of this interaction current into the form

$$\begin{aligned}&(\vec{\ell}\times\vec{k})^i(-\mathrm{i}\vec{k}\cdot\vec{x})+(-\mathrm{i}\vec{k}\cdot\vec{x})(\vec{\ell}\times\vec{k})^i \\ &=(\vec{k}\cdot\vec{x})p^i(-\mathrm{i}\vec{k}\cdot\vec{x})-x^i(\vec{k}\cdot\vec{p})(-\mathrm{i}\vec{k}\cdot\vec{x})+(-\mathrm{i}\vec{k}\cdot\vec{x})(\vec{k}\cdot\vec{x})p^i-(-\mathrm{i}\vec{k}\cdot\vec{x})x^i(\vec{k}\cdot\vec{p}).\end{aligned} \tag{443}$$

For the proof of gauge invariance of the quadrupole correction, it is more convenient to start from the length gauge expression. As the quadrupole term is a correction to the interaction current, only the terms $\delta\zeta_{9\ldots12}$ are relevant. Applying the same relations as in the last section, the first correction term $\delta\zeta_9$ is transformed with the result

$$\begin{aligned}-\omega_1\omega_2\delta\zeta_9 &= \omega_2\frac{1}{6}\left\langle\Phi_f\left|x^i\frac{1}{H_S-E_{\Phi_i}+\omega_1}\left(\omega_1(\vec{k}_1\cdot\vec{x})^2x^j\right.\right.\right. \\ &\qquad \left.\left.\left.+\frac{\mathrm{i}}{m_e}\left[(\vec{\ell}\times\vec{k}_1)^j(\vec{k}_1\cdot\vec{x})+(\vec{k}_1\cdot\vec{x})(\vec{\ell}\times\vec{k}_1)^j\right]\right)\right|\Phi_i\right\rangle \\ &= \left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{H_S-E_{\Phi_i}+\omega_1}\left[-\frac{1}{2}\left(\vec{k}_1\cdot\vec{x}\right)\right]\frac{p^j}{m_e}\right|\Phi_i\right\rangle \\ &\quad -\frac{1}{6}\omega_1\left\langle\Phi_f\left|x^i(\vec{k}_1\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle+\frac{\mathrm{i}}{6}\left\langle\Phi_f\left|\frac{p^i}{m_e}(\vec{k}_1\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle \\ &\quad -\left(\frac{\mathrm{i}}{6}k_1^lk_1^m\right)\left\langle\Phi_f\left|x^ix^l\frac{p^j}{m_e}x^m-x^ix^j\frac{p^l}{m_e}x^m+x^ix^mx^l\frac{p^j}{m_e}-x^ix^mx^j\frac{p^l}{m_e}\right|\Phi_i\right\rangle.\end{aligned} \tag{444}$$

The analogue transformation of $\delta\zeta_{10}$ leads to

$$
\begin{aligned}
-\omega_1\omega_2\delta\zeta_{10} &= \omega_1\frac{1}{6}\left\langle\Phi_f\left|x^i\frac{1}{H_S-E_{\Phi_f}-\omega_1}\left(\omega_2(\vec{k}_2\cdot\vec{x})^2x^j\right.\right.\right.\\
&\qquad\left.\left.\left.+\frac{\mathrm{i}}{m_e}\left[(\vec{\ell}\times\vec{k}_2)^j(\vec{k}_2\cdot\vec{x})+(\vec{k}_2\cdot\vec{x})(\vec{\ell}\times\vec{k}_2)^j\right]\right)\right|\Phi_i\right\rangle\\
&= \left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{H_S-E_{\Phi_f}-\omega_1}\left[-\frac{1}{2}\left(\vec{k}_2\cdot\vec{x}\right)\right]\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&\quad-\frac{1}{6}\omega_2\left\langle\Phi_f\left|x^i(\vec{k}_2\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle+\frac{\mathrm{i}}{6}\left\langle\Phi_f\left|\frac{p^i}{m_e}(\vec{k}_2\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle\\
&\quad-\left(\frac{\mathrm{i}}{6}k_2^lk_2^m\right)\left\langle\Phi_f\left|x^ix^l\frac{p^j}{m_e}x^m-x^ix^j\frac{p^l}{m_e}x^m+x^ix^mx^l\frac{p^j}{m_e}-x^ix^mx^j\frac{p^l}{m_e}\right|\Phi_i\right\rangle .
\end{aligned}
\tag{445}
$$

For the correction $\delta\zeta_{11}$ with the current acting on the left side this yields

$$
\begin{aligned}
-\omega_1\omega_2\delta\zeta_{11} &= \omega_1\frac{1}{6}\left\langle\Phi_f\left|\left(\omega_2(\vec{k}_2\cdot\vec{x})^2x^i+\frac{\mathrm{i}}{m_e}\left[(\vec{\ell}\times\vec{k}_2)^i(\vec{k}_2\cdot\vec{x})\right.\right.\right.\right.\\
&\qquad\left.\left.\left.\left.+(\vec{k}_2\cdot\vec{x})(\vec{\ell}\times\vec{k}_2)^i\right]\right)\frac{1}{H_S-E_{\Phi_i}+\omega_1}x^j\right|\Phi_i\right\rangle\\
&= \left\langle\Phi_f\left|\frac{p^i}{m_e}\left[-\frac{1}{2}\left(\vec{k}_2\cdot\vec{x}\right)\right]\frac{1}{H_S-E_{\Phi_i}+\omega_1}\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&\quad+\frac{1}{6}\omega_2\left\langle\Phi_f\left|x^i(\vec{k}_2\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle-\frac{\mathrm{i}}{6}\left\langle\Phi_f\left|x^i(\vec{k}_2\cdot\vec{x})^2\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&\quad+\left(\frac{\mathrm{i}}{6}k_2^lk_2^m\right)\left\langle\Phi_f\left|x^l\frac{p^i}{m_e}x^mx^j-x^i\frac{p^l}{m_e}x^mx^j+x^mx^l\frac{p^i}{m_e}x^j-x^mx^i\frac{p^l}{m_e}x^j\right|\Phi_i\right\rangle ,
\end{aligned}
\tag{446}
$$

and finally for $\delta\zeta_{12}$,

$$
\begin{aligned}
-\omega_1\omega_2\delta\zeta_{12} &= \omega_2\frac{1}{6}\left\langle\Phi_f\left|\left(\omega_1(\vec{k}_1\cdot\vec{x})^2x^i+\frac{\mathrm{i}}{m_e}\left[(\vec{\ell}\times\vec{k}_1)^i(\vec{k}_1\cdot\vec{x})\right.\right.\right.\right.\\
&\qquad\left.\left.\left.\left.+(\vec{k}_1\cdot\vec{x})(\vec{\ell}\times\vec{k}_1)^i\right]\right)\frac{1}{H_S-E_{\Phi_f}-\omega_1}x^j\right|\Phi_i\right\rangle\\
&= \left\langle\Phi_f\left|\frac{p^i}{m_e}\left[-\frac{1}{2}\left(\vec{k}_1\cdot\vec{x}\right)\right]\frac{1}{H_S-E_{\Phi_f}-\omega_1}\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&\quad+\frac{1}{6}\omega_1\left\langle\Phi_f\left|x^i(\vec{k}_1\cdot\vec{x})^2x^j\right|\Phi_i\right\rangle-\frac{\mathrm{i}}{6}\left\langle\Phi_f\left|x^i(\vec{k}_1\cdot\vec{x})^2\frac{p^j}{m_e}\right|\Phi_i\right\rangle\\
&\quad+\left(\frac{\mathrm{i}}{6}k_1^lk_1^m\right)\left\langle\Phi_f\left|x^l\frac{p^i}{m_e}x^mx^j-x^i\frac{p^l}{m_e}x^mx^j+x^mx^l\frac{p^i}{m_e}x^j-x^mx^i\frac{p^l}{m_e}x^j\right|\Phi_i\right\rangle .
\end{aligned}
\tag{447}
$$

The sum of these four corrections then gives

$$
\begin{aligned}
-\omega_1\omega_2 \sum_{i=9}^{12} \delta\zeta\Big|_{\delta I=\delta I_Q} &= \sum_{i=9}^{12} \delta\xi\Big|_{\delta J=\delta J_Q} - \left(\frac{\mathrm{i}}{6}k_1^l k_1^m\right)\left\langle \Phi_f \left| x^i x^l \frac{p^j}{m_e} x^m - x^i x^j \frac{p^l}{m_e} x^m \right.\right. \\
&+ x^i x^m x^l \frac{p^j}{m_e} - x^i x^m x^j \frac{p^l}{m_e} - \left.\left. \frac{p^i}{m_e} x^l x^m x^j \right| \Phi_i \right\rangle - \left(\frac{\mathrm{i}}{6}k_2^l k_2^m\right)\left\langle \Phi_f \left| x^i x^l \frac{p^j}{m_e} x^m \right.\right. \\
&- x^i x^j \frac{p^l}{m_e} x^m + x^i x^m x^l \frac{p^j}{m_e} - x^i x^m x^j \frac{p^l}{m_e} - \left.\left. \frac{p^i}{m_e} x^l x^m x^j \right| \Phi_i \right\rangle + \left(\frac{\mathrm{i}}{6}k_2^l k_2^m\right) \\
&\times \left\langle \Phi_f \left| x^l \frac{p^i}{m_e} x^m x^j - x^i \frac{p^l}{m_e} x^m x^j + x^m x^l \frac{p^i}{m_e} x^j - x^m x^i \frac{p^l}{m_e} x^j \right.\right. \\
&- x^i x^l x^m \frac{p^j}{m_e} \left.\left| \Phi_i \right\rangle + \left(\frac{\mathrm{i}}{6}k_1^l k_1^m\right)\left\langle \Phi_f \left| x^l \frac{p^i}{m_e} x^m x^j - x^i \frac{p^l}{m_e} x^m x^j \right.\right. \\
&+ x^m x^l \frac{p^i}{m_e} x^j - x^m x^i \frac{p^l}{m_e} x^j - \left.\left. x^i x^l x^m \frac{p^j}{m_e} \right| \Phi_i \right\rangle .
\end{aligned}
\tag{448}
$$

The rather long remainder terms can be greatly simplified by commuting the momentum operators to the right side, which leads to the much shorter expression

$$
\begin{aligned}
&-\omega_1\omega_2 \sum_{i=9}^{12} \delta\zeta\Big|_{\delta I=\delta I_Q} \\
&\quad = \sum_{i=9}^{12} \delta\xi\Big|_{\delta J=\delta J_Q} + \left\langle \Phi_f \left| \frac{1}{2m_e}\delta^{ij}\left(\vec{k}_1\cdot\vec{x}\right)^2 \right| \Phi_i \right\rangle + \left\langle \Phi_f \left| \frac{1}{2m_e}\delta^{ij}\left(\vec{k}_2\cdot\vec{x}\right)^2 \right| \Phi_i \right\rangle .
\end{aligned}
\tag{449}
$$

The last two terms on the right-hand side of the equation can be identified as the quadrupole correction to the seagull term in velocity gauge and thus this can be written as

$$
-\omega_1\omega_2 \sum_{i=9}^{12} \delta\zeta\Big|_{\delta I=\delta I_Q} = \sum_{i=9}^{12} \delta\xi\Big|_{\delta J=\delta J_Q} + \delta\xi_{13}\Big|_{\delta S=\delta S_Q} . \tag{450}
$$

Defining the quadrupole correction in velocity gauge as

$$
\delta\xi_Q = \sum_{i=9}^{12} \delta\xi_i\Big|_{\delta J=\delta J_Q} + \delta\xi_{13}\Big|_{\delta S=\delta S_Q} , \tag{451}
$$

and the corresponding correction in length gauge as

$$\delta\zeta_Q = \sum_{i=9}^{12} \delta\zeta_i \Big|_{\delta I = \delta I_Q} , \tag{452}$$

the above gauge relation takes the simple form

$$\delta\xi_Q = -\omega_1\omega_2\delta\zeta_Q \, . \tag{453}$$

Having now obtained the gauge relation for the quadrupole correction, it can be shown that

$$\begin{aligned} \delta\Gamma^{\xi}_{Q} &= 2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{max}} d\omega_1\, \omega_1\, \omega_2\, \xi\delta\xi_Q \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{max}} d\omega_1\, \omega_1\, \omega_2\, (-\omega_1\omega_2\zeta)\, [-\omega_1\omega_2\delta\zeta_Q] \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{\omega_{max}} d\omega_1\, \omega_1^3\, \omega_2^3\, \zeta\delta\zeta_Q = \delta\Gamma^{\zeta}_{Q} \, , \end{aligned} \tag{454}$$

which proves the gauge invariance of the quadrupole correction to the two-photon decay rate.

6.4.3. Spin-Dependent Corrections. So far all corrections due to the Hamiltonian, the quadrupole and the seagull term have been treated. The remaining corrections are all spin-dependent corrections to the interaction current. In velocity gauge these remaining terms are

$$\begin{aligned} \delta J^i_R &= \delta J^i - \delta J^i_H - \delta J^i_Q \\ &= -\frac{\mathrm{i}}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^i - \frac{1}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^i\left(\vec{k}\cdot\vec{x}\right) - \frac{1}{4m_e^2}\frac{Z\alpha}{r^3}\left(\vec{x}\times\vec{\sigma}\right)^i . \end{aligned} \tag{455}$$

From the considerations at the end of Sec. 4.4, the following replacements can be recalled

$$\begin{aligned} &-\frac{1}{2m_e}\left(\vec{\sigma}\times\vec{k}\right)^i\left(\vec{k}\cdot\vec{x}\right)\rightarrow-\frac{\mathrm{i}\omega}{4m_e^2}\left(\vec{\sigma}\times\vec{p}\right)^i\,, \\ &-\frac{1}{4m_e^2}\frac{Z\alpha}{r^3}\left(\vec{x}\times\vec{\sigma}\right)^i\rightarrow\frac{\mathrm{i}\omega}{4m_e^2}\left(\vec{\sigma}\times\vec{p}\right)^i\,, \end{aligned} \tag{456}$$

which occur when the terms on the left-hand side are contracted with the photon propagator [42, 77]. Therefore, the last two terms of Eq. (455) cancel. For the remaining term, the sum of the two corrections $\delta\xi_9$ and $\delta\xi_{11}$ with it is considered

$$\begin{aligned} \delta\xi_9+\delta\xi_{11}=&\left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{H_S-E_{\Phi_i}+\omega_1}(\vec{\sigma}\times\vec{k}_1)^i\right|\Phi_i\right\rangle \\ &+\left\langle\Phi_f\left|(\vec{\sigma}\times\vec{k}_1)^j\frac{1}{H_S-E_{\Phi_f}-\omega_1}\frac{p^i}{m_e}\right|\Phi_i\right\rangle\,. \end{aligned} \tag{457}$$

The Schrödinger Hamiltonian does not contain any spin dependence and does therefore commute with the spin operator. This allows to let the denominator act on one of the outer wave functions and leads to

$$\begin{aligned} \delta\xi_9+\delta\xi_{11}=&\left\langle\Phi_f\left|\frac{p^i}{m_e}\frac{1}{E_{\Phi_i}-E_{\Phi_i}+\omega_1}(\vec{\sigma}\times\vec{k}_1)^i\right|\Phi_i\right\rangle \\ &+\left\langle\Phi_f\left|(\vec{\sigma}\times\vec{k}_1)^j\frac{1}{E_{\Phi_f}-E_{\Phi_f}-\omega_1}\frac{p^i}{m_e}\right|\Phi_i\right\rangle \\ =&\frac{1}{\omega_1}\left(\left\langle\Phi_f\left|\frac{p^i}{m_e}(\vec{\sigma}\times\vec{k}_1)^i\right|\Phi_i\right\rangle-\left\langle\Phi_f\left|\frac{p^i}{m_e}(\vec{\sigma}\times\vec{k}_1)^i\right|\Phi_i\right\rangle\right)=0 \end{aligned} \tag{458}$$

because the momentum operator also commutes with $\vec{\sigma}$ and $\vec{k}_1$. The same can be shown for the sum of $\delta\xi_{10}$ and $\delta\xi_{12}$ where the $\vec{k}_1$ has to be replaced with $\vec{k}_2$. Therefore, the entire contribution from the remaining corrections to the current vanishes in the velocity gauge.

The remaining spin-dependent corrections to interaction current in length gauge are

$$\delta I_R^i=\frac{1}{2m_e\omega}\left(\vec{\sigma}\times\vec{k}\right)^i-\frac{\mathrm{i}}{2m_e\omega}\left(\vec{\sigma}\times\vec{k}\right)^i\left(\vec{k}\cdot\vec{x}\right)+\frac{\mathrm{i}\omega}{4m_e}\left(\vec{\sigma}\times\vec{x}\right)^i\,. \tag{459}$$

Because the position operator also commutes with both $\vec{\sigma}$ and $\vec{k}$, the considerations in Eq. (458) are also valid for the corresponding length gauge expression. Consequently, the contribution from the first term in Eq. (459) vanishes. Contracting the second term with the photon propagator leads to

$$-\frac{\mathrm{i}}{2m_e\omega}\left(\vec{\sigma}\times\vec{k}\right)^i\left(\vec{k}\cdot\vec{x}\right)=-\frac{\mathrm{i}\omega}{4m_e}\left(\vec{\sigma}\times\vec{x}\right)^i\,, \tag{460}$$

which exactly cancels the third term of Eq. (459).

Hence, the corresponding corrections

$$\delta\xi_R=\sum_{i=9}^{12}\delta\xi_i\Big|_{\delta J=\delta J_R}=0 \tag{461}$$

and

$$\delta\zeta_R=\sum_{i=9}^{12}\delta\zeta_i\Big|_{\delta I=\delta I_R}=0 \tag{462}$$

are both equal to 0 and thus trivially gauge independent. This completes the proof of the gauge invariance of the two-photon decay rate.

6.5. NUMERICAL RESULTS

Numerical results for the relativistic corrections to the two-photon decay rate are obtained by carrying out the integration with respect to ω_1 for both the velocity gauge expression in Eq. (404) as well as the length gauge expression in Eq. (412). The propagator is represented by a sum over the complete bound spectrum and an integral over all continuum states as in the case of the self-energy in Sec. 4. For a numerical evaluation of the expression the angular integration is carried out using algebraic methods detailed in Ref. [23]. The remaining radial integration is carried out by lattice techniques developed in Ref. [78]. In this method the intermediate basis set in the equation is represented by eigenstates of the Hamiltonian which is a matrix in a finite lattice. Thus, its eigenstates are then just the eigenvectors of this matrix. They represent the discrete bound states but also yield a pseudo spectrum of the continuum unbound states. Then letting both the operators act

on the reference state and discretizing the resulting wave function on the lattice, the matrix element of these with all the intermediate states can be evaluated. For this purpose, the lattice code employed for the calculation of self-energy corrections, described in detail in Ref. [42], is generalized to the calculation of the two-photon decay rate. The evaluation is carried out in both length and velocity gauge and the results are seen to agree.

6.5.1. 2S–1S Decay. For the results it is interesting to see them and have them discussed on one particular example. Due to the absence of cascade contributions and its importance for high-precision spectroscopy, here, the $2S$–$1S$ decay is chosen. The results from the different contributions are all given separately.

For the gauge-invariant result of the correction to the decay rate due to the relativistic Hamiltonian, from Sec. 6.4.1,

$$\delta\Gamma_H = \Gamma_0 \left[-0.5082\,(Z\alpha)^2\right] \tag{463}$$

is obtained. For the quadrupole correction, the gauge-invariant result is (see Sec. 6.4.2)

$$\delta\Gamma_Q = \Gamma_0 \left[-0.1555\,(Z\alpha)^2\right] . \tag{464}$$

As shown in Sec. 6.4.3, the remaining current corrections vanish, i.e.

$$\delta\Gamma_R = 0 . \tag{465}$$

The total result for the relativistic correction to the two-photon decay rate is the sum of the above terms and thus reads

$$\delta\Gamma = \delta\Gamma_H + \delta\Gamma_Q + \delta\Gamma_R = \Gamma_0 \left[-0.6636\,(Z\alpha)^2\right] . \tag{466}$$

The coefficient γ_2 is then

$$\gamma_2 = -0.6636 . \tag{467}$$

It can be interesting to consider the different contributions which make up the the total Hamiltonian correction. This is particularly helpful because the zitterbewegung

term is up to a different scaling identical to the leading radiative correction. Following Eq. (393), the different Hamiltonian corrections are the zitterbewegung (zb) term,

$$\delta H_{\rm zb} = \frac{\pi Z\alpha}{2m_e}\delta(\vec{x})\,, \tag{468}$$

the kinetic energy (ke) term,

$$\delta H_{\rm ke} = -\frac{p^4}{8m_e^3}\,, \tag{469}$$

and the spin-orbit (LS) coupling

$$\delta H_{LS} = \frac{Z\alpha}{4m_e^2}\frac{\vec{\ell}\cdot\vec{\sigma}}{r^3}\,. \tag{470}$$

The corresponding results read, for the $2S$–$1S$ decay,

$$\delta\Gamma_{\rm zb} = \Gamma_0\,\left[-0.7577\,(Z\alpha)^2\right]\,, \tag{471a}$$

$$\delta\Gamma_{\rm ke} = \Gamma_0\,\left[0.2495\,(Z\alpha)^2\right]\,, \tag{471b}$$

$$\delta\Gamma_{LS} = 0\,. \tag{471c}$$

6.5.2. Higher Excited States. When this approach is generalized for higher-excited states, there is one particular problem which requires special attention, the cascade decay. In this process a higher-excited states decays via two one-photon decays over a real intermediate state. For example the $3S$ state can decay via such cascade through the $2P$ state. In the two-photon decay this means that, when the $2P$ state is the virtual intermediate state in both denominators, a double pole in the photon energy integration arises. This causes the problem, how this pole is treated in the integration because in principle a quadratic singularity is *a priori* not integrable. In fact, such a case, where the decay can take place through a cascade of intermediate states, even the exact definition of the two-photon decay rate is troublesome [60–65, 67–69].

Here, a principal value prescription for the problematic double poles is used. It is based on the principles of the deformation of the integration contour from Ref. [7], which are discussed in Sec. 3, and an rigorous handling of the $i\epsilon$ prescriptions in

the denominators. The details of this procedure for the two-photon decay rate are explained in Refs. [67,68]. While the gauge invariance of the corrections is preserved, discriminating between the cascade decay, which consists of two one-photon decays, and the "real" two-photon decay is troublesome. This problem is still being discussed in the community [67–69].

With the lattice methods using the described procedure to deal with the poles, the relativistic corrections are calculated for many higher excited. The results are given in Table 6.1 which is published Ref. [59].

Table 6.1. Results for the γ_2 coefficient as defined in Eq. (382). This coefficient gives the relativistic corrections to the two-photon decay rate.

	$\|\Phi_f\rangle = \|1S_{1/2}\rangle$	$\|\Phi_f\rangle = \|2S_{1/2}\rangle$
$\|\Phi_i\rangle = \|2S_{1/2}\rangle$	−0.6636	-
$\|\Phi_i\rangle = \|3S_{1/2}\rangle$	−2.6637	− 1.7038
$\|\Phi_i\rangle = \|4S_{1/2}\rangle$	−4.5192	− 7.8530
$\|\Phi_i\rangle = \|3D_{3/2}\rangle$	−2.2978	7.8533
$\|\Phi_i\rangle = \|3D_{5/2}\rangle$	−1.0981	−22.2671

6.5.3. Leading Logarithmic QED Corrections. In the calculation of the low and the high-energy part in Sec. 4, it becomes apparent that the leading QED radiative correction is basically given by the effective Lamb-shift radiation Hamiltonian [79,80]

$$\delta H_{\rm rad} = \frac{4\,\alpha}{3}\,(Z\alpha)\,\ln[(Z\alpha)^{-2}]\,\frac{\delta(\vec{x})}{m_e^2}\,. \tag{472}$$

Because the difference between this Hamiltonian and the zitterbewegung term in the relativistic Hamiltonian

$$\delta H_{\rm zb} = \pi Z\alpha \frac{\delta(\vec{x})}{2m_e} \tag{473}$$

is only a prefactor, the γ_3 coefficient can be obtained as $8\gamma_{2,\rm zb}/3$ from $\gamma_{2,\rm zb}$, which is the contribution to γ_2 caused exclusively by the zitterbewegung term. The result found in this way for the $2S$–$1S$ transition, which according to Eq. (471a) is given by $\gamma_3 = \frac{8}{3}(-0.7577) = -2.0205$, agrees with the results previously obtained for this correction in Refs. [58, 74]. The result for other transition, which are presented in Ref. [59], are given in Table 6.2.

Table 6.2. Results for γ_3 as defined in Eq. (382).

	$\|\Phi_f\rangle = \|1S_{1/2}\rangle$	$\|\Phi_f\rangle = \|2S_{1/2}\rangle$
$\|\Phi_i\rangle = \|2S_{1/2}\rangle$	− 2.0203	-
$\|\Phi_i\rangle = \|3S_{1/2}\rangle$	9.6521	16.0424
$\|\Phi_i\rangle = \|4S_{1/2}\rangle$	20.7364	61.7499
$\|\Phi_i\rangle = \|3D_{3/2}\rangle$	− 5.4681	144.3639
$\|\Phi_i\rangle = \|3D_{5/2}\rangle$	− 5.4681	144.3639

6.5.4. Comparison of Analytic and Numerical Results. The results presented in this section are obtained using the methods of NRQED described in Sec. 4. Also calculations exist which were carried using the approach discussed in Sec. 3 and employ fully relativistic, numerical QED calculations. In this work both of these approaches have been discussed. Here, the opportunity is taken to compare the results obtained with both methods and to show that they agree. Such a comparison

provides a highly nontrivial and rigorous check of the results and allows to excludes conceivable errors.

A fully relativistic numerical calculation of the $2S$–$1S$ two-photon decay rate has been carried out in Ref. [81]. From these results a fit to a convenient functional form in $Z\alpha$ leading to an approximate formula valid across the whole range of nuclear charge numbers Z was obtained. It is given in Refs. [81,82] and reads

$$\Gamma \approx \Gamma_0 \frac{1 + 3.9448\,(Z\alpha)^2 - 2.040\,(Z\alpha)^4}{1 + 4.6019(Z\alpha)^2}\,. \tag{474}$$

In order for this to yield an estimate for the correction term in relative order $(Z\alpha)^2$, this expression has to be re-expanded in $Z\alpha$. Indeed, the coefficient of relative order $(Z\alpha)^2$, which this expansion yields, $\gamma_2 \approx -0.6571$, is in fair agreement with the result with the NRQED result in Eq. (467), $\gamma_2 = -0.6636$.

In Ref. [66] fully relativistic, numerical results for the $3S$–$1S$ two-photon decay rate were presented. In it the decay rate, including all corrections, has been determined for different values of the nuclear charge number Z. To allow for a comparison in this case, the relativistic correction γ_2 of relative order $(Z\alpha)^2$, presented in this work, has to be used to correct the nonrelativistic decay rate for different values of Z. The corrected decay rate for the $3S$–$1S$ two-photon decay is then $\Gamma \approx 1.61\,(Z = 40)^6\,\mathrm{rad/s}$. In Ref. [66] the result for the $E1E1$ two-photon decay rate is given as $\Gamma = 1.60\,(Z = 40)^6\,\mathrm{rad/s}$. Both of these results are again in good agreement.

7. CALCULATION: SELF-ENERGY AND THE LAMB SHIFT

7.1. ORIENTATION

In this section, the nonrelativistic theory is applied in order to obtain corrections of relative order $(Z\alpha)^2$ to the self-energy correction of the Lamb shift. In contrast to the previous section there is only one photon but this photon is virtual. The obtained correction are therefore additional QED corrections to the Lamb shift. The focus is on highly-excited Rydberg states because these calculations are required for an ongoing project at NIST. The QED results obtained for this project in Ref. [83,84] are necessary to reduce theoretical uncertainties and could allow to deduce a more accurate value for the Rydberg constant. Starting from the theory explained in Sec. 4, it is shown how the corrections are evaluated for Rydberg states.

Following Sec. 4 the calculation is split into two parts. In the low-energy part only contributions from virtual photon at low photon energies are considered, whereas in the high-energy part the effect from highly energetic virtual photons are determined. This separation is necessary because of the two energy scales in the problem from the virtual photon and the binding Coulomb potential. The investigation start with the low-energy part.

7.2. LOW-ENERGY PART

7.2.1. Orientation. Here, the relativistic corrections of order $(Z\alpha)^2$ to Bethe's result for the self-energy correction for highly excited Rydberg states are calculated. Following the theoretical derivation in Sec. 4, the low-energy part of the self-energy correction is given by

$$\mathrm{Re}\Delta E^{(2)}_{L,\psi} = \int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij} - \frac{k^i k^j}{\vec{k}^2}\right)\tilde{P}^{ij}\,. \tag{475}$$

According to Sec. 4.5, the matrix element $\tilde{P}^{ij}$ reads

$$\begin{aligned}\tilde{P}^{ij} = &\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle \\ &+ 2\cdot\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\delta j^j|\Phi\rangle \\ &- \langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\delta E\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle \\ &+ \langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\delta H_S\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle \\ &+ 2\cdot\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\delta\Phi\rangle + \mathcal{O}((Z\alpha)^4)\,,\end{aligned} \tag{476}$$

where the first term is Bethe's classic result [6] and the other terms are the relativistic corrections of order $(Z\alpha)^2$ to it, which are investigated here. The effective correction operators have been derived in Sec. 4.4 by a Foldy-Wouthuysen transformation of the fully relativistic Hamiltonian and current operator. While the resulting correction are given in Sec. 4.5, they are restated here for easier referencing. It is convenient to break up the **interaction current** correction into its constituents in Eq. (297) because the angular integration is different for each of the terms. This results in the following terms:

the **nonrelativistic multipole correction**

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = &\int_{\omega_{\vec{k}}<\epsilon}\frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij} - \frac{k^ik^j}{\vec{k}^2}\right) \\ &\times\left\{\langle\Phi|\frac{p^i}{m_e}\left(\mathrm{i}\vec{k}\cdot\vec{x}\right)\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}\left(-\mathrm{i}\vec{k}\cdot\vec{x}\right)|\Phi\rangle\right. \\ &\left. - \langle\Phi|\frac{p^i}{m_e}\left(\vec{k}\cdot\vec{x}\right)^2\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\right\}.\end{aligned} \tag{477}$$

the **relativistic momentum correction**

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,p^ip^2} = &\int_{\omega_{\vec{k}}<\epsilon}\frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij} - \frac{k^ik^j}{\vec{k}^2}\right) \\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{-p^jp^2}{m_e^3}|\Phi\rangle\,,\end{aligned} \tag{478}$$

the **correction due to the spin coupling to the physical momentum**

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,r\times\sigma} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\left(\frac{-Z\alpha\,(\vec{x}\times\vec{\sigma})^j}{m_e^2r^3}\right)|\Phi\rangle\ ,\end{aligned} \tag{479}$$

the **quadrupole correction to the magnetic coupling**

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\left(\frac{\left(\vec{k}\cdot\vec{x}\right)\left(\vec{k}\times\vec{\sigma}\right)^j}{m_e}\right)|\Phi\rangle\ .\end{aligned} \tag{480}$$

This concludes the corrections due to the relativistic corrections of the interaction current.

The next correction arise because of the **relativistic correction to the reference-state energy**

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta E} = -&\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\delta E\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\ .\end{aligned} \tag{481}$$

The **relativistic correction of the Hamiltonian** leads to the contribution

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta H_S} = -&\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\\ &\times\left(\frac{\vec{p}^4}{8m_e^3}-\frac{Z\alpha}{4m_e^2r^3}\vec{\ell}\cdot\vec{\sigma}\right)\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\ .\end{aligned} \tag{482}$$

In δH_S the Darwin term is neglected because Rydberg states are considered here and this term vanishes for states with angular momentum $\ell \geq 1$.

The last correction is due to the **relativistic correction of the wave function** and is

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta\Phi} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}\left(\frac{1}{E_\Phi-H_S}\right)'\delta H_S|\Phi\rangle\ .\end{aligned} \tag{483}$$

These terms are now derived and evaluated separately.

7.2.2. Nonrelativistic Multipole Correction. The nonrelativistic multipole corrections are due to the expansion $e^{i\vec{k}\cdot\vec{x}}$ in the nonrelativistic interaction current and are given in Eq. (477) as

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\left\{\langle\Phi|\frac{p^i}{m_e}\left(i\vec{k}\cdot\vec{x}\right)\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}\left(-i\vec{k}\cdot\vec{x}\right)|\Phi\rangle\right.\\ &\left.-\langle\Phi|\frac{p^i}{m_e}\left(\vec{k}\cdot\vec{x}\right)^2\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\right\}.\end{aligned} \tag{484}$$

In order to extract the $\vec{k}$ dependence from the matrix element, the index notation is used, in which the expression takes the form

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = &\int_{|\vec{k}|<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{m_e^2\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\left\{\langle\Phi|p^ik^ax^a\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}p^jk^bx^b|\Phi\rangle\right.\\ &\left.-\langle\Phi|p^ik^ak^bx^ax^b\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}p^j|\Phi\rangle\right\}.\end{aligned} \tag{485}$$

Writing $d^3k = d\Omega_{\vec{k}}\,\omega_{\vec{k}}^2\,d\omega_{\vec{k}}$ and multiplying out the transverse δ, yields

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = &\int_{\omega_{\vec{k}}<\epsilon} d\Omega_{\vec{k}}\frac{d\omega_{\vec{k}}}{(2\pi)^2}\frac{\alpha}{m_e^2}\frac{k^ak^b}{\vec{k}^2}\left\{\langle\Phi|p^ix^a\frac{\omega_{\vec{k}}^3}{E_\Phi-H_S-\omega_{\vec{k}}}p^ix^b|\Phi\rangle\right.\\ &-\langle\Phi|p^ix^ax^b\frac{\omega_{\vec{k}}^3}{E_\Phi-H_S-\omega_{\vec{k}}}p^j|\Phi\rangle\\ &-\frac{k^ik^j}{\vec{k}^2}\langle\Phi|p^ix^a\frac{\omega_{\vec{k}}^3}{E_\Phi-H_S-\omega_{\vec{k}}}p^jx^b|\Phi\rangle\\ &\left.+\frac{k^ik^j}{\vec{k}^2}\langle\Phi|p^ix^ax^b\frac{\omega_{\vec{k}}^3}{E_\Phi-H_S-\omega_{\vec{k}}}p^j|\Phi\rangle\right\}.\end{aligned} \tag{486}$$

The dependence on $\vec{k}$ is extracted and the integration with respect to $d\Omega_{\vec{k}}$ can be carried out again using Eqs. (214) and (215) as well as

$$\int d\Omega_k \frac{k^i k^j}{\vec{k}^2} \frac{k^a k^c}{\vec{k}^2} = \frac{4\pi}{15} \left(\delta^{ij}\delta^{ac} + \delta^{ia}\delta^{jc} + \delta^{ic}\delta^{ja} \right) . \tag{487}$$

When the momentum operator is also replaced according to $p^i \to \mathrm{i}\nabla^i$, the result is

$$\begin{aligned} \mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} = -\int_0^\epsilon d\omega_{\vec{k}} \, \frac{\alpha}{\pi m_e^2} \Bigg\{ & \frac{4}{15} \langle \Phi | \, \nabla^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} x^j \nabla^i \, | \Phi \rangle \\ & - \frac{1}{15} \langle \Phi | \, \nabla^i x^i \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} x^i \nabla^i \, | \Phi \rangle \\ & - \frac{1}{15} \langle \Phi | \, \nabla^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} x^i \nabla^j \, | \Phi \rangle \\ & - \frac{4}{15} \langle \Phi | \, \nabla^i x^j x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} \nabla^i \, | \Phi \rangle \\ & + \frac{2}{15} \langle \Phi | \, \nabla^i x^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} \nabla^j \, | \Phi \rangle \Bigg\} . \end{aligned} \tag{488}$$

The angular integration is carried out for each of the five terms separately in the following. Thereby, the Wigner-Eckhart theorem as well as the Racah algebra [23] are employed and the calculation is carried out algebraically. This algebraic methods requires the use of spherical coordinates. The Cartesian scalar product in spherical coordinates is given by

$$A^i B^i = \sum_q (-1)^q A_q B_{-q} \, , \tag{489}$$

which makes an easy change of coordinates in these calculations possible.

The first term of Eq. (488) is denoted as M_a in the following and is

$$M_a = \langle \Phi | \, \nabla^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} x^j \nabla^i \, | \Phi \rangle \, . \tag{490}$$

Similar to the evaluation of the leading low-energy part in Sec. 4, a complete set of Schrödinger eigenfunctions of the hydrogen atom is introduced. Both the reference state as well as the basis set are expressed in terms of the relevant quantum numbers.

M_a is thus written as

$$M_a = \sum_{n'\ell'm'} \langle n\ell m|\, \nabla^i x^j \,|n'\ell'm'\rangle \, \frac{\omega_{\vec{k}}^3}{E_n - H_{n'} - \omega_{\vec{k}}} \, \langle n'\ell'm'|\, x^j \nabla^i \,|n\ell m\rangle \ . \tag{491}$$

The Wigner-Eckhart theorem now allows to reduce the manifold of magnetic projections m of the orbital angular momentum ℓ to one particular choice, which is $m = 0$ in this section. Moreover, switching to spherical coordinates yields

$$M_a = \sum_{n'\ell'm'} \sum_{q,q'} (-1)^q (-1)^{q'} \langle n\ell 0|\nabla^q x^{q'}|n'\ell'm'\rangle \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \langle n'\ell'm'|x^{-q'}\nabla^{-q}|n\ell 0\rangle \ . \tag{492}$$

Because it allows some simplifications later, a complete set of angular basis states is introduced between the x and the ∇-operator which leads to

$$\begin{aligned} M_a = & \sum_{n',\ell',m'} \sum_{q,q'} \sum_{\ell'',m'',\ell''',m'''} (-1)^q (-1)^{q'} \, \langle n\ell 0|\, \nabla^q \,|\ell''m''\rangle \, \langle \ell''m''|\, x^{q'} \,|n'\ell'm'\rangle \\ & \times \frac{\omega^3}{E_n - E_{n'} - \omega_{\vec{k}}} \, \langle n'\ell'm'|\, x^{-q'} \,|\ell'''m'''\rangle \, \langle \ell'''m'''|\, \nabla^{-q} \,|n\ell 0\rangle \ . \end{aligned} \tag{493}$$

Using formulas from Ref. [23] and grouping terms with q and q' together, one obtains

$$\begin{aligned} M_a = & \sum_{n',\ell',m'} \sum_{\ell'',m'',\ell''',m'''} \sum_{q} (-1)^q (-1)^{m'''} (-1)^{m''} \, \langle n\ell 0|\, \nabla^0 \,|\ell''0\rangle \, \langle \ell'''0|\, \nabla^0 \,|n\ell 0\rangle \\ & \times \frac{\begin{pmatrix} \ell & 1 & \ell'' \\ 0 & q & m'' \end{pmatrix} \begin{pmatrix} \ell''' & 1 & \ell \\ -m''' & -q & 0 \end{pmatrix}}{\begin{pmatrix} \ell & 1 & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell''' & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}} \sum_{q'} (-1)^{q'} (-1)^{m'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \\ & \times \langle \ell''0|\, x^0 \,|n'\ell'0\rangle \, \langle n'\ell'0|\, x^0 \,|\ell'''0\rangle \, \frac{\begin{pmatrix} \ell' & 1 & \ell''' \\ -m' & -q' & m''' \end{pmatrix} \begin{pmatrix} \ell'' & 1 & \ell' \\ -m'' & q' & m' \end{pmatrix}}{\begin{pmatrix} \ell' & 1 & \ell''' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell'' & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix}} \ . \end{aligned} \tag{494}$$

Combining the sum over q' can be achieved by making use of Eq. (8.4.5/6) and Eq. (12.1.3) from Ref. [23] and gives

$$\begin{aligned}
&\sum_{q',m'}(-1)^{q'}(-1)^{m'}\begin{pmatrix}\ell' & 1 & \ell'''\\ -m' & -q' & m'''\end{pmatrix}\begin{pmatrix}\ell'' & 1 & \ell'\\ -m'' & q' & m'\end{pmatrix}\\
&=\sum_{q',m'}(-1)^{q'}(-1)^{m'}\begin{pmatrix}\ell'' & 1 & \ell'\\ -m'' & q' & m'\end{pmatrix}(-1)^{1+\ell'+\ell}\begin{pmatrix}1 & \ell' & \ell\\ -q' & -m' & m'''\end{pmatrix}\\
&=\frac{(-1)^{m''}}{2\ell''+1}\delta_{\ell''',\ell''}\delta_{m''',m''}\,.
\end{aligned}\tag{495}$$

The resulting Kronecker delta allows to contract the sum over q in a similar manner, which leads to

$$\begin{aligned}
&\sum_{q,m''}(-1)^{q}(-1)^{m''}\begin{pmatrix}\ell'' & 1 & \ell\\ -m'' & -q & 0\end{pmatrix}\begin{pmatrix}\ell & 1 & \ell''\\ 0 & q & m''\end{pmatrix}\\
&=\sum_{q,m''}(-1)^{q}(-1)^{m''}(-1)^{1+\ell+\ell''}\begin{pmatrix}1 & \ell'' & \ell\\ -q & -m'' & 0\end{pmatrix}\begin{pmatrix}\ell & 1 & \ell''\\ 0 & q & m''\end{pmatrix}\\
&=\frac{1}{2\ell+1}\,.
\end{aligned}\tag{496}$$

Through these simplifications the matrix element can be expressed as

$$\begin{aligned}
M_a=\frac{1}{2\ell+1}\sum_{n',\ell',\ell''}\frac{1}{2\ell''+1}&\begin{pmatrix}\ell'' & 1 & \ell\\ 0 & 0 & 0\end{pmatrix}^{-2}\begin{pmatrix}\ell' & 1 & \ell''\\ 0 & 0 & 0\end{pmatrix}^{-2}\frac{\omega^3}{E_n-E_{n'}-\omega_{\vec{k}}}\\
&\times\langle n\ell 0|\,\nabla^0\,|\ell''0\rangle\,\langle\ell''0|\,x^0\,|n'\ell'0\rangle\,\langle n'\ell'0|\,x^0\,|\ell''0\rangle\,\langle\ell''0|\,\nabla^0\,|n\ell 0\rangle\,.
\end{aligned}\tag{497}$$

The action of the ∇-operator on the wave function is given by Eqs. (13.2.23/24) of Ref. [23] and reads

$$\begin{aligned}
&\langle nL+10|\nabla_{10}\,|NL0\rangle\\
&\qquad=\frac{L+1}{\sqrt{(2L+1)(2L+3)}}\int_0^\infty dr r^2 R_{nL+1}(r)\left(\frac{d}{dr}-\frac{L}{r}\right)R_{NL}(r)
\end{aligned}\tag{498}$$

and

$$\langle nL-10|\nabla_{10}|NL0\rangle = \frac{L}{\sqrt{(2L+1)(2L-1)}}\int_0^\infty dr r^2 R_{nL-1}(r)\left(\frac{d}{dr}+\frac{L+1}{r}\right)R_{NL}(r)\,. \tag{499}$$

The squares of the $3j$-symbols can be obtained by

$$\begin{pmatrix}\ell' & 1 & \ell\\ 0 & 0 & 0\end{pmatrix}^2 = \begin{cases}\frac{\ell}{(2\ell+1)(2\ell-1)} & \text{for } \ell'=\ell-1\,,\\ \frac{\ell+1}{(2\ell+1)(2\ell+3)} & \text{for } \ell'=\ell+1\,.\end{cases} \tag{500}$$

Consequently, the final result for M_a is found to be

$$\begin{aligned} M_a = \sum_{n'}\frac{\omega_{\vec{k}}^3}{E_n-E_{n'}-\omega_{\vec{k}}}\Bigg\{ & \frac{\ell+1}{2\ell+1}\frac{\ell+2}{2\ell+3}\\ & \times\left(\int_0^\infty dr r^2 R_{n'\ell+2}(r)\left(r\frac{d}{dr}-\ell\right)R_{n\ell}(r)\right)^2\\ & +\frac{\ell+1}{2\ell+1}\frac{\ell+1}{2\ell+3}\left(\int_0^\infty dr r^2 R_{n'\ell}(r)\left(r\frac{d}{dr}-\ell\right)R_{n\ell}(r)\right)^2\\ & +\frac{\ell}{2\ell+1}\frac{\ell}{2\ell-1}\left(\int_0^\infty dr r^2 R_{n'\ell}(r)\left(r\frac{d}{dr}+(\ell+1)\right)R_{n\ell}(r)\right)^2\\ & +\frac{\ell}{2\ell+1}\frac{\ell-1}{2\ell-1}\left(\int_0^\infty dr r^2 R_{n'\ell-2}(r)\left(r\frac{d}{dr}+(\ell+1)\right)R_{n\ell}(r)\right)^2\Bigg\}\,, \end{aligned} \tag{501}$$

where $R_{n\ell}(r)$ are the radial eigenfunctions of the Schrödinger equation defined in Eq. (162).

The second term in Eq. (488), which is denoted here as M_b can be calculated following an analogue procedure. There is, however, a shorter way to solve the angular integration. It is based upon the observation that in

$$M_b = \langle\Phi|\,\nabla^i x^i\frac{\omega_{\vec{k}}^3}{E_\Phi-H_S-\omega_{\vec{k}}}x^j\nabla^j\,|\Phi\rangle \tag{502}$$

both operators are scalar products. The scalar product

$$\vec{x} \cdot \vec{\nabla} = r \frac{d}{dr} \tag{503}$$

does not carry any dependence on the angular coordinates. Thus M_b is simply given by

$$M_b = \sum_{n'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \left(\int_0^\infty dr r^2 R_{n'\ell}(r) r \frac{d}{dr} R_{n\ell}(r) \right)^2 , \tag{504}$$

where again a complete basis set was used to represent the propagator.

The third term in Eq. (488)

$$M_c = \langle \Phi | \nabla^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} x^i \nabla^j | \Phi \rangle \tag{505}$$

is again determined following the same steps as for the first term. After the introduction of a complete set of basis states and the transition to spherical coordinates, it is found to be

$$\begin{aligned} M_c = & \sum_{n',\ell',m'} \sum_{q,q'} \sum_{\ell'',m'',\ell''',m'''} (-1)^q (-1)^{q'} \langle n\ell 0 | \nabla^q | \ell'' m'' \rangle \langle \ell'' m'' | x^{q'} | n'\ell' m' \rangle \\ & \times \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \langle n'\ell' m' | x^{-q} | \ell''' m''' \rangle \langle \ell''' m''' | \nabla^{-q'} | n\ell 0 \rangle . \end{aligned} \tag{506}$$

Reducing the matrix elements to the z component and the projection $m = 0$ leads to

$$
\begin{aligned}
M_c = & \sum_{n',\ell',m'} \sum_{\ell'',m'',\ell''',m'''} \sum_{q,q'} (-1)^q (-1)^{m'''} (-1)^{m''} (-1)^{q'} (-1)^{m'} \langle n\ell 0 | \nabla^0 | \ell'' 0 \rangle \\
& \times \langle \ell'' 0 | x^0 | n'\ell' 0 \rangle \frac{\begin{pmatrix} \ell & 1 & \ell'' \\ 0 & q & m'' \end{pmatrix} \begin{pmatrix} \ell'' & 1 & \ell' \\ -m'' & q' & m' \end{pmatrix}}{\begin{pmatrix} \ell & 1 & \ell'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell'' & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix}} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \\
& \times \langle n'\ell' 0 | x^0 | \ell''' 0 \rangle \langle \ell''' 0 | \nabla^0 | n\ell 0 \rangle \frac{\begin{pmatrix} \ell' & 1 & \ell''' \\ -m' & -q & m''' \end{pmatrix} \begin{pmatrix} \ell''' & 1 & \ell \\ -m''' & -q' & 0 \end{pmatrix}}{\begin{pmatrix} \ell' & 1 & \ell''' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell''' & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}} .
\end{aligned}
\tag{507}
$$

With Eq. (12.1.8) from Ref. [23] this can be simplified to give

$$
\begin{aligned}
M_c = & \frac{1}{2\ell + 1} \sum_{n',\ell''',\ell'',\ell'} \begin{Bmatrix} 1 & \ell'' & \ell \\ 1 & \ell''' & \ell' \end{Bmatrix} \begin{pmatrix} \ell''' & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} \ell' & 1 & \ell''' \\ 0 & 0 & 0 \end{pmatrix}^{-1} \\
& \times \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \begin{pmatrix} \ell & 1 & \ell'' \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} \ell'' & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix}^{-1} \\
& \times \langle n\ell 0 | \nabla^0 | \ell'' 0 \rangle \langle \ell'' 0 | x^0 | n'\ell' 0 \rangle \langle n'\ell' 0 | x^0 | \ell''' 0 \rangle \langle \ell''' 0 | \nabla^0 | n\ell 0 \rangle .
\end{aligned}
\tag{508}
$$

Evaluation of all expression allows to write the final result as

$$
\begin{aligned}
M_c = \sum_{n'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \Bigg\{ & \frac{\ell+1}{2\ell+1}\frac{\ell+2}{2\ell+3} \\
& \times \left(\int_0^\infty dr r^2 R_{n'\ell+2}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right)^2 \\
& + \frac{\ell+1}{(2\ell+1)^2}\frac{1}{2\ell+3} \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right)^2 \\
& + 2\frac{\ell}{2\ell+1}\frac{\ell+1}{2\ell+1} \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right) \\
& \times \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right) \\
& + \frac{\ell}{(2\ell+1)^2}\frac{1}{2\ell-1} \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right)^2 \\
& + \frac{\ell}{2\ell+1}\frac{\ell-1}{2\ell-1} \left(\int_0^\infty dr r^2 R_{n'\ell-2}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right)^2 \Bigg\} .
\end{aligned}
\tag{509}
$$

The fourth term of Eq. (488):

$$
M_d = \langle \Phi | \nabla^i r^2 \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} \nabla^i | \Phi \rangle \tag{510}
$$

is relatively easy to determine. The reason is that r^2 is scalar and, thus, only the radial equation compared to Eq. (227) has to be changed with the result

$$\begin{aligned} M_d = \sum_{n'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \Bigg\{ & \frac{\ell}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(\frac{d}{dr} + \frac{\ell+1}{r} \right) R_{n\ell}(r) \\ & \times \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(r^2 \frac{d}{dr} + (\ell+1) r \right) R_{n\ell}(r) \\ & + \frac{\ell+1}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(\frac{d}{dr} - \frac{\ell}{r} \right) R_{n\ell}(r) \\ & \times \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(r^2 \frac{d}{dr} - \ell r \right) R_{n\ell}(r) \Bigg\}. \end{aligned} \tag{511}$$

Finally, the last contribution from the nonrelativistic multipole is given by

$$M_e = \langle \Phi | \nabla^i x^i x^j \frac{\omega_{\vec{k}}^3}{E_\Phi - H_S - \omega_{\vec{k}}} \nabla^j | \Phi \rangle \ . \tag{512}$$

Recalling that $p^i x^i$ is a scalar, the determination of this term is completely analogue to the one before with the result

$$\begin{aligned} M_e = \sum_{n'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} \Bigg\{ & \frac{\ell+1}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell+1}(r) r^2 \frac{d}{dr} R_{n\ell}(r) \\ & \times \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(\frac{d}{dr} - \frac{\ell}{r} \right) R_{n\ell}(r) \\ & + \frac{\ell}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell-1}(r) r^2 \frac{d}{dr} R_{n\ell}(r) \\ & \times \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(\frac{d}{dr} + \frac{\ell+1}{r} \right) R_{n\ell}(r) \Bigg\}. \end{aligned} \tag{513}$$

The dependence on the energy can be extracted from each of the terms. If the remaining integrals without the energy dependence is denoted as $M_{n'}$, then the

photon energy integration can be carried out as follows

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq} &= -\frac{\alpha}{\pi m_e^2}\int_0^{\epsilon} d\omega_{\vec{k}} \sum_{n'} \frac{\omega_{\vec{k}}^3}{E_n - E_{n'} - \omega_{\vec{k}}} M_{n'} \\ &= \frac{\alpha}{\pi m^2}\sum_{n'} M_{n'}\left\{\frac{\epsilon^3}{3} - \frac{\epsilon^2}{2}(E_{n'} - E_n) + \epsilon(E_{n'} - E_n)^2\right. \\ &\quad \left. - (E_{n'} - E_n)^3 \ln\left(\frac{\epsilon}{(Z\alpha)^2 m_e}\right) + (E_{n'} - E_n)^3 \ln\left(\frac{|E_{n'} - E_S|}{(Z\alpha)^2 m_e}\right)\right\}.\end{aligned} \tag{514}$$

Following the explanation of the analytical method in Sec. 4, only the finite term contributes to the low-energy part. It leads to a Bethe logarithm type of correction. Consequently, the order in α and $Z\alpha$ is extracted from this finite part to define what is called the relativistic Bethe logarithm β_{SE}

$$\mathrm{Re}\Delta E^{(2)}_{L,\Phi,nq,f} = \frac{\alpha}{\pi}\frac{(Z\alpha)^6 m_e}{n^3}\beta_{\mathrm{SE},nq}(n\ell_j)\,. \tag{515}$$

The nonrelativistic multipole correction to this relativistic Bethe logarithm is thus

$$\begin{aligned}
\beta_{\mathrm{SE},nq}(n\ell_j) = {} & \frac{n^3}{(Z\alpha)^6 m_e^3} \sum_{n'} (E_{n'} - E_n)^3 \ln\left(\frac{|E_{n'} - E_n|}{(Z\alpha)^2 m_e}\right) \frac{1}{15} \Bigg[-3 \frac{\ell+2}{2\ell+3} \frac{(\ell+1)}{2\ell+1} \\
& \times \left(\int_0^\infty dr r^2 R_{n'\ell+2}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right)^2 + 4 \frac{\ell+1}{2\ell+1} \\
& \times \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(\frac{d}{dr} - \frac{\ell}{r} \right) R_{n\ell}(r) \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(r^2 \frac{d}{dr} - \ell r \right) R_{n\ell}(r) \\
& - 2 \frac{\ell+1}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell+1}(r) r^2 \frac{d}{dr} R_{n\ell}(r) \int_0^\infty dr r^2 R_{n'\ell+1}(r) \left(\frac{d}{dr} - \frac{\ell}{r} \right) R_{n\ell}(r) \\
& - \left(\frac{4(2\ell+1)(\ell+1)^2 - (\ell+1)}{(2\ell+1)^2(2\ell+3)} \right) \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right)^2 \\
& - 2 \frac{\ell}{2\ell+1} \frac{\ell+1}{2\ell+1} \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right) \\
& \times \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} - \ell \right) R_{n\ell}(r) \right) + \left(\int_0^\infty dr r^2 R_{n'\ell}(r) r \frac{d}{dr} R_{n\ell}(r) \right)^2 \\
& - \left(4 \frac{\ell}{2\ell+1} \frac{\ell}{2\ell-1} - \frac{\ell}{(2\ell+1)^2} \frac{1}{2\ell-1} \right) \\
& \times \left(\int_0^\infty dr r^2 R_{n'\ell}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right)^2 \\
& + 4 \frac{\ell}{2\ell+1} \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(r^2 \frac{d}{dr} + (\ell+1) r \right) R_{n\ell}(r) \\
& \times \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(\frac{d}{dr} + \frac{\ell+1}{r} \right) R_{n\ell}(r) - 2 \frac{\ell}{2\ell+1} \\
& \times \int_0^\infty dr r^2 R_{n'\ell-1}(r) r^2 \frac{d}{dr} R_{n\ell}(r) \int_0^\infty dr r^2 R_{n'\ell-1}(r) \left(\frac{d}{dr} + \frac{\ell+1}{r} \right) R_{n\ell}(r) \\
& - 3 \frac{\ell}{2\ell+1} \frac{\ell-1}{2\ell-1} \left(\int_0^\infty dr r^2 R_{n'\ell-2}(r) \left(r\frac{d}{dr} + (\ell+1) \right) R_{n\ell}(r) \right)^2 \Bigg].
\end{aligned} \tag{516}$$

7.2.3. Relativistic Momentum Correction. The relativistic momentum correction in Eq. (478) has a structure very similar to the leading term evaluated in Eq. (227). Therefore, the angular integration as well as the integration with respect to the photon energy are completely analog. For this purpose the reference state is written in terms of the hydrogen quantum numbers and a complete set of basis is used. This yields

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,p^i p^2} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^i k^j}{\vec{k}^2}\right)\sum_{n'\ell'm'}\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle \\ &\times\frac{1}{E_n-E_{n'}-\omega_{\vec{k}}}\left\langle n'\ell'm'\left|\frac{-p^j p^2}{m_e^3}\right|n\ell m\right\rangle ,\end{aligned} \tag{517}$$

where the sum extends over all bound and unbound states. Because the operators do not depend on $\vec{k}$, the angular integration with respect to $\vec{k}$ can be carried out with the relations in Eqs. (214) and (215) with the result

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,p^i p^2} = &\frac{2\alpha}{3\pi}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}}\sum_{n'\ell'm'}\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle \\ &\times\frac{1}{E_n-E_{n'}-\omega_{\vec{k}}}\left\langle n'\ell'm'\left|\frac{-p^i p^2}{m_e^3}\right|n\ell m\right\rangle ,\end{aligned} \tag{518}$$

In the integration with respect to the photon energy, only the finite term contributes to the low-energy part, as shown in Sec. 4. From Eq. (223) the analogue finite contribution here can be identified. With $(Z\alpha)^2 m_e$ as the scaling parameter in the logarithm, the finite contribution for the relativistic momentum correction yields

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,p^i p^2,f} = &\frac{2\alpha}{3\pi}(E_n-E_{n'})\ln\left[\frac{|E_n-E_{n'}|}{(Z\alpha)^2 m_e}\right] \\ &\times\sum_{n'\ell'm'}\left\langle n\ell m\left|\frac{p^i}{m_e}\right|n'\ell'm'\right\rangle\left\langle n'\ell'm'\left|\frac{-p^i p^2}{m_e^3}\right|n\ell m\right\rangle ,\end{aligned} \tag{519}$$

Recalling the relation

$$-p^2=\Delta=-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\vec{\ell}^{\,2}}{r^2}, \tag{520}$$

as well as that $|n\ell m\rangle$ is an eigenstate of $\vec{\ell}^{\,2}$ and the result for the Bethe logarithm in Eq. (227), one obtains for the relativistic Bethe logarithm contribution $\beta_{\mathrm{SE},p^ip^2}$

$$\begin{aligned}
\beta_{\mathrm{SE},p^ip^2}(n\ell_j) = \frac{2\alpha}{3\pi}\frac{n^3}{(Z\alpha)^6 m_e^5}\sum_{n'}(E_n - E_{n'})\,\ln\left[\frac{|E_n - E_{n'}|}{(Z\alpha)^2 m_e}\right]\Bigg\{\frac{\ell+1}{2\ell+1} \\
\times\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r) \\
\times\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R_{n\ell}(r) \\
+\frac{\ell}{2\ell+1}\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r) \\
\times\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R_{n\ell}(r) \\
-\frac{\ell+1}{2\ell+1}\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r) \\
\times\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)\frac{\ell(\ell+1)}{r^2}R_{n\ell}(r) \\
-\frac{\ell}{2\ell+1}\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r) \\
\times\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)\frac{\ell(\ell+1)}{r^2}R_{n\ell}(r)\Bigg\}\,.
\end{aligned} \tag{521}$$

7.2.4. Spin Coupling to Physical Momentum Correction. The spin dependence of the next correction given in Eq. (479) necessitates the use of the Pauli wave function from Eq. (165), which includes the spin into the Schrödinger wave function and is denoted by $|n\ell jm\rangle$. The integration with respect to the photon energy is again completely analogue because there is no k dependence in the integral

and the finite part is

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,r\times\sigma,f} = -Z\alpha\frac{2\alpha}{3\pi}\sum_{n'}(E_n - E_{n'})\,\ln\left[\frac{|E_n - E_{n'}|}{(Z\alpha)^2 m_e}\right]\sum_{j',\ell',m',q}(-1)^q \\ \times\langle n\ell jm|\,\frac{p^q}{m_e}\,|n'\ell'j'm'\rangle\,\langle n'\ell'j'm'|\,\frac{(\vec{x}\times\vec{\sigma})^{-q}}{m_e^2 r^3}\,|n\ell jm\rangle\ .\end{aligned} \tag{522}$$

Compared to the angular integration in Sec. 7.2.2 the addition of the spin leads to a few complications. For example, the matrix elements are no longer reduced to the orbital angular momentum projection $m = 0$ but rather to the total angular momentum projection $m = \frac{1}{2}$. The reduction process here now has the form

$$\langle n\ell jm|\,p^q\,|n'\ell'j'm'\rangle = (-1)^{-m+\frac{1}{2}}\frac{\begin{pmatrix} j & 1 & j' \\ -m & q & m'\end{pmatrix}}{\begin{pmatrix} j & 1 & j' \\ -\frac{1}{2} & 0 & \frac{1}{2}\end{pmatrix}}\left\langle n\ell j\frac{1}{2}\right|\,p^0\,\left|n'\ell'j'\frac{1}{2}\right\rangle \tag{523}$$

and

$$\begin{aligned}&\langle n'\ell'j'm'|\frac{(\vec{x}\times\vec{\sigma})^{-q}}{r^3}\,|n\ell jm\rangle \\ &\quad = (-1)^{-m+\frac{1}{2}}\frac{\begin{pmatrix} j' & 1 & j \\ -m' & -q & m\end{pmatrix}}{\begin{pmatrix} j' & 1 & j \\ -\frac{1}{2} & 0 & \frac{1}{2}\end{pmatrix}}\left\langle n'\ell'j'\frac{1}{2}\right|\,\frac{(\vec{x}\times\vec{\sigma})^0}{r^3}\,\left|n\ell j\frac{1}{2}\right\rangle\ .\end{aligned} \tag{524}$$

One of these $3j$-symbols can be rewritten as

$$\begin{pmatrix} j & 1 & j' \\ -m & q & m'\end{pmatrix} = (-1)^{j+1+j'}\begin{pmatrix} j & j' & 1 \\ -m & m' & q\end{pmatrix}\ . \tag{525}$$

Analogue, one of the $3j$-symbols in the denominator can be transformed into the other. The $3j$-symbols in the numerator can be combined using relations from Ref. [23] to

give

$$\begin{aligned}
&\sum_{m'q}(-1)^{-m'+1-m+q}(-1)^{j'+1+j}\begin{pmatrix} j & j' & 1 \\ -m & m' & q \end{pmatrix}\begin{pmatrix} j' & 1 & j \\ -m' & -q & m \end{pmatrix} \\
=&(-1)^{j-m+1}\sum_{m'q}(-1)^{1+j'-m'-q}\begin{pmatrix} j & j' & 1 \\ -m & m' & q \end{pmatrix}\begin{pmatrix} j' & 1 & j \\ -m' & -q & m \end{pmatrix} \\
=&(-1)^{2j+1}\frac{1}{2j+1},
\end{aligned} \tag{526}$$

where $(-1)^q = (-1)^{-q}$ is employed because q is a whole number. A formula for the matrix element with p is given in Eq. (7.1.24) in Ref. [23]. The $\vec{x}\times\vec{\sigma}$ matrix element can be determined with the following relation for the cross product

$$(\vec{x}\times\vec{\sigma})^0 = -\mathrm{i}\,(x_1\sigma_{-1} - x_{-1}\sigma_1) \tag{527}$$

and a combination of Eqs. (7.1.26) and (7.1.28) from Ref. [23]. The finite contribution from the spin coupling to the physical momentum to the low-energy part is thus given by

$$\begin{aligned}
\beta_{\mathrm{SE},r\times\sigma}(n\ell_j) = -\frac{2\alpha}{3\pi}\frac{n^3}{(Z\alpha)^5 m_e^4}\sum_{n'}(E_n - E_{n'})\,\ln\left[\frac{|E_n - E_{n'}|}{(Z\alpha)^2 m_e}\right]\Bigg\{&\frac{\kappa+1}{2\ell+1} \\
&\times\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr} - \frac{\ell}{r}\right)R_{n\ell}(r) \\
&\times\int_0^\infty dr r^2 R_{n'\ell+1}(r)\frac{1}{r^2}R_{n\ell}(r) \\
&+\frac{\kappa+1}{2\ell+1}\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr} + \frac{\ell+1}{r}\right)R_{n\ell}(r) \\
&\times\int_0^\infty dr r^2 R_{n'\ell-1}(r)\frac{1}{r^2}R_{n\ell}(r)\Bigg\},
\end{aligned} \tag{528}$$

where $\kappa = (-1)^{j+\ell+\frac{1}{2}}(j+\frac{1}{2})$ is the Dirac quantum number.

7.2.5. Quadrupole Correction to the Magnetic Coupling. This correction given in Eq. (480) is

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\left[\frac{1}{m_e}\left(\vec{k}\cdot\vec{x}\right)\left(\vec{k}\times\vec{\sigma}\right)^j\right]|\Phi\rangle\ .\end{aligned} \tag{529}$$

As this depends on $\vec{k}$, a similar procedure to Sec. 7.2.2 has to be applied and the $\vec{k}$ dependence has to be extracted. For this the index notation is employed in which

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{|\vec{k}|<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{m_e^2\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}k^ax^a\epsilon^{jcd}k^c\sigma^d\,|\Phi\rangle\end{aligned} \tag{530}$$

is obtained. Taking $\omega=|\vec{k}|$ out of the first $\vec{k}$, yields

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} &= \int_{|\vec{k}|<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{m_e^2\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\quad\times\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{k^a}{|\vec{k}|}r^a\epsilon^{jcd}k^c\sigma^d\,|\Phi\rangle\\ &= \int_{|\vec{k}|<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{m_e^2\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\quad\times\langle\Phi|\,p^i\frac{(\omega_{\vec{k}}-E_\Phi+H_S)-(H_S-E_S)}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{k^a}{|\vec{k}|}r^a\epsilon^{jcd}k^c\sigma^d\,|\Phi\rangle\ .\end{aligned} \tag{531}$$

The first of the terms in the numerator cancels the denominator. Consequently, it would be proportional to ϵ after the integration and does not contribute in the finite order ϵ^0. Therefore, the terms is neglected. The second term can be taken care off with the relation in Eq. (416), which leads to

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{|\vec{k}|<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{m_e^3\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{k^a}{|\vec{k}|}(ip^a)\epsilon^{jcd}k^c\sigma^d\,|\Phi\rangle\ .\end{aligned} \tag{532}$$

Analogue for the second $\vec{k}$ it is found

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = &\int_{\omega<\epsilon}\frac{d\omega}{(2\pi)^3}\frac{2\pi\alpha}{m_e^3\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}k^ar^a\epsilon^{jcd}k^c\sigma^d\,|\Phi\rangle\,.\end{aligned} \tag{533}$$

where the relation

$$[(H_S-E_S),p^a] = \mathrm{i}Z\alpha\frac{r^a}{r^3} \tag{534}$$

is used. The identities in Eqs. (214),(215) and (487) allow to carry out the angular integration with respect to $\vec{k}$ which gives

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} = \frac{\alpha}{\pi m_e^3}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}}\Bigg(&\frac{1}{3}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\epsilon^{iad}r^a\sigma^d\,|\Phi\rangle\\ &+\frac{1}{15}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\epsilon^{iad}r^a\sigma^d\,|\Phi\rangle\\ &+\frac{1}{15}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\epsilon^{jjd}r^i\sigma_d\,|\Phi\rangle\\ &+\frac{1}{15}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\epsilon^{aid}r^a\sigma^d\,|\Phi\rangle\Bigg).\end{aligned} \tag{535}$$

Because of the total antisymmetry of the ϵ-tensor the third term vanishes while the second and fourth term cancel exactly, thus

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,krk\times\sigma} &= \frac{\alpha}{\pi m_e^3}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}}\frac{1}{3}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\epsilon^{iad}r^a\sigma^d\,|\Phi\rangle\\ &= -\frac{\alpha}{3\pi m_e^3}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}}\langle\Phi|\,p^i\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{Z\alpha}{r^3}\left(\vec{r}\times\vec{\sigma}\right)^i|\Phi\rangle\\ &= -\frac{1}{2}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,r\times\sigma}\end{aligned} \tag{536}$$

and accordingly

$$\beta_{\mathrm{SE},krk\times\sigma}(n\ell_j) = -\frac{1}{2}\beta_{\mathrm{SE},r\times\sigma}(n\ell_j). \tag{537}$$

7.2.6. Correction to Energy, Hamiltonian and Wave Function. The relativistic correction of the reference-state energy is given in Eq. (481) as

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta E} = &-\int_{\omega_{\vec{k}}<\epsilon}\frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\\ &\times\langle\Phi|\,\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\delta E\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}\,|\Phi\rangle\ .\end{aligned} \tag{538}$$

Once more, a complete set of basis states is introduced to yield

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta E} = &-\int_{\omega_{\vec{k}}<\epsilon}\frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}m_e^2}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\delta E\sum_{n',j,\ell,m'}\left(\frac{1}{E_n-E_{n'}-\omega_{\vec{k}}}\right)^2\\ &\times\langle n\ell jm|\,p^i\,|n'\ell'j'm'\rangle\,\langle n'\ell'j'm'|\,p^j\,|n\ell jm\rangle\ .\end{aligned} \tag{539}$$

The relativistic correction of the reference-state energy is found in the literature [38] to be

$$\delta E=\frac{(Z\alpha)^4m_e}{2n^3}\left(\frac{3}{4n}-\frac{1}{j+\frac{1}{2}}\right)\ ,\ j=\ell\pm\frac{1}{2}. \tag{540}$$

The evaluation of the matrix element is now the same as for the previous corrections and therefore not discussed. Carrying out the remaining integration with respect to the photon energy the contribution to the relativistic Bethe logarithm is obtained as

$$\begin{aligned}\beta_{\mathrm{SE},\delta E}(n\ell_j) = &\frac{1}{3m_e^2(Z\alpha)^2}\left(\frac{3}{4n}-\frac{1}{j+\frac{1}{2}}\right)\sum_{n'}\left[\ln\left(\frac{|E_n-E_{n'}|}{(Z\alpha)^2m_e}\right)+1\right]\\ &\times\left\{\frac{\ell+1}{2\ell+1}\left(\int_0^\infty drr^2R_{n\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r)\right)^2\right.\\ &\left.+\frac{\ell}{2\ell+1}\left(\int_0^\infty drr^2R_{n\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r)\right)^2\right\}.\end{aligned} \tag{541}$$

As it turns out, the evaluation of the contribution from the relativistic corrections to the Hamiltonian is the most complicated in the low-energy part. Discussing the spin-orbit coupling and the relativistic kinetic energy correction separately, has proven to be the most convenient approach. Here, the starting point is the spin-orbit

coupling correction from Eq. (482), which is found to be

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta H(LS)} = \int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}} \\ \times\frac{Z\alpha}{4m_e^2r^3}\left(\vec{\ell}\cdot\vec{\sigma}\right)\frac{1}{E_\Phi-H_S-\omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\ .\end{aligned} \tag{542}$$

For this correction a new Hamiltonian is defined, in which the spin-orbit coupling is infinitesimally included

$$H(\eta) = \frac{\vec{p}^2}{2m_e} - \frac{Z\alpha}{r} + \eta\frac{Z\alpha}{4m_e^2r^3}\vec{\ell}\cdot\vec{\sigma}\,. \tag{543}$$

The above correction can then be obtained by taking the derivative with respect to η, which gives

$$\frac{\partial}{\partial\eta}\frac{1}{E_\Phi-H(\eta)-\omega_{\vec{k}}}\bigg|_{\eta=0} = \frac{1}{E_\Phi-H(\eta)-\omega_{\vec{k}}}\frac{Z\alpha}{4m_e^2r^3}\vec{\ell}\cdot\vec{\sigma}\frac{1}{E_\Phi-H(\eta)-\omega_{\vec{k}}}\,. \tag{544}$$

The idea is now to calculate the contribution just like for the Bethe logarithm only with this perturbed Hamiltonian, and obtain the contribution from the energy correction as the derivative of it with respect to η. For this the matrix element

$$M_{\delta H(LS)} = \langle\Phi|p^i\frac{1}{H(\eta)-(E_S-\omega)}p^i|\Phi\rangle \tag{545}$$

has to be evaluated. Due to the dependence of the Hamiltonian on both spin and orbital angular momentum, the angular algebra has to be considered very carefully and all possible configurations in the intermediate states have to be taken into account. In the usual way a complete basis set is used to represent the propagator, here, however, it is the complete basis of $H(\eta)$ and not that of the Schrödinger Hamiltonian. These basis states of $H(\eta)$ are denoted as $|\ \rangle'$ and allow to write

$$\begin{aligned}M_{\delta H(LS)} = \sum_{n',j',\ell',m',q}(-1)^q\langle n\ell jm|\nabla_{1q}|n'\ell'j'm'\rangle' \\ \times\,'\langle n'\ell'j'm'|\frac{1}{E_\Phi-H(\eta)-\omega_{\vec{k}}}|n'\ell'j'm'\rangle'\,'\langle n'\ell'j'm'|\nabla_{1-q}|n\ell jm\rangle\end{aligned} \tag{546}$$

in spherical coordinates. It is possible to extract the angular dependence of the perturbed Hamiltonian, which is just given by $\vec{\ell}\cdot\vec{\sigma}$, in order to obtain a perturbed energy $E'_{n'}(\eta)$ independent of it. Together with the equations from Sec. 7.2.4 the matrix element can be written as

$$\begin{aligned} M_{\delta H(LS)} = \frac{(-1)^{2j+1}}{2j+1}\sum_{n',j'}\begin{pmatrix} j' & 1 & j \\ -\frac{1}{2} & 0 & \frac{1}{2}\end{pmatrix}^{-2}\frac{1}{E_n - E'_{n'}(\eta)-\omega_{\vec{k}}} \\ \times\left\{(-1)^{2j+1}(2j+1)(\ell+1)\left[j'(j'+1)-(\ell+1)(\ell+2)-\frac{3}{4}\right]\right. \\ \times\left[\int_0^\infty dr r^2 R'_{n'\ell+1}(r,\eta)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r)\right]^2 \\ \times\begin{Bmatrix} j & j' & 1 \\ \ell+1 & \ell & \frac{1}{2}\end{Bmatrix}^2\left(C^{j'\frac{1}{2}}_{j\frac{1}{2}10}\right)^2+(-1)^{2j+1}(2j+1)\ell \\ \times\left[j'(j'+1)-\ell(\ell-1)-\frac{3}{4}\right]\begin{Bmatrix} j & j' & 1 \\ \ell-1 & \ell & \frac{1}{2}\end{Bmatrix}^2\left(C^{j'\frac{1}{2}}_{j\frac{1}{2}10}\right)^2 \\ \left.\times\left[\int_0^\infty dr r^2 R'_{n'\ell-1}(r,\eta)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r)\right]^2\right\}. \end{aligned} \tag{547}$$

It is possible to simplify this further and obtain an expression in which the sum over the intermediate total angular momenta is already carried out. For this, the two possible total angular momenta j for the reference state, $j=\ell-\frac{1}{2}$ and $j=\ell+\frac{1}{2}$, are considered. Moreover, the results for $\ell'\to\ell-1$ and $\ell'\to\ell+1$ in the intermediate state without the factor $\vec{\ell}\cdot\vec{\sigma}$ are denoted as Q_{L-1} and Q_{L+1} respectively. If the reference state has $j=\ell-\frac{1}{2}$, then for $\ell'\to\ell+1$ the total angular momentum j' in the intermediate state can only be $j'\to j+1$. This means the sum over j' in the case $\ell'\to\ell+1$ contains only one term and one finds

$$\begin{aligned}\left(\vec{\ell}\cdot\vec{\sigma}\right)Q_{\ell+1} &= \left((\ell+1)^2-\frac{1}{4}-\ell^2-3\ell-2-\frac{3}{4}\right)Q_{L+1} \\ &= -(\ell+2)Q_{\ell+1}\,.\end{aligned} \tag{548}$$

If the the intermediate orbital angular momentum is now $\ell'\to\ell-1$, there are two terms with different total angular momentum j', which have to be added weighted

by the factor $\vec{\ell}\cdot\vec{\sigma}$. Unfortunately, this also contains pre-factors which are contained in Q_{L-1}, thus making it necessary to divide by these pre-factors. Denoting the total angular factor as VQ yields

$$VQ = \frac{\left(\vec{\ell}\cdot\vec{\sigma}\right)A + \left(\vec{\ell}\cdot\vec{\sigma}\right)B}{A+B}, \tag{549}$$

where A and B are the pre-factors, which would arise from the angular algebra without $\vec{\ell}\cdot\vec{\sigma}$. The result is

$$VQ = \frac{(\ell-1)(1-\ell-2\ell^2)}{\ell(2\ell-1)}Q_{\ell-1} = -\frac{(\ell+1)(\ell-1)}{\ell}Q_{\ell-1}\,. \tag{550}$$

The calculation for total angular momentum j of the reference state being $j=\ell+\frac{1}{2}$ is analogue, but now there are two terms for the case $\ell'\to\ell+1$ and only one for $\ell'\to\ell-1$. As the result

$$\begin{aligned}\left(\vec{L}\cdot\vec{\sigma}\right)Q_{L-1} &= \left(L^2-\frac{1}{4}-L^2+L-\frac{3}{4}\right)Q_{L-1}\\ &= (L-1)Q_{L-1} \qquad (551)\\ VQ = \frac{(L+2)(1-(L+1)(2L+1))}{(L+1)(2L+3)}Q_{L+1} &= \frac{L(L+2)}{L+1}Q_{L+1} \qquad (552)\end{aligned}$$

is obtained. Using $R'_{n\ell}(r,\eta)$ to denote the radial eigenfunction of the perturbed Hamiltonian, the finite contribution to the low-energy part is found to be

$$\begin{aligned}\beta_{\mathrm{SE},\delta H(LS)}(n\ell_j) = \frac{2n^3}{3(Z\alpha)^6 m_e^3}\frac{\partial}{\partial\eta}\sum_{n'}(E'_{n'}(\eta)-E_n)\ln\left(\frac{|E_n-E'_{n'}(\eta)|}{(Z\alpha)^2 m_e}\right)\\ \times\left\{\left[(\ell+2)\delta_{j,\ell-\frac{1}{2}}-\frac{\ell(\ell+2)}{\ell+1}\delta_{j,\ell+\frac{1}{2}}\right]\right.\\ \times\frac{\ell+1}{2\ell+1}\left(\int_0^\infty dr r^2 R'_{n'\ell+1}(r,\eta)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r)\right)^2\\ +\left[\frac{(\ell+1)(\ell-1)}{\ell}\delta_{j,\ell-\frac{1}{2}}-(\ell-1)\delta_{j,\ell+\frac{1}{2}}\right]\\ \left.\times\frac{\ell}{2\ell+1}\left(\int_0^\infty dr r^2 R'_{n'\ell-1}(r,\eta)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r)\right)^2\right\}\Bigg|_{\eta=0}.\end{aligned} \tag{553}$$

For the relativistic kinetic energy correction the same approach is used. Based upon its contribution

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi,\delta H(p^4)} = -\int_{\omega_{\vec{k}}<\epsilon} \frac{d^3k}{(2\pi)^3}\frac{2\pi\alpha}{\omega_{\vec{k}}}\left(\delta^{ij}-\frac{k^ik^j}{\vec{k}^2}\right)\langle\Phi|\frac{p^i}{m_e}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}} \\ \times \frac{\vec{p}^4}{8m_e^3}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{p^j}{m_e}|\Phi\rangle\end{aligned} \tag{554}$$

again a perturbed Hamiltonian is defined by

$$H(\eta) = \frac{\vec{p}^2}{2m_e} - \frac{Z\alpha}{r} - \eta\frac{\vec{p}^4}{8m_e^3}\,. \tag{555}$$

Due to

$$\frac{\partial}{\partial\eta}\frac{1}{E_\Phi - H(\eta) - \omega_{\vec{k}}}\bigg|_{\eta=0} = -\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\frac{\vec{p}^4}{8m_e^3}\frac{1}{E_\Phi - H_S - \omega_{\vec{k}}}\,. \tag{556}$$

the finite contribution to the low-energy part can be found in an analogous manner by taking a derivative of the term calculated with the perturbed energy and wave function. While the numerical lattice method, which is used to calculate the radial integrals, is able to obtain basis states for the Hamiltonian perturbed by $1/r^3$, the even more singular behavior of p^4 requires a different method to find the perturbed radial functions. In this case one resorts to first order perturbation theory in order to find the perturbed eigenstates which are given by [38]

$$|n\ell jm\rangle' = |n\ell jm\rangle - \eta\sum_{k\neq n}|k\ell jm\rangle\frac{1}{E_n - E_k}\langle k\ell jm|\frac{\vec{p}^4}{8m_e^3}|n\ell jm\rangle\,. \tag{557}$$

The matrix element is diagonal in the angular quantum numbers and can be further simplified by expressing p^2 in terms of the Schrödinger Hamiltonian minus the Coulomb potential, i.e.

$$\frac{\vec{p}^4}{8m_e^3} = \frac{1}{2m_e}\left(\frac{\vec{p}^2}{2m_e}\right)^2 = \frac{1}{2m_e}\left(H_S + \frac{Z\alpha}{r}\right)^2\,. \tag{558}$$

Thus the perturbed radial eigenfunctions can be determined by

$$R'_{n\ell}(r,\eta) = R_{n\ell}(r) - \frac{\eta}{2m_e}\sum_{k\neq n} R_{k\ell}(r)\frac{1}{E_n - E_k}\Big(E_k E_n \delta_{k,n} + \int_0^\infty dr r^2 R_{k\ell}(r)\left((E_k + E_n)\frac{Z\alpha}{r} + \frac{(Z\alpha)^2}{r^2}\right) R_{n\ell}(r)\Big)\,. \tag{559}$$

Additionally, the perturbed eigenenergy has to be found which is again determined using first order perturbation theory. From the literature [38] one finds the equation

$$E'_n(\eta) = E_n - \eta\,\langle n\ell jm|\,\frac{\vec{p}^{\,4}}{8m^3}\,|njlm\rangle\ , \tag{560}$$

which in this case can be evaluated to be

$$E_n(\eta) = E_n - \frac{\eta}{2m}\Big(E_n^2 + \int_0^\infty dr r^2\left(2E_n\frac{Z\alpha}{r} + \frac{(Z\alpha)^2}{r^2}\right) R_{nl}^2(r)\Big)\,. \tag{561}$$

With the such determined perturbed wave function and energy the contribution to the low-energy part of this term is

$$\begin{aligned}\beta_{\mathrm{SE},\delta H(p^4)}(n\ell_j) = {}& \frac{2n^3}{3(Z\alpha)^6\, m_e^3}\frac{\partial}{\partial\eta}\sum_n (E'_{n'}(\eta) - E_n)\ln\left(\frac{|E_n - E'_{n'}(\eta)|}{(Z\alpha)^2 m_e}\right) \\ &\times\Big\{\frac{\ell+1}{2\ell+1}\Big(\int_0^\infty dr r^2 R'_{n'\ell+1}(r,\eta)\left(\frac{d}{dr} - \frac{\ell}{r}\right) R_{n\ell}(r)\Big)^2 \\ &+ \frac{\ell}{2\ell+1}\Big(\int_0^\infty dr r^2 R'_{n'\ell-1}(r,\eta)\left(\frac{d}{dr} + \frac{\ell+1}{r}\right) R_{n\ell}(r)\Big)^2\Big\}\,.\end{aligned} \tag{562}$$

The final low-energy contribution arise from the first order, relativistic correction of the wave function given in Eq. (483). The evaluation of the angular algebra is in principle analogue to the Bethe logarithm in Eq. (227) with the only difference being the multiplication of the wave function correction matrix element. Fortunately, this matrix element is diagonal in the angular quantum numbers. The finite contribution

to the low-energy part is then just

$$\begin{aligned}\beta_{\mathrm{SE},\delta\Phi}(n\ell_j) = \frac{2n^3}{3m_e^3(Z\alpha)^6}\sum_{n'}\sum_{k\neq n}\frac{E_{n'}-E_n}{E_n-E_k}\ln\left(\frac{|E_n-E_{n'}|}{(Z\alpha)^2 m_e}\right)\\ \times\int_0^\infty dr r^2 R_{k\ell}(r)\Big[\frac{1}{4m_e^3}\left(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{\ell(\ell+1)}{r^2}\right)^2+\frac{\kappa+1}{2m_e^2r^3}\Big]R_{n\ell}(r)\\ \times\left\{\frac{\ell+1}{2\ell+1}\Big(\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{k\ell}(r)\Big)\right.\\ \times\Big(\int_0^\infty dr r^2 R_{n'\ell+1}(r)\left(\frac{d}{dr}-\frac{\ell}{r}\right)R_{n\ell}(r)\Big)\\ +\frac{\ell}{2\ell+1}\Big(\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{k\ell}(r)\Big)\\ \left.\times\Big(\int_0^\infty dr r^2 R_{n'\ell-1}(r)\left(\frac{d}{dr}+\frac{\ell+1}{r}\right)R_{n\ell}(r)\Big)\right\},\end{aligned} \tag{563}$$

where $\kappa=(-1)^{j+\ell+\frac{1}{2}}(j+\frac{1}{2})$ again is the Dirac quantum number.

7.2.7. Summary of Corrections in the Low-Energy Part. In order to obtain the total low-energy part of the self-energy correction all these separate contributions have to be added. However, there is also a contribution of order $\alpha(Z\alpha)^6$, which contains a logarithm of ϵ and thus the non finite contribution to the low-energy part. So far this term has been neglected. While its derivation is not given here (it can be found for example in Ref. [46]), it has to be included to receive the complete result. By also taking into account Bethe's results, which is shown in Eq. (227), the low-energy part of the self-energy correction for highly excited Rydberg states with $\ell\geq 2$ is found to be

$$\begin{aligned}\mathrm{Re}\Delta E^{(2)}_{L,\Phi}(n\ell_j,Z\alpha,\epsilon) = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3}\Big\{-\frac{4}{3}\ln k_0+(Z\alpha)^2\Big[\beta_{\mathrm{SE}}(n\ell_j)\\ +\frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\left(\ln\left[\frac{\epsilon}{(Z\alpha)^2 m_e}\right]+\frac{1}{\epsilon}\right)\Big]\Big\}.\end{aligned} \tag{564}$$

or in terms of the scaled self-energy function F defined in Secs. 3 and 4 by

$$\mathrm{Re}\Delta E^{(2)}_{L,\Phi} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3} F_L(n\ell_j, Z\alpha, \epsilon)\,, \tag{565}$$

as

$$\begin{aligned} F_L(n\ell_j, Z\alpha, \epsilon) = -\frac{4}{3}\ln k_0 + (Z\alpha)^2 \Bigg\{ & \beta_{\mathrm{SE}}(n\ell_j) \\ & + \frac{3n^2 - \ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})} \left(\ln\left[\frac{\epsilon}{(Z\alpha)^2 m_e}\right] + \frac{1}{\epsilon} \right) \Bigg\}\,. \end{aligned} \tag{566}$$

In both cases $\ln k_0$ denotes the Bethe logarithm given in Eq. (227) and β_{SE} denotes the relativistic Bethe logarithm which is given by the sum of all the finite contributions from the terms discussed in this section

$$\begin{aligned} \beta_{\mathrm{SE}}(n\ell_j) = {} & \beta_{\mathrm{SE},nq}(n\ell_j) + \beta_{\mathrm{SE},p^ip^2}(n\ell_j) + \beta_{\mathrm{SE},r\times\sigma} n\ell_j) + \beta_{\mathrm{SE},kr\,k\times\sigma}(n\ell_j) \\ & + \beta_{\mathrm{SE},\delta E}(n\ell_j) + \beta_{\mathrm{SE},\delta H(LS)}(n\ell_j) + \beta_{\mathrm{SE},\delta H(p^4)}(n\ell_j) + \beta_{\mathrm{SE},\delta\Phi}(n\ell_j)\,. \end{aligned} \tag{567}$$

7.2.8. Numerical Evaluation and Results. So far the functional form of the relativistic Bethe logarithms has been given as integrals involving the sum over all bound and unbound radial eigenfunctions of the Schrödinger equation, these are evaluated numerically using lattice methods. The values for the relativistic Bethe logarithm obtained by us with this method for numerous highly excited states are given in Table 7.1. These results have been published in Refs. [83–85].

A detailed description of the lattice method can be found in Ref. [78] and here only a short overview over the most important points is given. A finite lattice is used to represent the remaining radial variable in the expressions obtained for β_{SE}. Due to the structure of the wave function the lattice spacing is not equidistant but exponentially scaled such that the lattice spacing closer to the origin is denser than far away from the origin. This allows for a better representation of the wave function with fewer lattice points. Consequently, the integrals reduce to sum over all lattice points.

Moreover, the Schrödinger equation in this exponential lattice spacing also becomes discrete. It is given in Ref. [78]. The derivative in it is consequently replaced by a discretized derivative, for which a 11-point discrete derivative formula is employed

in our calculations in this work. For the first points closest to the origin this formula is altered as described in Ref. [78] to account for the missing points outside of the lattice.

Table 7.1. Values obtained by the numerical lattice method for the relativistic Bethe logarithm β_{SE}. The numbers in parentheses are standard uncertainties in the last figure.

n	ℓ	$2j$	κ	β_{SE}	$2j$	κ	β_{SE}
16	15	29	15	$0.629\,871(5) \times 10^{-5}$	31	-16	$0.625\,545(5) \times 10^{-5}$
16	14	27	14	$0.902\,533(5) \times 10^{-5}$	29	-15	$0.895\,491(5) \times 10^{-5}$
15	14	27	14	$0.859\,850(5) \times 10^{-5}$	29	-15	$0.853\,375(5) \times 10^{-5}$
15	13	25	13	$1.262\,399(5) \times 10^{-5}$	27	-14	$1.251\,506(5) \times 10^{-5}$
14	13	25	13	$1.199\,921(5) \times 10^{-5}$	27	-14	$1.189\,658(5) \times 10^{-5}$
14	12	23	12	$1.811\,052(5) \times 10^{-5}$	25	-13	$1.793\,624(5) \times 10^{-5}$
13	12	23	12	$1.716\,173(5) \times 10^{-5}$	25	-13	$1.700\,273(5) \times 10^{-5}$
13	11	21	11	$2.675\,867(5) \times 10^{-5}$	23	-12	$2.646\,861(5) \times 10^{-5}$
12	11	21	11	$2.527\,776(5) \times 10^{-5}$	23	-12	$2.501\,428(5) \times 10^{-5}$
12	10	19	10	$3.962\,364(5) \times 10^{-5}$	21	-11	$3.898\,005(5) \times 10^{-5}$
11	10	19	10	$3.853\,354(5) \times 10^{-5}$	21	-11	$3.807\,626(5) \times 10^{-5}$
11	9	17	9	$6.526\,732(5) \times 10^{-5}$	19	-10	$6.433\,497(5) \times 10^{-5}$
10	9	17	9	$6.120\,418(5) \times 10^{-5}$	19	-10	$6.036\,525(5) \times 10^{-5}$
10	8	15	8	$10.945\,050(5) \times 10^{-5}$	17	- 9	$10.761\,067(5) \times 10^{-5}$
9	8	15	8	$10.219\,540(5) \times 10^{-5}$	17	- 9	$10.054\,823(5) \times 10^{-5}$
9	7	13	7	$19.539\,646(5) \times 10^{-5}$	15	- 8	$19.144\,495(5) \times 10^{-5}$
8	7	13	7	$18.157\,546(5) \times 10^{-5}$	15	- 8	$17.805\,538(5) \times 10^{-5}$
8	6	11	6	$37.774\,523(5) \times 10^{-5}$	13	- 7	$36.828\,860(5) \times 10^{-5}$
7	6	11	6	$34.920\,620(5) \times 10^{-5}$	13	- 7	$34.081\,999(5) \times 10^{-5}$
7	5	9	5	$81.068\,312(5) \times 10^{-5}$	11	- 6	$78.458\,727(5) \times 10^{-5}$
6	5	9	5	$74.539\,820(5) \times 10^{-5}$	11	- 6	$72.232\,654(5) \times 10^{-5}$
6	4	7	4	$200.519\,845(5) \times 10^{-5}$	9	- 5	$191.776\,916(5) \times 10^{-5}$
5	4	7	4	$183.482\,753(5) \times 10^{-5}$	9	- 5	$175.747\,109(5) \times 10^{-5}$
5	3	5	3	$604.539\,039(5) \times 10^{-5}$	7	- 4	$566.224\,291(5) \times 10^{-5}$

In this way, a matrix for the Schrödinger equation at every lattice point is obtained. Using the LAPACK package for FORTRAN, this matrix is diagonalized and its eigenvectors and eigenvalues are determined. The eigenvalues give the energy of the intermediate state and the eigenvectors are used as the intermediate states at every lattice point. A certain amount of these eigenvectors have a negative eigenvalue and thus represent the complete bound spectrum, but eigenvectors with a positive eigenvalue are also obtained. This is the big advantage of the lattice method because it yields a pseudo spectrum representing the continuum of unbound states as well. The operator acting on the reference state wave function is calculated in continuum space and then discretized to the lattice.

7.3. HIGH-ENERGY PART

7.3.1. One-Vertex Contribution. As explained in Sec. 4.6, for high photon energy it is possible to expand in the binding Coulomb potential and consider the contributions separately for each number of interactions with the Coulomb potential. Because here only the self-energy correction of order $\alpha(Z\alpha)^6$ is determined, the zero-vertex part, which cancels the mass renormalization, as well as the the one-vertex contribution of order $\alpha(Z\alpha)^4$ given in Eq. (324), which also vanishes for the highly excited states investigated here, are not discussed. The contribution from the one-vertex part of order $\alpha(Z\alpha)^6$ is due to the F_2 form factor correction to the electric interaction. From Eq. (325) it is found to be

$$\Delta E_H^1(n\ell_j) = \left\langle \psi^+ \right| F_2(\nabla^2) \frac{e}{2m_e} \mathrm{i}\vec{\gamma} \cdot \vec{E} \left| \psi \right\rangle \,. \tag{568}$$

Expanding $F_2(\nabla^2)$ in powers of $Z\alpha$ in lowest order leads to the term

$$\Delta E_{H,0}^1(n\ell_j) = \left\langle \psi^+ \right| F_2(0) \frac{e}{2m_e} \mathrm{i}\vec{\gamma} \cdot \vec{E} \left| \psi \right\rangle \,, \tag{569}$$

with $F_2(0) = \alpha/2\pi$. Counting the orders of $Z\alpha$, it becomes clear that in order to obtain the correction of order $\alpha(Z\alpha)^6$ this has to be evaluated on the relativistic wave function expanded in $Z\alpha$ up to relative order $(Z\alpha)^2$. The reason is that this correction evaluated on the nonrelativistic wave function would lead to a contribution in order $\alpha(Z\alpha)^4$, so in order to get to $\alpha(Z\alpha)^6$ corrections of the wave function of relative

order $(Z\alpha)^2$ have to be included as well. This matrix element has been evaluated in Ref. [47] for general states with $\ell \geq 2$ based upon results in Ref. [48] to be

$$\begin{aligned}\Delta E^1_{H,0}(n\ell_j) = &-\frac{\alpha}{\pi}\frac{(Z\alpha)^4\, m_e}{n^3}\frac{1}{2\kappa\,(2\ell+1)} \\ &+\frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left(-\frac{12\kappa^2-1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2}\right. \\ &\left.-\frac{1}{n}\frac{3}{4\kappa^2\,(2\kappa+1)}+\frac{1}{n^2}\frac{8\kappa-3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)}\right).\end{aligned} \tag{570}$$

The first part is actually of order $\alpha(Z\alpha)^4$ and part of the magnetic moment anomaly of the electron, which contributes to the self-energy in basically all orders of α but every time in order $(Z\alpha)^4$ in the nonrelativistic expansion.

The contribution from the first order term of the expansion of $F_2(\nabla^2)$ is

$$\Delta E^1_{H,1}(n\ell_j) = \left\langle \psi^+ \right| F_2'(0)\nabla^2 \frac{e}{2m_e} \mathrm{i}\vec{\gamma}\cdot\vec{E}\left|\psi\right\rangle . \tag{571}$$

Because this is already of order $\alpha(Z\alpha)^6$, it can be evaluated on the nonrelativistic wave function. For higher excited states though this correction vanishes. The reason lies in the fact that $\nabla^2\vec{E}$ is proportional to $\vec{\nabla}\delta(\vec{x})$ which evaluated on the nonrelativistic wave function is zero for states with $\ell \geq 2$.

Thus, there is only one contribution from the one-vertex part.

7.3.2. Two-Vertex Contribution. For this contribution in Ref. [46], a Hamiltonian has been found. There, it is given in dimensional regularization, for the infinitesimal overlapping parameter ϵ used here, the so-called photon-energy regularization, it is given in Ref. [47] as

$$H_{2v}(\epsilon) = \frac{\alpha}{\pi}\left[\frac{2}{3}\ln\left(\frac{m_e}{2\epsilon}\right)-\frac{2}{3\epsilon}+\frac{34}{45}\right]\frac{(\vec{\nabla}V)^2}{m_e^3} . \tag{572}$$

This Hamiltonian is directly of order $\alpha(Z\alpha)^6$ and can, therefore, be evaluated on the nonrelativistic wave function. Using $\nabla V = Z\alpha/r^2$ and the result in Eq. (328), the

corresponding energy shift is found to be

$$\Delta E_H^2(n\ell_j,\epsilon) = \frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right] \times \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\,. \tag{573}$$

7.3.3. Summary of Corrections in the High-Energy Part. For highly excited Rydberg states the total contribution from the high-energy part is given by the sum of the two non-vanishing terms as

$$\begin{aligned}\Delta E_H(n\ell_j,\epsilon) &= \Delta E_{H,0}^1(n\ell_j) + \Delta E_H^2(n\ell_j,\epsilon)\\ &= -\frac{\alpha}{\pi}\frac{(Z\alpha)^4\, m_e}{n^3}\frac{1}{2\kappa\,(2\ell+1)}\\ &\quad + \frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left(-\frac{12\kappa^2-1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2}\right.\\ &\quad \left. -\frac{1}{n}\frac{3}{4\kappa^2\,(2\kappa+1)} + \frac{1}{n^2}\frac{8\kappa-3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)}\right)\\ &\quad + \frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right]\\ &\quad \times \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\,.\end{aligned} \tag{574}$$

As the first term of the last equation, which is already contained in Bethe's result, is of order $\alpha(Z\alpha)^4$, the high-energy part of the self-energy correction of order $\alpha(Z\alpha)^6$ is found to be

$$\begin{aligned}\Delta E_{H,(Z\alpha)^6}(n\ell_j,\epsilon) &= \frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left(-\frac{12\kappa^2-1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2}\right.\\ &\quad \left. -\frac{1}{n}\frac{3}{4\kappa^2\,(2\kappa+1)} + \frac{1}{n^2}\frac{8\kappa-3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)}\right)\\ &\quad + \frac{\alpha}{\pi}\frac{(Z\alpha)^6\, m_e}{n^3}\left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right]\\ &\quad \times \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\,.\end{aligned} \tag{575}$$

Due to common scaling of the corrections, the corrections are generally expressed in terms of the scaled self-energy function F, as was already done in Secs. 3 and 4. The

high-energy part of this function is given by

$$\Delta E_H(n\ell_j,\epsilon) = \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3} F_H(n\ell_j, Z\alpha, \epsilon)\,. \tag{576}$$

Consequently, for highly excited Rydberg states F_H is

$$\begin{aligned} F_H(n\ell_j, Z\alpha, \epsilon) = \frac{1}{2\kappa\,(2\ell+1)} + (Z\alpha)^2 \Bigg(& -\frac{12\kappa^2-1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2} \\ & - \frac{1}{n}\,\frac{3}{4\kappa^2\,(2\kappa+1)} + \frac{1}{n^2}\,\frac{8\kappa-3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)} \\ & + \left[\ln\left(\frac{m_e}{2\epsilon}\right) - \frac{1}{\epsilon} + \frac{17}{15}\right] \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})} \Bigg)\,. \end{aligned} \tag{577}$$

7.4. RESULTS

The complete self-energy correction can be obtained by adding the low- and the high-energy part. As explained in Sec. 4, the terms, which are dependent on the overlapping parameter ϵ, exactly cancel each other in this matching procedure (see Eq. (332)). The results for both parts from Eqs. (566) and (574) for highly excited Rydberg states lead to

$$\begin{aligned} \Delta E(n\ell_j) &= \Delta E_L(n\ell_j,\epsilon) + \Delta E_H(n\ell_j,\epsilon) \\ &= \frac{\alpha}{\pi}\frac{(Z\alpha)^4 m_e}{n^3} F(n\ell_j, Z\alpha) \end{aligned} \tag{578}$$

with the scaled self-energy function F, defined in Secs. 3 and 4, which for these states is given as the sum of its low- and high-energy part as

$$\begin{aligned} F(n\ell_j, Z\alpha) &= F_L(n\ell_j, Z\alpha, \epsilon) + F_H(n\ell_j, Z\alpha, \epsilon) \\ &= -\frac{1}{2\kappa\,(2\ell+1)} - \frac{4}{3}\ln k_0 + (Z\alpha)^2 \Bigg\{ \left[\ln\left(\frac{1}{2(Z\alpha)^2}\right) + \frac{17}{15}\right] \\ &\quad \times \frac{3n^2-\ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})} \\ &\quad - \frac{12\kappa^2-1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2} - \frac{1}{n}\,\frac{3}{4\kappa^2\,(2\kappa+1)} \\ &\quad + \frac{1}{n^2}\,\frac{8\kappa-3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)} + \beta_{\mathrm{SE}}(n\ell_j) \Bigg\}\,. \end{aligned} \tag{579}$$

In the common QED notation, F is usually written as

$$\begin{aligned} F(n\ell_j, Z\alpha) &= A_{41}(n\ell_j)\ln\left[(Z\alpha)^{-2}\right] + A_{40}(n\ell_j) + (Z\alpha)A_{50}(n\ell_j) + (Z\alpha)^2 \\ &\times \left\{A_{62}(n\ell_j)\ln^2\left[(Z\alpha)^{-2}\right] + A_{61}(n\ell_j)\ln\left[(Z\alpha)^{-2}\right] + A_{60}(n\ell_j) + \right\} + \ldots . \end{aligned} \tag{580}$$

The letter denotes the order in α and A thus is order α. Within the $Z\alpha$ expansion the first subscript denotes the order in $Z\alpha$, and the second the power of the logarithm $\ln[(Z\alpha)^{-2}]$ which goes with this coefficient. In this way the coefficients can be identified for highly excited Rydberg states with $\ell \geq 2$ as

$$A_{40}(n\ell_j) = -\frac{1}{2\kappa\,(2\ell+1)} - \frac{4}{3}\ln k_0(n,\ell)\,, \tag{581}$$

$$A_{61}(n\ell_j) = \frac{3n^2 - \ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})} \tag{582}$$

and

$$\begin{aligned} A_{60}(n\ell_j) = {} & \frac{3n^2 - \ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}\left\{\frac{17}{15} - \ln(2)\right\} + \beta_{\rm SE}(n\ell_j) \\ & - \frac{12\kappa^2 - 1}{2\,(2j+1)\,\kappa^2\,(2\kappa-1)\,(2\kappa+1)^2} \\ & - \frac{1}{n}\,\frac{3}{4\kappa^2\,(2\kappa+1)} + \frac{1}{n^2}\,\frac{8\kappa - 3}{2\,(2j+1)\,(2\kappa-1)\,(2\kappa+1)}\,, \end{aligned} \tag{583}$$

while all other explicitly written coefficients vanish. Higher-order terms denoted as ellipsis are so far unknown.

Numerical Results for the A_{60} coefficient for highly excited Rydberg states based upon the results for the relativistic Bethe logarithm $\beta_{\rm SE}$ obtained with the numerical lattice method and presented here in Table 7.1, are given in Table 7.2. These results have been published in Refs. [83–85]. Their application for predictions of transition frequencies in one-electron ions is explained in the next section.

Table 7.2. Values obtained for the A_{60} coefficient in Eq. (583) with the values for $\beta_{\rm SE}$ from Table 7.1. The numbers in parentheses are standard uncertainties in the last figure.

n	ℓ	$2j$	κ	A_{60}	$2j$	κ	A_{60}
16	15	29	15	$0.121\,749(5) \times 10^{-5}$	31	-16	$1.059\,674(5) \times 10^{-5}$
16	14	27	14	$0.155\,786(5) \times 10^{-5}$	29	-15	$0.540\,181(5) \times 10^{-5}$
15	14	27	14	$0.189\,309(5) \times 10^{-5}$	29	-15	$1.420\,631(5) \times 10^{-5}$
15	13	25	13	$0.252\,108(5) \times 10^{-5}$	27	-14	$2.116\,050(5) \times 10^{-5}$
14	13	25	13	$0.296\,641(5) \times 10^{-5}$	27	-14	$1.945\,279(5) \times 10^{-5}$
14	12	23	12	$0.410\,825(5) \times 10^{-5}$	25	-13	$2.979\,937(5) \times 10^{-5}$
13	12	23	12	$0.469\,973(5) \times 10^{-5}$	25	-13	$2.729\,475(5) \times 10^{-5}$
13	11	21	11	$0.679\,575(5) \times 10^{-5}$	23	-12	$4.318\,998(5) \times 10^{-5}$
12	11	21	11	$0.759\,620(5) \times 10^{-5}$	23	-12	$3.940\,256(5) \times 10^{-5}$
12	10	19	10	$1.019\,187(5) \times 10^{-5}$	21	-11	$6.331\,080(5) \times 10^{-5}$
11	10	19	10	$1.259\,580(5) \times 10^{-5}$	21	-11	$5.882\,197(5) \times 10^{-5}$
11	9	17	9	$2.008\,438(5) \times 10^{-5}$	19	-10	$10.111\,871(5) \times 10^{-5}$
10	9	17	9	$2.158\,923(5) \times 10^{-5}$	19	-10	$9.141\,150(5) \times 10^{-5}$
10	8	15	8	$3.655\,111(5) \times 10^{-5}$	17	- 9	$16.589\,245(5) \times 10^{-5}$
9	8	15	8	$3.860\,349(5) \times 10^{-5}$	17	- 9	$14.918\,400(5) \times 10^{-5}$
9	7	13	7	$7.018\,373(5) \times 10^{-5}$	15	- 8	$28.939\,225(5) \times 10^{-5}$
8	7	13	7	$7.286\,141(5) \times 10^{-5}$	15	- 8	$25.876\,638(5) \times 10^{-5}$
8	6	11	6	$14.449\,671(5) \times 10^{-5}$	13	- 7	$54.593\,341(5) \times 10^{-5}$
7	6	11	6	$14.743\,922(5) \times 10^{-5}$	13	- 7	$48.518\,597(5) \times 10^{-5}$
7	5	9	5	$32.590\,282(5) \times 10^{-5}$	11	- 6	$114.160\,310(5) \times 10^{-5}$
6	5	9	5	$32.667\,627(5) \times 10^{-5}$	11	- 6	$100.820\,108(5) \times 10^{-5}$
6	4	7	4	$82.746\,781(5) \times 10^{-5}$	9	- 5	$274.825\,060(5) \times 10^{-5}$
5	4	7	4	$81.441\,471(5) \times 10^{-5}$	9	- 5	$241.292\,908(5) \times 10^{-5}$
5	3	5	3	$240.315\,141(5) \times 10^{-5}$	7	- 4	$808.701\,545(5) \times 10^{-5}$

7.5. IMPACT OF THE QED RESULTS

7.5.1. Overview of Corrections. In the previous sections the energy shift due to the self-energy was given in terms of the scaled function F (see Eqs. (157) and (331)). When switching to SI units this relation is given by

$$\Delta E(n\ell_j) = 2hR_\infty c \frac{\alpha}{\pi} \frac{Z^4\alpha^2}{n^3} F(n\ell_j, Z\alpha)\,, \tag{584}$$

where c is the speed of light, h Planck's constant and $R_\infty = \alpha^2 m_e c/2h$ the Rydberg constant. Here, the states are denoted in the spectroscopic notation $n\ell_j$. The scaled self-energy function is commonly expanded into a semi-analytic series in $Z\alpha$ whose general from is [22, 84, 86]

$$\begin{aligned} F(n\ell_j, Z\alpha) &= A_{41}(n\ell_j) \ln\left[(Z\alpha)^{-2}\right] + A_{40}(n\ell_j) + (Z\alpha) A_{50}(n\ell_j) \\ &\quad + (Z\alpha)^2 \left\{A_{62}(n\ell_j) \ln^2\left[(Z\alpha)^{-2}\right] + A_{61}(n\ell_j) \ln\left[(Z\alpha)^{-2}\right] + G_{\mathrm{SE}}(n\ell_j, Z\alpha)\right\} \\ &\quad + \frac{\alpha}{\pi}\left[B_{40} + \ldots\right] + \left(\frac{\alpha}{\pi}\right)^2 \left[C_{40} + \ldots\right] + \ldots\,. \end{aligned} \tag{585}$$

The A coefficients arise from the one-photon QED corrections, while the B and C coefficients are due to two- and three-photon corrections respectively. The first of subscript numbers gives the power in $Z\alpha$ and the second denotes the power of the logarithm $\ln\left[(Z\alpha)^{-2}\right]$. G_{SE} is the one-photon QED self-energy remainder function. Comparing this general expression to the result of Sec. 4, it becomes clear that a lot of these term vanish for the highly excited states considered in this work. Indeed, the overview over the general expressions which can be found in Refs. [22, 86] confirms this and for $\ell \geq 2$ the expression takes the simpler form

$$\begin{aligned} F(n\ell_j, Z\alpha) &= A_{40}(n\ell_j) + (Z\alpha)^2 \left\{A_{61}(n\ell_j) \ln\left[(Z\alpha)^{-2}\right] + G_{\mathrm{SE}}(n\ell_j, Z\alpha)\right\} \\ &\quad + \frac{\alpha}{\pi}\left[B_{40} + \ldots\right] + \left(\frac{\alpha}{\pi}\right)^2 \left[C_{40} + \ldots\right] + \ldots\,. \end{aligned} \tag{586}$$

At the end of Sec. 4, the A_{61} coefficient is already stated for the states considered in Eq. (328) to be

$$\begin{aligned} A_{61}(n\ell_j) &= \frac{3n^2 - \ell(\ell+1)}{3n^2\,(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})} \\ &= \frac{32}{3}\frac{3n^2-\ell(\ell+1)}{n^2}\frac{(2\ell-2)!}{(2\ell+3)!}\,. \end{aligned} \tag{587}$$

The leading term of Eq. (332), is identified as the A_{40} coefficient in Eq. (581), which is

$$A_{40}(n\ell_j) = -\frac{1}{2\kappa\,(2\ell+1)} - \frac{4}{3}\ln k_0(n,\ell)\,, \tag{588}$$

with the Dirac quantum number $\kappa = (-1)^{j-\ell+1/2}(j+\frac{1}{2})$. The source of first term in the above equation is in fact the one-photon contribution from the magnetic moment anomaly of the electron $a_e = (g-2)/2$. The contributions from the two- and three-photon level to this electric moment anomaly are known [87] and thus all known terms of F lead to

$$\begin{aligned} F(n\ell_j, Z\alpha) = &-\frac{a_e}{\kappa(2\ell+1)}\frac{\pi}{\alpha} - \frac{4}{3}\ln k_0(n,\ell) + \frac{32}{3}\frac{3n^2-\ell(\ell+1)}{n^2} \\ &\times \frac{(2\ell-2)!}{(2\ell+3)!}(Z\alpha)^2\ln\left[(Z\alpha)^{-2}\right] + (Z\alpha)^2\,G_{\mathrm{SE}}(n\ell_j, Z\alpha)\,. \end{aligned} \tag{589}$$

The self-energy remainder function G_{SE} can be calculated by either the fully relativistic numerical method described in Sec. 3 or by the analytic expansion in $Z\alpha$ described in Sec. 4.

For the fully relativistic numerical evaluation the complete one-photon, self-energy function G_{SE} is considered. Its calculation follows the methods outlined in Sec. 3. For higher excited states only the extraction procedure of lower order terms also includes term of order $(Z\alpha)^4$, i.e the nonrelativistic result is extracted with the spurious lower order terms. This slightly different procedure to the one described here, which allows for results even for low Z, is explained in Ref. [86]. The problems which have to be faced in order to obtain results for highly excited states and how they have been overcome are detailed in Ref. [88].

For the method of Sec. 4, a nonrelativistic expansion of G_{SE} is carried out. Again, the nonrelativistic expansion is given by the semi-analytic expansion in $Z\alpha$ and it is here

$$G_{\mathrm{SE}}(n\ell_j, Z\alpha) = A_{60}(n\ell_j) + (Z\alpha)^2 \left\{ A_{81}(n\ell_j) \ln\left[(Z\alpha)^{-2}\right] + A_{80}(n\ell_j) + \ldots \right\} . \quad (590)$$

From a comparison to Eq. (332) the A_{60} coefficient can be found to be

$$A_{60}(n\ell_j) = \Xi(n\ell_j) + A_{61}(n\ell_j) \left\{ \frac{17}{15} - \ln(2) \right\} + \beta_{\mathrm{SE}}(n\ell_j) , \quad (591)$$

with $\Xi(n\ell_j)$ defined in Eq. (326) and the relativistic Bethe logarithm $\beta_{\mathrm{SE}}(n\ell_j)$. While for the most terms of A_{60} general expression for arbitrary states are known, the relativistic Bethe logarithm β_{SE} has to be determined numerically with the numerical lattice method, based on Ref. [78] and detailed in Ref. [42], for every state under study.

Of the higher order terms, only for B_{60} calculations exist for states with $\ell \leq 5$ [89] and the vacuum polarization contribution to A_{80} is known which is given in Ref. [90] and is extremely small. All other terms are unknown. Based on the trend exhibited for highly excited states compared to lower lying states, the magnitude of the QED correction decreases with higher principal quantum number n and orbital angular momentum ℓ, which for example can be seen from the values of A_{60} in Table 7.2. Therefore it becomes possible to neglect the unknown higher order terms in G_{SE} and approximate it by its value for $(Z\alpha) \to 0$ which is

$$\lim_{Z\alpha \to 0} G_{\mathrm{SE}}(n\ell_j, Z\alpha) = A_{60}(n\ell_j) . \quad (592)$$

In general, this definition is used to compare the results obtained with the methods of Secs. 3 and 4. For this, G_{SE} is evaluated with the fully relativistic, numerical method for different values of Z and the results are extrapolated to $Z = 0$. The value extrapolated from the numerical method should then agree with the A_{60} coefficient obtained through the $Z\alpha$ expansion. Such an analysis is for example carried out and described in Ref. [86].

Due to the described trend for highly excited Rydberg states the results of both methods can basically be compared directly because it is assumed that the higher order corrections are very small. Indeed, a comparison of the A_{60} coefficients, which are obtained for Rydberg states and presented in Ref. [83], and a nonperturbative (in $Z\alpha$) calculation of G_{SE}, with the results given in Ref. [88], shows a excellent agreement of both values even for rather high nuclear charge numbers Z up to $Z = 16$. In this way errors, which cannot be excluded in such complicated computations otherwise, seem rather unlikely because the results are checked in a highly nontrivial way. It is important to note that numerical calculations for highly excited Rydberg states constitute a highly complicated task. Moreover, an additional comparison for the lower Rydberg states in Ref. [85] shows a very good agreement of both values. In fact, the deviation $|G_{\mathrm{SE}}(Z\alpha) - A_{60}|$ numerically is less than 10^{-4} for all states and all nuclear charge numbers considered therein.

Therefore, for the states considered in this work the scaled self-energy function F can be written as

$$\begin{aligned} F(n\ell_j, Z\alpha) = &-\frac{a_e}{\kappa(2\ell+1)}\frac{\pi}{\alpha} - \frac{4}{3}\ln k_0(n,\ell) + \frac{32}{3}\frac{3n^2-\ell(\ell+1)}{n^2} \\ &\times \frac{(2\ell-2)!}{(2\ell+3)!}(Z\alpha)^2 \ln\left[(Z\alpha)^{-2}\right] + (Z\alpha)^2 A_{60}(n\ell_j) + \dots , \end{aligned} \tag{593}$$

where the dots denote the contributions from higher loop orders.

Hence, the energy shift due to QED radiative effects of a state with $\ell \geq 2$ can be formulated by plugging this into Eq. (584) which leads to

$$\begin{aligned} \Delta E(n\ell_j) = 2hR_\infty c\frac{Z^4\alpha^2}{n^3}\Bigg\{ &-\frac{a_e}{\kappa(2\ell+1)} - \frac{\alpha}{\pi}\Bigg[\frac{4}{3}\ln k_0(n,\ell) + \frac{32}{3}\frac{3n^2-\ell(\ell+1)}{n^2} \\ &\times \frac{(2\ell-2)!}{(2\ell+3)!}(Z\alpha)^2 \ln\left[(Z\alpha)^{-2}\right] + (Z\alpha)^2 A_{60}(n\ell_j)\Bigg]\Bigg\} + \dots . \end{aligned} \tag{594}$$

One may now ask why in Sec. 3 the effort is undertaken to describe the fully relativistic QED theory, which allows to evaluate G_{SE}, while it is not used here. The reason is that it not only helps to understand the efforts and techniques involved in the determination of G_{SE} to allow for such a comparison, but also illustrates many of the challenges in QED for bound states. It also provides the reasons and incentive

for the development of the nonrelativistic formalism. Indeed, as explained in Sec. 4, the nonrelativistic theory is directly based upon the nonrelativistic expansion of the fully relativistic expression.

In addition, Sec. 3 illustratively and thoroughly describes the formal separation of the integral into the two parts using a deformation of the integration contour. For the nonrelativistic theory in Sec. 4 just the separation point is the infinitesimal ϵ instead of E_n. This then enables the nonrelativistic expansion in the low-energy part. As shown in the model example in Sec. 5, with the infinitesimal overlapping parameter, no spurious lower order terms, which are present in the fully relativistic method, arise. These lower-order remainder terms are the reason, why the fully relativistic method requires demanding high precision calculations because, as seen in the model in Sec. 5, they induce a severe loss of numerical precision. This loss is especially prevalent for low Z.

The region of low nuclear charge number Z is where the nonrelativistic formalism particularly excels because it is an expansion in $Z\alpha$, which is small in this region. With results also available for low Z from the fully relativistic formalism, the theory can be cross checked in a highly nontrivial way and shows outstanding agreement of both approaches. In addition, the overview over both methods allows to appreciate the clarity of the nonrelativistic formalism as well as its illustrative power to provide a more accessible physical origin of the correction terms.

So far, the expressions are given in the non recoil limit, where the nuclear mass is assumed to be infinite, in order to simplify the calculations. The effects from a finite nuclear mass can be included into the QED radiative level shift by use of the reduced mass

$$m_r = \frac{m_e}{1 + r(\mathcal{N})} \tag{595}$$

with the electron to nucleus mass ratio $r(\mathcal{N}) = m_e/m_N(\mathcal{N})$ and the mass of the nucleus $m_N(\mathcal{N})$, instead of the electron mass m_e. In writing $m_N(\mathcal{N})$, the subscript N is used in order to denote the nuclear mass, and the argument $\mathcal{N}$ is reserved in order to differentiate a specific nucleus under investigation. Thereby the notation used in Ref. [85] is adopted.

Experimentally, transition frequencies for a transition between different levels are measured. This transition frequency is related to the energy of the levels by

$$\nu_{1\leftrightarrow 2} = \frac{1}{h}\left(E_2 - E_1\right) \tag{596}$$

for a transition between quantum states $|1\rangle$ and $|2\rangle$, where h is Planck's constant. This is used here to define the bound-state energy as a bound-state frequency

$$\nu_i = E_i/h \tag{597}$$

which means

$$\nu_{1\leftrightarrow 2} = \nu_2 - \nu_1\,. \tag{598}$$

In this way, the energy shift due to QED radiative correction can be reformulated into a frequency. Out of Eq. (594) it is obtained with the inclusion of the reduced mass effects for the highly excited states under investigation to be

$$\begin{aligned}\nu_{\mathrm{QED}}(n\ell_j) = \frac{R_\infty c}{1+r(\mathcal{N})}\frac{2Z^4\alpha^2}{n^3}\Bigg\{&-\frac{1}{1+r(\mathcal{N})}\frac{a_e}{\kappa(2\ell+1)} + \frac{1}{[1+r(\mathcal{N})]^2}\\ &\times\frac{\alpha}{\pi}\Bigg[-\frac{4}{3}\ln k_0(n,\ell) + \frac{32}{3}\frac{3n^2-\ell(\ell+1)}{n^2}\frac{(2\ell-2)!}{(2\ell+3)!}\\ &\times(Z\alpha)^2\ln\left(\frac{1+r(\mathcal{N})}{(Z\alpha)^2}\right) + (Z\alpha)^2 A_{60}(n\ell_j)\Bigg]\Bigg\} + \ldots\,.\end{aligned} \tag{599}$$

However, with the inclusion of effects from finite nuclear mass also the non recoil limit was dropped. In turn, this implies that recoil effects have to be considered and for a accurate prediction of transition frequencies of one-electron atoms more corrections arise. Now, these other necessary contribution of the transition frequency between atomic states will be discussed. A more detailed overview over these terms and their derivation and concerning references can be found in Refs. [22,83,84,91,92].

The by far largest term is evidently the contribution from the Dirac energy, which here is expressed as a Dirac frequency ν_D. With the rest mass subtracted and

corrections from the nuclear motion included it is commonly given as

$$\nu_D = \frac{R_\infty c}{1+r(\mathcal{N})} 2\left\{ f(n,j) - 1 - \frac{r(\mathcal{N})\,\alpha^2}{2\,[1+r(\mathcal{N})]^2}\,[f(n,j)-1]^2 \right\}, \tag{600}$$

with the function $f(n,j)$ given as

$$f(n,j) = \left[1 + \frac{(Z\alpha)^2}{\left(n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - (Z\alpha)^2}\right)^2} \right]^{-\frac{1}{2}}. \tag{601}$$

The next term arises for finite nuclear mass from the two-body Breit-Hamiltonian, it is called the Barker-Glover term [93] and is

$$\nu_{\mathrm{BG}} = \frac{R_\infty c}{1+r(\mathcal{N})} \frac{r(\mathcal{N})^2 Z^4 \alpha^2}{n^3\,[1+r(\mathcal{N})]^2} \left(\frac{1}{j+\frac{1}{2}} - \frac{1}{\ell+\frac{1}{2}} \right) (1-\delta_{\ell 0})\,. \tag{602}$$

The final contribution is then from relativistic recoil corrections which lead to a change of the frequency for states with $\ell \geq 2$ by [94–97]

$$\begin{aligned} \nu_{\mathrm{RR}} = \frac{R_\infty c}{1+r(\mathcal{N})} \frac{2\,r(\mathcal{N})\,Z^5\alpha^3}{\pi n^3} \Bigg\{ & \frac{1}{[1+r(\mathcal{N})]^2} \left[-\frac{8}{3} \ln k_0(n,\ell) \right. \\ & \left. - \frac{7}{3} \frac{1}{\ell(\ell+1)(2\ell+1)} \right] + \pi Z\alpha\,[1+r(\mathcal{N})] \\ & \times \left[3 - \frac{\ell(\ell+1)}{n^2} \frac{2}{(4l^2-1)(2\ell+3)} \right] + \ldots \Bigg\}, \end{aligned} \tag{603}$$

where $\ln k_0$ again is the (nonrelativistic) Bethe logarithm that depends on n and ℓ. The ellipses at the end, stand for the unknown terms of higher order.

If the nucleus has a non zero spin, this spin can couple to the total angular momentum of the electron. This cause the hyperfine structure of the electron levels. The corresponding frequency for the hyperfine splitting can be found from Ref. [98]

to be

$$\begin{aligned}\nu_{\rm hfs} = & \frac{R_\infty c}{1+r(\mathcal{N})}\frac{Z^3\alpha^2}{n^3}\frac{r(\mathcal{N})}{1+r(\mathcal{N})}\frac{\kappa}{|\kappa|} \\ & \times \frac{g_N}{(2\kappa+1)(\kappa^2-\frac{1}{4})}\left[f(f+1)-I(I+1)-j(j+1)\right] \\ & \times n^3|\kappa|(2\kappa+1)\frac{2\kappa(\gamma+n-|\kappa|)-N}{N^4\gamma(4\gamma^2-1)}\left\{1+\frac{\alpha}{\pi}\frac{1}{4\kappa}\right\},\end{aligned} \tag{604}$$

where g_N is the nuclear g factor, $\vec{f}=\vec{I}+\vec{j}$ the total angular momentum of the one-electron ion, $\gamma=\sqrt{\kappa^2-(Z\alpha)^2}$ and $N=\sqrt{(n-|\kappa|)^2+2(n-|\kappa|)\gamma+\kappa^2}$. The self-energy corrections to this result, of which the lowest order term is already included, are derived in Sec. 8. The additional self-energy corrections of relative order $(Z\alpha)^2$ can be found in Eq. (692).

This concludes the discussion of all contributions to the transition frequencies between states with $\ell \geq 2$ in one-electron atoms known so far. A comparison with similar investigations for states with lower orbital angular momentum like in Refs. [22, 86] reveals that the expression simplify considerably.

Especially, the troublesome nuclear-size correction is absent. Moreover, as already mentioned in the discussion of the QED radiative corrections, the magnitude of the contribution reduces. In turn, this increases the accuracy of the theoretical prediction which can be achieved with the known terms. The total frequency of a specific level is then the sum

$$\nu_i = \nu_{\rm D} + \nu_{\rm BG} + \nu_{\rm RR} + \nu_{\rm QED}\,. \tag{605}$$

where $i=1,2$ is defined in the spirit of Eq. (598) and $\nu_{\rm hfs}$ is assumed to have been subtracted; if necessary, the hyperfine-fine structure mixing terms can be calculated according to the approach outline in Sec. III of Ref. [99].

The most important advantage of Rydberg states is however the absence of the nuclear size correction for these states, which is negligible small. The reason lies in the fact that these states are so far away from the nucleus and the overlap with the nucleus is extremely small. In fact, the probability for a Rydberg state of an one-electron ion with principal quantum number n and orbital momentum $\ell = n-1$ to

be within a radius r within the nucleus is [84]

$$P(r) = \int_{|\vec{x}|<r} d^3x \; |\Psi(\vec{x})|^2 \approx \frac{1}{(2n+1)!} \left(\frac{2Zr}{na_0} \right)^{2n+1} , \tag{606}$$

where a_0 is the Bohr radius. If r is assumed to be the nuclear charge radius, then the high-power $(r/a_0)^{2n+1}$ together with the factorial lead to an almost complete suppression of effects from the nuclear radius for the states under investigation. Especially, in view of the recent measurement in Ref. [100] of the proton charge radius in muonic hydrogen which disagrees with the charge radius obtained in electronic hydrogen through spectroscopy [22] as well as with the proton charge radius from scattering experiments [101], this fact becomes even more important.

7.5.2. Estimate of Theoretical Uncertainties. After the overview over all relevant theoretical expressions to calculate transition frequencies between Rydberg states, it is important to investigate how accurate the predictions are which can be made with them. Otherwise, a sensible comparison between the theoretical predictions and experimental measurements is not possible.

There are, in fact, two different sources of uncertainty in the theoretical predictions. The first is due to the fundamental constants and nuclear masses required for the evaluation of the theoretical frequencies. These cannot be determined by theory from first principle but rather have to be measured in experiments and their value determined by a comparison of theory and experiment. Therefore, their values carry an uncertainty. All fundamental constants and nuclear masses, as well as their associated uncertainties, which have been employed in the calculations of the transition frequencies, are given in Table 7.3. The values of the fundamental constants have been taken from CODATA2006 [22], the values for the required nuclear masses are from the 2003 Atomic Mass Evaluation [102] (AME2003). It is important to note that the masses given therein are the atomic masses of the nucleus and the electrons. The nuclear mass is obtained by subtracting the mass of the electrons and their binding energies from the atomic mass. This procedure is explained in Ref. [103]. The values for the ionization energies are taken from Refs. [103,104]. All of the masses are given in the atomic mass unit u, in which they are more accurately known than in kg. In fact, currently there are efforts to use the atomic mass unit to define the SI unit

kilogram. Unfortunately, they have not been met with success so far and therefore the conversion factor, which is the Avogadro number N_A, still has a rather large relative uncertainty of 5.0×10^{-8}. However, because the theoretical expression for the transition frequency only depend on the mass ratio and also masses determined in Penning traps are given in the atomic mass unit, it will be used throughout this work. In order to reduce uncertainties from the theoretical determination of the electron's magnetic moment anomaly a_e, the experimentally determined value [105] is used.

Table 7.3. Fundamental constants and masses used as input parameters for the evaluation of the theoretical expression and error estimates. In parentheses, the standard uncertainty is indicated. The masses $m_A(\mathcal{N})$ correspond to the atomic mass of an atom (including the bound electrons) with nucleus $\mathcal{N}$. By contrast, the nuclear mass is denoted as $m_N(\mathcal{N})$ in this work (it excludes the mass of the bound electrons and their binding energies).

Constant	Value
$R_\infty c$	$3.289\,841\,960\,361(22) \times 10^{15}$ Hz
α	$7.297\,352\,5376(50) \times 10^{-3}$
a_e	$1.159\,652\,180\,73(28) \times 10^{-3}$
m_e	$5.485\,799\,0943(23) \times 10^{-4}$ u
$m_A(^1\mathrm{H})$	1.007 825 032 07(10) u
$m_A(^2\mathrm{H})$	2.014 101 778 040(80) u
$m_A(^4\mathrm{He})$	4.002 603 254 131(62) u
$m_A(^{20}\mathrm{Ne})$	19.992 440 1754(19) u

The other source of uncertainty for the theoretical prediction arises because higher order terms in the theoretical formulas are not known and so a prediction made from them is only accurate up to effects from these higher order terms. In order to obtain the uncertainty of the theoretical prediction, the effects from the uncalculated higher-order terms, denoted as dots in the expressions in the last section, have to be estimated. The uncertainty of the QED radiative corrections is assumed to be dominated by the B_{60} coefficient, which is not known for Rydberg states. Form a

comparison of B_{60} and A_{60} for lower lying states, B_{60} seems to be about four times larger in magnitude. Thus, $4A_{60}\alpha/\pi$ is used as the uncertainty of the QED corrections involving more photons. Because not for all transitions so far results for $G_{\rm SE}$ exist, also an uncertainty estimate for the higher order terms in $Z\alpha$ is included for safety. For this the magnitude of A_{81} is estimated as that of A_{60}, which means the associated uncertainty is estimated as $(Z\alpha)^2 \ln[(Z\alpha)^{-2}]A_{60}$. For the relativistic recoil corrections the uncertainty is estimated as $Z\alpha \ln[(Z\alpha)^{-2}]$ times the last known term. These are the estimates which are already used in Refs. [83–85]. Possible asymmetries of the line-shape have been investigated by Low in Ref. [106] and found to be of the order $\alpha(Z\alpha)^2 E_{\rm QED}$. They can be calculated with the formalism therein if required.

As an example, the theoretical prediction for transition frequency between Rydberg states is evaluated. The results for different nuclei are given in Table 7.4. In the following two subsections applications of such very accurate theoretical predictions for Rydberg states are investigated.

Table 7.4. Theoretical predictions for transition frequencies in the one-electron ion of helium and neon. The transition from the initial level $|1\rangle$ with quantum numbers $n = 15$, $\ell = 14$, and $j = 29/2$ to the level $|2\rangle$ with quantum numbers $n = 16$, $\ell = 15$, and $j = 31/2$ is considered. The individual contributions are listed in Eq. (605).

Term	^{4}He$^+$ ν(THz)	^{20}He^{9+} ν(THz)
ν_D	7.081 331 011 067 13(4736)	177.054 575 479 0197(11840)
$\nu_{\rm BG}$	0.000 000 000 000 01	0.000 000 000 0002
$\nu_{\rm RR}$	0.000 000 000 000 11	0.000 000 000 0625
$\nu_{\rm QED}$	−0.000 000 001 261 66	− 0.000 000 788 808 8
Total	7.081 331 009 805 59(4736)	177.054 574 690 2737(11840)

7.5.3. Rydberg States and the Rydberg Constant. While the $1S$–$2S$ transition in hydrogen has been measured with the astonishing relative accuracy of 1.4×10^{-14} [9], the Rydberg constant is only known with a relative accuracy of 6.6×10^{-12} [22]. This is due to theoretical uncertainties from the nuclear size

correction. Though the measurement of the transition frequency can be used to deduce a value for the root mean squared (RMS) charge radius of the proton, the uncertainty of other measurements of this charge radius do not allow a deduction of a more accurate value for the Rydberg constant.

As stated before, highly excited Rydberg states are now basically independent of the nuclear size. Thereby, a problematic theoretical uncertainty can be avoided. The second discussed advantage of Rydberg states, is the reduction of the magnitude of QED and other corrections. For example the A_{60} coefficient for the Rydberg states, which are considered in Ref. [83], is about a factor 10^{-6} times smaller than the A_{60} coefficient for the $2S$ state. Moreover as evident from the comparison carried out in Ref. [88] the A_{60} coefficient accounts for bulk of the one-photon QED corrections in Rydberg states. This is not the case for S states which can be seen from the values for G_{SE} and A_{60} given in Ref. [22]. Also, in the two-photon self-energy some of the known terms have been shown to vanish for Rydberg states. All of this makes Rydberg states very attractive for a determination of the Rydberg constant, from a theoretical point of view. Apart from the Rydberg constant which limits the accuracy of the theoretical prediction, all other uncertainties appear to be on or even below the level of accuracy as in the seminal measurements of the $1S$–$2S$ transition in hydrogen in Ref. [9].

In Table 7.4 transition frequencies between the highest-j states with $n = 15$ and $n = 16$ in the one-electron ion of helium and neon have been calculated using the formulas in Eqs. (599),(600),(602),(603) and the fundamental constants in Table 7.3. Because the nuclei considered have zero nuclear spin, no hyperfine structure corrections are necessary. The sources of uncertainties and an estimate of their size based upon the discussion in Sec. 7.5.2 are given in Table 7.5 for the transition frequencies from Table 7.4. As evident form Table 7.5 the highest uncertainty arise from the Rydberg constant. Assuming the theory is correct, a comparison of an experimental measurement for the transition frequency with an accuracy higher than the accuracy of the Rydberg constant, can thus be used in order to deduce a more accurate value for the Rydberg constant. Because the uncertainty of the electron to nucleus mass ration can be a limiting factor, it is important to carry out the measurement in systems with a well known nuclear mass.

Experimentally, transition frequencies between Rydberg states of hydrogen have been measured in an 80 K atomic beam in the millimeter region [107]. Though the achieved accuracy of 2.1×10^{-11} [107, 108] is not enough to reduce the uncertainty of the Rydberg constant, it shows the feasibility of high-precision spectroscopy in Rydberg states. In lower-lying states the unprecedented precision in the measurements become possible with the advent of optical frequency combs [109], which can, in principle, provide relative frequency measurements with uncertainties approaching 10^{19} over 100 THz of bandwidth [110]. Considering recent advances in the accuracy of frequency standards [111], a further increase of spectroscopical precision over even today's impressive level [9], could be possible. Efforts are currently underway at NIST [83,84,88] to measure transitions between Rydberg states with optical frequency combs.

Table 7.5. Sources and estimated relative standard uncertainties in the theoretical value of the transition frequency between the highest-j states with $n = 15$ and $n = 16$ in hydrogen-like helium and hydrogen-like neon.

Source	He^+	Ne^{9+}
Rydberg constant	6.6×10^{-12}	6.6×10^{-12}
Fine-structure constant	6.1×10^{-16}	1.5×10^{-14}
Electron-nucleus mass ratio	5.8×10^{-14}	1.2×10^{-14}
a_e	4.2×10^{-20}	1.0×10^{-18}
Theory	1.6×10^{-17}	2.7×10^{-14}

For an interrogation with optical frequency combs circular Rydberg states in one-electron ions with a low nuclear charge number Z seem to most favorable. Perturbations from the laser field and other sources are smaller for heavier ions with a larger Z, though. In general, a large variety of measurements in ions with different Z and for many different transitions could be useful for experimental optimization and internal consistency checks. Achieving a relative uncertainty smaller than the relative uncertainty of the Rydberg constant in the experimental measurements of

the transition frequency, a comparison of theory and experiment could thus allow to determine a more accurate value for the Rydberg constant.

A more accurate value for the Rydberg constant is not only interesting for a deeper understanding of fundamental constants in general but can also help to clear up the current problem of disagreeing values for the RMS charge radius of the proton. If the measurements can be reproduced and conceivable errors ruled out, using the RMS charge radius determined in muonic hydrogen would require to alter the Rydberg constant to keep the frequency predictions in hydrogen in agreement. A measurement of the Rydberg constant in a system, which is independent of nuclear size effects, is therefore very desirable to uncover the source of the disagreement. A Rydberg constant determined in such a way would thus be free of any possible mixing of QED and nuclear effects, which might be contained in the Rydberg constant determined in lower-lying states. Moreover, the exact magnitude of the non QED effects i.e. nuclear size or possible other effects can be quantified.

The investigation provided that nuclear masses can be a limiting factor in highly precise theoretical predictions for Rydberg states. This opens up the possibility to envision the determination of electron to nucleus mass ratios and nuclear masses, which will be studied in the next section.

7.5.4. Rydberg States and the Nuclear Masses. Due to the unprecedented precision of measurements of transition frequencies, which can reached with optical frequency combs, and the very accurate theoretical predictions, which can be made for Rydberg states, they are interesting for more than the determination of the Rydberg constant. For such a possible determination of the Rydberg constant in highly excited states, atoms with a well known nuclear mass are most interesting because the electron to nucleus mass ratio can constitute a large portion of the theoretical uncertainty. In one-electron ions, where the nuclear mass has a large uncertainty, this uncertainty could prohibit to deduce a more accurate value for the Rydberg constant. In such an ion, though, a comparison of highly precise experimental frequency measurements and the theoretical prediction can be used to deduce a more accurate value for the nuclear mass. While the possibility of a determination of nuclear mass with high-precision spectroscopy has been investigated for molecules in Ref. [112, 113], the described simplifications for Rydberg states, make them appear

more attractive for such efforts. Therefore, the possible determination of nuclear mass with high-precision spectroscopy in highly excited Rydberg states of one-electron ions is investigated here, based on our analysis in Ref. [85].

Now the question is how can the masses be determined with high-precision spectroscopy. For this purpose it is instructive to recall the expression for the frequencies of Rydberg states in Eqs. (599), (600), (602), and (603). It can be observed that all frequencies are directly proportional to the Rydberg constant but even to rather high accuracy ($\sim 10^{-14}$) they are also nearly proportional to $(1 + r(\mathcal{N}))^{-1}$. This dependence on the electron to nucleus mass ratio and therefore on the nuclear mass, allows the determination of the nuclear mass from the transition frequency.

In principle, there are now two methods to do that. For the first method (*method I*) isotopes of a given charge number Z are considered. The transition frequencies of one specific transition is only different between the isotopes because of the different nuclear masses. If one isotope has a very well determined mass, its mass can be used as a reference. This nucleus is denoted as $\mathcal{N}_R$ and its mass as $m_N(\mathcal{N}_R)$. The other isotope, whose mass $m_N(\mathcal{N}_M)$ is to be determined, is denoted as $\mathcal{N}_M$. A specific transition frequency is then measured in the reference isotope, which is denoted as $\nu^R_{1\leftrightarrow 2}$. The same transition is also measured in the isotope, whose mass is to be determined, which gives the frequency $\nu^M_{1\leftrightarrow 2}$. The measured frequencies can then be written as equations by using the experimental value as the left-hand side in Eq. (605) and the theoretical expression as the right-hand side. The resulting system of two equations can be solved for two variables, namely the Rydberg constant and the unknown nuclear mass $m_N(\mathcal{N}_M)$. The general idea behind it is that the Rydberg constant currently is the biggest source of uncertainty and the current uncertainty is not enough to enable accurate mass determinations. This point was elucidated in the discussion of Tables 7.4 and 7.5. With the isotope shift, this problem can be avoided because the Rydberg constant can be eliminated in the system of two equations.

For the next method in principle again two frequencies have to be measured, one in a system with a well-known reference mass and one in a the system, whose mass is to be determined. The first resulting equation in the system with the well-known mass is solved for the Rydberg constant. This is plugged into the second equation, which is then solved for the unknown mass. Hence, the first measurement is in

fact a determination of the Rydberg constant. As discussed in Sec. 7.5.3 efforts are undertaken at NIST to deduce a improved value for the Rydberg constant in Rydberg states. There is also an experiment at the National Physics Laboratory (NPL) in the United Kingdom, where the $2S$-$8D$ transition in hydrogen is investigated with the aim of determining the Rydberg constant [114]. Should these efforts be crowned with success and the uncertainty of the Rydberg constant be reduced significantly to a relative accuracy between $10^{-13} \ldots 10^{-14}$, using the frequency in the reference system to solve for the Rydberg constant is no longer necessary. Thus, a transition frequency $\nu^{M}_{1\leftrightarrow 2}$ measured in an one-electron ion with an inaccurately known nuclear mass can directly be compared to the theoretical value and the mass $m_N(\mathcal{N}_M)$ determined by solving for it. This is known as *method II* in this work. Alternatively, the equation can be solved for the electron to nucleus mass ratio $r(\mathcal{N}_M)$ instead, this is *method III*.

After these considerations the explicit formulas for each method will be derived. As explained earlier the theoretical expressions are all directly proportional to the Rydberg constant but carry very different dependencies on the electron to nucleus mass ratio. In the Dirac value Eq. (600) for example, the first term is directly proportional to the ratio of the reduced mass to the electron mass $\mu_r/m_e = 1/(1 + r(\mathcal{N})))$, while the second is proportional to $r(\mathcal{N})(\mu_r/m_e)^3$. Despite this complicated dependence, it is possible to assume an approximate proportionality to the ratio of the reduced mass to the electron mass. Extracting these two proportionalities out of the transition frequency $\nu_{1\leftrightarrow 2}$ a scaled frequency $f_{1\leftrightarrow 2}$ can be defined by

$$\nu_{1\leftrightarrow 2} = R_\infty c \, \frac{1}{1 + r(\mathcal{N})} \, f_{1\leftrightarrow 2} \, . \tag{607}$$

Because the proportionality to $(1+r(\mathcal{N}))^{-1}$ is only approximate, the scaled frequency $f_{1\leftrightarrow 2}$, which is given by theory, still carries a residual mass dependence. Fortunately, at least for stable/long living nuclei equal in mass or heavier than lithium, if known electron to nucleus mass ratios are used for the residual dependence of $f_{1\leftrightarrow 2}$, the uncertainty introduced by this does not contribute to the uncertainty on a level required for the nuclear mass determination. With this the required formulas can now be derived.

Formulas for *method I*: one isotope with a well determined mass is required. It acts as the reference mass and accordingly, its transition frequency, mass ratio and theoretical value are labeled $\nu^R_{1\leftrightarrow 2}$, $r(\mathcal{N}_R)$, and $f^R_{1\leftrightarrow 2}$, respectively. The transition frequency, mass ratio and theoretical value, which will be labeled $\nu^M_{1\leftrightarrow 2}$, $r(\mathcal{N}_M)$, and $f^M_{1\leftrightarrow 2}$, of another isotope with a inaccurately known mass, are then determined. The mass of this isotope $m_N(\mathcal{N}_M)$ can then by expressed in terms of the reference mass $m_N(\mathcal{N}_R)$ by solving the equations

$$\nu^R_{1\leftrightarrow 2} = R_\infty c \, \frac{1}{1+r(\mathcal{N}_R)} \, f^R_{1\leftrightarrow 2} \,, \tag{608}$$

$$\nu^M_{1\leftrightarrow 2} = R_\infty c \, \frac{1}{1+r(\mathcal{N}_M)} \, f^M_{1\leftrightarrow 2} \,. \tag{609}$$

By taking the ratio of the two frequencies the Rydberg constant cancels and

$$\begin{aligned} \frac{\nu^R_{1\leftrightarrow 2}}{\nu^M_{1\leftrightarrow 2}} &= \frac{f^R_{1\leftrightarrow 2}}{f^M_{1\leftrightarrow 2}} \, \frac{1+r(\mathcal{N}_M)}{1+r(\mathcal{N}_R)} \\ &= \frac{m_N(\mathcal{N}_R) f^R_{1\leftrightarrow 2}}{m_N(\mathcal{N}_M) f^M_{1\leftrightarrow 2}} \, \frac{m_N(\mathcal{N}_M)+m_e}{m_N(\mathcal{N}_R)+m_e} \end{aligned} \tag{610}$$

is obtained. Solving for the nuclear mass $m_N(\mathcal{N}_M)$ yields

$$m_N(\mathcal{N}_M) = m_N(\mathcal{N}_R) \, m_e \left[\frac{\nu^R_{1\leftrightarrow 2} \, f^M_{1\leftrightarrow 2}}{\nu^M_{1\leftrightarrow 2} \, f^R_{1\leftrightarrow 2}} \, (m_N(\mathcal{N}_R)+m_e) - m_N(\mathcal{N}_R) \right]^{-1} . \tag{611}$$

This allows us to determine the nuclear mass of one isotope $m_N(\mathcal{N}_M)$ from a measurement of a transition frequency $\nu^M_{1\leftrightarrow 2}$ in this isotope, and a reference transition frequency $\nu^R_{1\leftrightarrow 2}$ in an isotope with nuclear mass $m_N(\mathcal{N}_R)$.

Formulas for *method II*: For the second method it is assumed that a more precise value for the Rydberg constant is available with a relative uncertainty between $10^{-13} \ldots 10^{-14}$. This could be provided by the on-going experiments with this aim like the joint theoretical and experimental project with the National Institute of Standards and Technology (NIST), presented in Refs. [83, 84, 88]. Its details have been discussed in the previous section Sec. 7.5.3. Furthermore, there is a project at the

National Physics Laboratory (NPL) in the United Kingdom where the $2S$–$8D$ transition in hydrogen is intended to be used in order to improve the accuracy of the Rydberg constant [114].

This would provide the first frequency solved for the Rydberg constant. Thus, only the transition frequency $\nu^M_{1\leftrightarrow 2}$ in the one-electron ion, whose mass is to be determined, has to be measured. The nuclear mass $m_N(\mathcal{N}_M)$ can directly be obtained by solving Eq. (607) yielding

$$m_N(\mathcal{N}_M) = m_e \left(\frac{f^M_{1\leftrightarrow 2} R_\infty c}{\nu^M_{1\leftrightarrow 2}} - 1 \right)^{-1} . \tag{612}$$

The crux of the mass determination lies in the numerical loss in the conversion of frequency measurements into a determination of the mass. This numerical loss arises because

$$\frac{f^M_{1\leftrightarrow 2} R_\infty c}{\nu^M_{1\leftrightarrow 2}} - 1 = r(\mathcal{N}_M) , \tag{613}$$

where $r(\mathcal{N}_M)$ is rather small ($\approx 10^{-4} \ldots 10^{-5}$ in typical cases), whereas the two terms on the left hand side are of order unity.

Alternatively, this equation can be solved for the electron to nucleus mass ratio, which gives

$$r(\mathcal{N}_M) = \frac{f^M_{1\leftrightarrow 2} R_\infty c}{\nu^M_{1\leftrightarrow 2}} - 1 . \tag{614}$$

The resulting determination of $r(\mathcal{N}_M)$ is denoted as *method III* in the following. Again, there is a loss in numerical significance of about four decimals.

For illustrative purposes the determination of the electron to nucleus mass ratio using *method III* for ^{1}H, ^{2}H from Ref. [85] is reiterated here. The electron to nucleus mass ratios in hydrogen and deuterium are important for precision spectroscopy in these systems and can be very helpful for the on-going efforts of a comparison of transition frequencies in hydrogen and anti-hydrogen [115]. Examples for *method I* and *method II* are treated in Ref. [85].

One specific transition is considered, which is the two-photon transition from the state $|1\rangle$ with quantum numbers $n = 9$, $\ell = 8$, $j = 15/2$ to a state $|2\rangle$ with quantum

numbers $n = 16$, $\ell = 10$, $j = 19/2$. This specific transition is studied because for states with $j = \ell - \frac{1}{2}$ the QED correction are generally smaller and therefore also their associated uncertainties. Moreover, two-photon transitions are interesting due to the smaller line width. Based upon the theoretical formulas in Sec. 7.5 with the fundamental constants and masses from Table 7.3 the transition frequencies for hydrogen and deuterium have been calculated, which are given in Table 7.6. The transition frequencies do not include the hyperfine structure. For hydrogen, which has a nuclear spin of $I = \frac{1}{2}$, and deuterium with $I = 1$, the hyperfine splitting can be evaluated using Eq. (604). Moreover, hyperfine-mixing corrections can be determined with the formalism described in Ref. [99]. It is assumed that these corrections have been subtracted from the experimentally measured frequencies.

Table 7.6. Theoretical predictions for two-photon transition frequencies in atomic hydrogen and deuterium. The transition from the initial level $|1\rangle$ with quantum numbers $n = 9$, $\ell = 8$, and $j = 15/2$ to the level $|2\rangle$ with quantum numbers $n = 16$, $\ell = 10$, and $j = 19/2$ is considered. For the upper state, the higher-order self-energy coefficient reads $A_{60}(n = 16, \ell = 10, j = \frac{19}{2}) = 1.026705(5) \times 10^{-5}$. The individual contributions are listed in Eq. (605).

Term	^{1}H ν(THz)	^{2}H ν(THz)
ν_D	27.749 282 698 7469(1857)	27.756 833 254 1589(1856)
$\nu_{\rm BG}$	− 0.000 000 000 0005	− 0.000 000 000 0001
$\nu_{\rm RR}$	0.000 000 000 0009	0.000 000 000 0004
$\nu_{\rm QED}$	0.000 000 003 4893	0.000 000 003 4911
Total	27.749 282 702 2366(1857)	27.756 833 257 6503(1856)

With a similar analysis of the sources of uncertainty as in the last section, one finds that the dominant source of uncertainty is again the Rydberg constant. However, the second largest contribution to the uncertainty in these systems comes from the electron to nucleus mass ratios which have the following relative accuracies:

$$\frac{\delta r(^1\mathrm{H})}{r(^1\mathrm{H})} = 4.3 \times 10^{-10}, \qquad \frac{\delta r(^2\mathrm{H})}{r(^2\mathrm{H})} = 4.2 \times 10^{-10}. \tag{615}$$

The relative uncertainty of the theoretical predicted transition frequency in both these systems caused by the uncertainty of the electron to nucleus mass ratio is of the order 10^{-13}, making them unattractive for improving the accuracy of the Rydberg constant. With a more accurate value for the Rydberg constant of the order of 10^{-14}, the accuracy of the electron to nucleus mass ratio would in fact be the limiting factor of the theoretical prediction. Thus, such an accurate value for the Rydberg constant and a frequency measurement of the same relative accuracy of about 10^{-14}, would allow to determine a more precise value for the electron to nucleus mass ratio in these systems.

The theoretically determined transition frequencies in Table 7.6 can be used for a more quantitative analysis of the sources of uncertainty and the reachable accuracy based on Eq. (614). Similar, to the last section the fundamental constants, the masses and the theoretical predictions lead to uncertainties. Based on the formal dependence given by Eq. (614) of the electron to nucleus mass ratio on them and the uncertainty introduced by them can be estimated. The attained experimental accuracy is kept as a variable. In this way, it can be illustrated how accurate a determination of the Rydberg constant and the transition frequency has to be for a certain accuracy of the electron to nucleus mass ratio. For the case of deuterium $\mathcal{N}_M = {}^2\mathrm{H}$ these are given in Table 7.7 and for the case of hydrogen $\mathcal{N}_M = {}^1\mathrm{H}$ they can be found in Table 7.8. The first contribution in both cases to the relative uncertainty $\delta r(\mathcal{N}_M)/r(\mathcal{N}_M)$ of the electron to nucleus mass ratio, $r(\mathcal{N}_M)$, to be measured, comes from the residual dependence of the scaled frequency f on $r(\mathcal{N}_M)$. It can be seen that it does not contribute on a relevant level to the total uncertainty, which also justifies the approximate proportionality used in the described methods. The second uncertainty is introduced by the fine-structure constant. Then the experimentally determined value for the electron magnetic moment anomaly a_e causes the uncertainty in the third line of both tables. The last contribution above the horizontal line is then due to the neglected higher-order terms in the theoretical prediction, which interestingly become very small due to the functional dependence for the mass ratio. This is not the case for both *method I* and *method II*, where the theoretical uncertainty plays a more important role (see Ref. [85]). Below the horizontal line, the uncertainty introduced by the experimental measurement of the transition frequency and the

experimentally determined Rydberg constant are given in terms of the respective relative accuracies.

Table 7.7. Application of *method III* (see text) for the determination of the electron to nucleus mass ratio for $\mathcal{N}_M = {}^2\mathrm{H}$. The transition is $|1\rangle \leftrightarrow |2\rangle$ where $|1\rangle$ is the state with quantum numbers $n = 9$, $\ell = 8$, and $j = 15/2$, and $|2\rangle$ has quantum numbers $n = 16$, $\ell = 10$ and $j = 19/2$. The contributions to the relative uncertainty $\delta r(\mathcal{N}_M)/r(\mathcal{N}_M)$ of the electron to deuteron mass ratio due to the 2006 CODATA values for the fundamental constants and masses required for the evaluation of the theoretical expressions are given above the horizontal line. Contributions due to the assumed spectroscopic measurements are given below the horizontal line.

Source	$\frac{\delta r(\mathcal{N}_M)}{r(\mathcal{N}_M)}$
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial r(\mathcal{N}_M)}\delta r(\mathcal{N}_M)$	9.1×10^{-17}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial \alpha}\delta\alpha$	1.4×10^{-12}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial a_e}\delta a_e$	1.2×10^{-16}
$\delta f^M_{1\leftrightarrow 2}$	6.8×10^{-33}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial \nu^M_{1\leftrightarrow 2}}\delta\nu^M_{1\leftrightarrow 2}$	$3.7 \times 10^3 \left(\frac{\delta\nu^M_{1\leftrightarrow 2}}{\nu^M_{1\leftrightarrow 2}}\right)$
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial R_\infty c}\delta R_\infty c$	$3.7 \times 10^3 \left(\frac{\delta R_\infty c}{R_\infty c}\right)$

For a conservative estimate of the experimentally possible accuracy of a measurement of the transition frequency in such a system a study of the ratio of the energy of the transition E to the decay width of the line Γ is required. From a general calculation of one-photon decay widths of Rydberg states in Ref. [116], Ref. [83] used the estimate for the Q factor for transitions from n to $n-1$ of near circular

Rydberg states

$$Q = \frac{E_n - E_{n-1}}{\Gamma_n + \Gamma_{n-1}} = \frac{3n^2}{4\alpha(Z\alpha)^2} \,. \tag{616}$$

Table 7.8. Application of *method III* (see text) for the determination of the electron to nucleus mass ratio for $\mathcal{N}_M = {}^1\mathrm{H}$. The transition is $|1\rangle \leftrightarrow |2\rangle$ where $|1\rangle$ is the state with quantum numbers $n = 9$, $\ell = 8$, and $j = 15/2$, and $|2\rangle$ has quantum numbers $n = 16$, $\ell = 10$ and $j = 19/2$. Again, contributions to the relative uncertainty $\delta r(\mathcal{N}_M)/r(\mathcal{N}_M)$ of the mass ratio are separated into those caused by theoretical input data which are given above the horizontal line, and contributions due to the assumed spectroscopic measurements are given below the horizontal line.

Source	$\frac{\delta r(\mathcal{N}_M)}{r(\mathcal{N}_M)}$
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial r(\mathcal{N}_M)}\delta r(\mathcal{N}_M)$	9.3×10^{-17}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial \alpha}\delta\alpha$	7.0×10^{-13}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial a_e}\delta a_e$	5.8×10^{-17}
$\delta f^M_{1\leftrightarrow 2}$	1.3×10^{-32}
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial \nu^M_{1\leftrightarrow 2}}\delta\nu^M_{1\leftrightarrow 2}$	$1.8 \times 10^3 \left(\frac{\delta\nu^M_{1\leftrightarrow 2}}{\nu^M_{1\leftrightarrow 2}}\right)$
$\frac{1}{r(\mathcal{N}_M)}\frac{\partial r(\mathcal{N}_M)}{\partial R_\infty c}\delta R_\infty c$	$1.8 \times 10^3 \left(\frac{\delta R_\infty c}{R_\infty c}\right)$

As different transitions are considered in this work a complete calculation of the decay width is carried out based on the formulas in Ref. [24] which are discussed shortly in Sec. 4. The result for the Q factor for the studied transition in hydrogen,

published in Ref. [85], is found to be

$$Q(\mathrm{H})[n = 16, \ell = 10 \rightarrow n = 9, \ell = 8] = 7.2 \times 10^{8} \,. \tag{617}$$

In experimental measurements of the $2P$ Lamb shift, the energy of the line has been measured within 10^{-4} of the width of the line [117, 118]. This corresponds to a conservative estimate of the relative uncertainty of the experimental determination of the transition frequency of 1.4×10^{-13} which is used as the relative uncertainty of the Rydberg constant as well. By adding all uncertainties quadratically, the electron to deuteron mass ratio could then by determined with a relative uncertainty of 7.3×10^{-10}. The value for the mass ratio in the 2006 CODATA has a relative uncertainty of 4.2×10^{-10} [22], so the level of accuracy is comparable.

In the same way and with the same relative uncertainty in the frequency and Rydberg measurement, in hydrogen the electron to proton mass ratio could be determine with a relative uncertainty of 3.6×10^{-10}. Here, a comparison to the relative uncertainty of the 2006 CODATA value with a relative uncertainty of 4.3×10^{-10} [22], reveals that this is even slightly better. Should the experimental techniques, which might have to be developed for the mentioned project at NIST [83, 84, 88], enable more accurate measurement of transition frequencies in Rydberg states, more accurate value for both mass ratios could be obtained as well.

8. CALCULATION: QED AND HYPERFINE SPLITTING

8.1. ORIENTATION

So far only the effect of QED on the plain states of the Dirac equation has been considered. This already includes the effect of the magnetic moment of the electron due to its spin in its rest frame interacting with the magnetic field of the nucleus circling the electron. Because the nucleus has a spin as well, the spin of the nucleus can also interact with the magnetic field generated by the electron circling the nucleus. Another level shift, the so called hyperfine structure is the consequence. All these discussed level shifts are illustrated in Fig. 8.1.

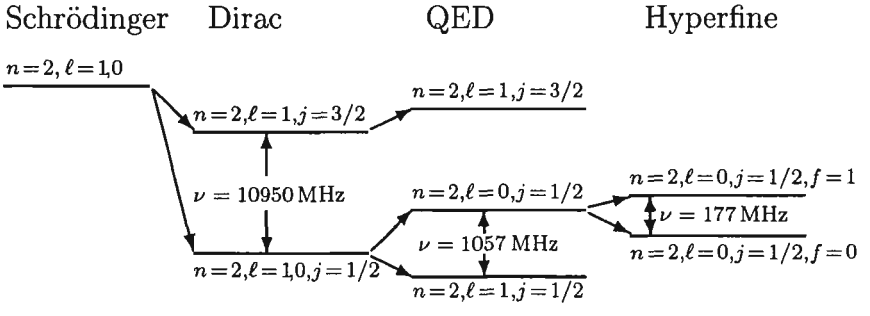

Figure 8.1. Level structure of the $n = 2$ states in atomic hydrogen.

From this figure, it can be seen that the effect from the hyperfine structure has to be considered in all predictions to the transition frequencies for nuclei with non-zero nuclear spin. Otherwise, the necessary accuracy cannot be reached. Interestingly, the hyperfine structure Hamiltonian does not commute with the Hamiltonian of the fine structure and therefore levels with different j coupling to the same total angular momentum of the ion f are mixed in the hyperfine structure. This is explained in detail for the muonic hydrogen in Refs. [51, 119]. This effect will however be neglected here. In this section the self-energy corrections to the hyperfine structure

for states with $\ell \leq 2$ are investigated. Basically, the effect of the magnetic moment of the nucleus is to generate an external magnetic field in which the electron moves. While so far in the Foldy-Wouthuysen transformation the external magnetic field was set to 0, the external magnetic field is now the magnetic field of the nucleus. Since the transformation starts from the fully relativistic Dirac Hamiltonian it is necessary to include the hyperfine interaction into this Hamiltonian first. The self-energy correction to the hyperfine structure can then identified to be the additional terms that will be obtained compared to the self-energy correction in the last section.

Following the derivation in Ref. [120] the magnetic field of the nucleus is given by the vector potential

$$\vec{A}_{\text{hfs}}(\vec{x}) = -\frac{1}{4\pi}\frac{\vec{\mu}\times\vec{x}}{r^3}\,, \tag{618}$$

where $\vec{\mu}$ denotes the the operator of the nuclear magnetic moment. As usual the curl of this vector potential yields the magnetic field

$$\vec{B}_{\text{hfs}} = \vec{\nabla}\times\vec{A}_{\text{hfs}}(\vec{x}) = -\frac{2}{3}\,\vec{\mu}\,\delta(\vec{x}) - \frac{3(\vec{\mu}\cdot\hat{\vec{x}})\hat{\vec{x}}-\vec{\mu}}{4\pi r^3}\,. \tag{619}$$

The coupling to the Dirac Hamiltonian is obtained by adding the vector potential of the hyperfine interaction to the quantized field. Returning to the approximation of an infinitely heavy nucleus without recoil effects, which was dropped in the last section, the relativistic magnetic dipole interaction of the nuclear magnetic moment and an electron can be expressed by the interaction Hamiltonian

$$H_{\text{hfs}} = -e\vec{\alpha}\cdot\vec{A}_{\text{hfs}}(\vec{x}) = \frac{e}{4\pi}\vec{\alpha}\cdot\frac{\vec{\mu}\times\vec{x}}{r^3} = \frac{e}{4\pi}\vec{\mu}\cdot\frac{\vec{x}\times\vec{\alpha}}{r^3} \tag{620}$$

Following the notation in Ref. [120], lowercase letters are used to label relativistic operators, whereas nonrelativistic operators are labeled by uppercase letters. As explained earlier, similar to the fine-structure, the hyperfine structure requires to couple the spin of the nucleus I to the total angular momentum of the electron j to receive the total angular momentum of the one electron ion f. Then the hyperfine

interaction Hamiltonian acts on the coupled states of the electron and the nucleus

$$|nfm_fIj\rangle = \sum_{M,m} C^{fm_f}_{IMjm} |IM\rangle |njm\rangle \ . \tag{621}$$

The magnetic quantum number of the nuclear spin is denoted as M while that of the total angular momentum of the ion f is labeled m_f. The hyperfine structure splitting is then the energy shift because of this interaction and given as

$$\Delta E_{\text{hfs}} = \langle nfm_fIj | H_{\text{hfs}} | nfm_fIj \rangle \ . \tag{622}$$

In order to extract how the hyperfine interaction acts on the electronic states the matrix element can be rewritten

$$\begin{aligned}
\Delta E_{\text{hfs}} = \langle nfm_fIj | H_{\text{hfs}} | nfm_fIj \rangle &= \frac{e}{4\pi} \left\langle nfm_fIj \left| \vec{\mu} \cdot \frac{\vec{x} \times \vec{\alpha}}{r^3} \right| nfm_fIj \right\rangle \\
&= \frac{e}{4\pi} \frac{|\vec{\mu}|}{I} \left\langle nfm_fIj \left| \vec{I} \cdot \frac{\vec{x} \times \vec{\alpha}}{r^3} \right| nfm_fIj \right\rangle \\
&= \frac{e}{4\pi} \frac{|\vec{\mu}|}{I} \langle nfm_fIj | \vec{I} \sum_{n'j'I'M'm'} C^{fm'_f}_{IM'jm'} |IM'\rangle |njm'\rangle \\
&\quad \times \sum_{n'j'I'M'm'} C^{f'm'_f}_{I'M'j'm'} \langle I'M' | \langle n'j'm' | \frac{\vec{x} \times \vec{\alpha}}{r^3} |nfm_fIj\rangle
\end{aligned} \tag{623}$$

The expression is multiplied by one in the right form, which yields

$$\begin{aligned}
\Delta E_{\text{hfs}} &= \frac{e}{4\pi} \frac{|\vec{\mu}|}{I} \langle nfm_fIj | \vec{I} \sum_{n'j'I'M'm'} C^{fm'_f}_{IM'jm'} |IM'\rangle |njm'\rangle \\
&\quad \times \sum_{n'j'I'M'm'} C^{f'm'_f}_{I'M'j'm'} \langle I'M' | \langle n'j'm' | \frac{\vec{x} \times \vec{\alpha}}{r^3} |nfm_fIj\rangle \\
&\quad \times \sum_{n'j'I'M'm'} \langle I'M' | \langle n'j'm' | 2\vec{j} |nfm_fIj\rangle \frac{C^{f'm'_f}_{I'M'j'm'}}{C^{f'm'_f}_{I'M'j'm'} \langle I'M' | \langle n'j'm' | 2\vec{j} |nfm_fIj\rangle} \\
&= \frac{e}{4\pi} \frac{|\vec{\mu}|}{I} \left\langle nfm_fIj \left| 2\vec{I} \cdot \vec{j} \right| nfm_fIj \right\rangle \sum_{n'j'm'} \frac{\langle n'j'm' | \frac{\vec{x} \times \vec{\alpha}}{r^3} |njm\rangle}{\langle n'j'm' | 2\vec{j} |njm\rangle} \ ,
\end{aligned} \tag{624}$$

where in the last step the nuclear spin degrees of freedom have been traces out in the right matrix element. The left matrix element can be evaluated with the known

expression

$$2\left(\vec{I}\cdot\vec{j}\right)=\vec{f}^{\,2}-\vec{I}^{\,2}-\vec{j}^{\,2}\,. \tag{625}$$

Moreover, $e^2=4\pi\alpha$ and $|\vec{\mu}|=g_N Ie/(2m_n)$, where g_N is the nuclear g factor, are used. Thus, the expression can be further simplified by employing orthogonality relations and the Wigner-Eckhart theorem with q denoting the vector component in the spherical basis

$$\begin{aligned}
\Delta E_{\rm hfs} &= \frac{\alpha g_N}{2}\frac{1}{m_N}\left[f(f+1)-I(I+1)-j(j+1)\right] \\
&\quad\times\sum_{n'j'm'}\left\langle n'j'm'\left|\frac{[\vec{x}\times\vec{\alpha}]_q}{r^3}\right|njm\right\rangle\left(2\left\langle n'j'm'\right|j_q\left|njm\right\rangle\right)^{-1} \\
&= \alpha\frac{g_N}{2}\frac{1}{m_N}\left[f(f+1)-I(I+1)-j(j+1)\right] \\
&\quad\times\left\langle njm\left|\frac{[\vec{x}\times\vec{\alpha}]_0}{r^3}\right|njm\right\rangle\left(2\left\langle njm\right|j_0\left|njm\right\rangle\right)^{-1} \\
&= \alpha\frac{g_N}{2}\frac{1}{m_N}\left[f(f+1)-I(I+1)-j(j+1)\right] \\
&\quad\times\frac{1}{2m}\left\langle njm\left|\frac{[\vec{x}\times\vec{\alpha}]_0}{r^3}\right|njm\right\rangle \\
&= \alpha\frac{g_N}{2}\frac{m_e}{m_N}\left[f(f+1)-I(I+1)-j(j+1)\right]\left\langle nj\tfrac{1}{2}\left|\frac{[\vec{x}\times\vec{\alpha}]_0}{m_e r^3}\right|nj\tfrac{1}{2}\right\rangle\,.
\end{aligned} \tag{626}$$

In this way, it has been achieved to separate the nuclear from the electronic variables, very similar to tracing out the photon degrees of freedom in Sec.4. A very detailed analysis of the separation of the nuclear variables can be found in Ref. [121]. This procedure allows to reduce the evaluations of the hyperfine structure and corrections to it, to the evaluation of matrix elements of operators acting solely on electronic states. The electronic matrix element will be denoted as $\Theta_e(nj\ell)$. Moreover, as can be seen from the above calculation, these electronic matrix elements are independent of the magnetic quantum number m. Hence, m is chosen to be $m=\frac{1}{2}$ to simplify the evaluation. This was used as well in the Lamb shift calculations. Consequently, $\Theta_e(nj\ell)$ is defined by

$$\Theta_e(n\ell_j)=\left\langle nj\tfrac{1}{2}\left|\frac{[\vec{x}\times\vec{\alpha}]_0}{m_e r^3}\right|nj\tfrac{1}{2}\right\rangle \tag{627}$$

and the energy shift due to the hyperfine interaction is thus

$$\Delta E_{\rm hfs} = \alpha \frac{g_N}{2} \frac{m_e}{m_N} \left[f(f+1) - I(I+1) - j(j+1) \right] \Theta_e(n\ell_j) \,. \tag{628}$$

A fully relativistic evaluation of $\Theta_e(n\ell_j)$ has been carried out in Ref. [98] with the result

$$\Theta_e(n\ell_j) = \frac{\kappa}{|\kappa|} \frac{(Z\alpha)^3 m_e}{n^3(2\kappa+1)(\kappa^2-\frac{1}{4})} n^3 |\kappa| (2\kappa+1) \frac{2\kappa(\gamma+n-|\kappa|)-N}{N^4\gamma(4\gamma^2-1)} \,, \tag{629}$$

with the notation used in Sec. 3, i.e. $\gamma = \sqrt{\kappa^2-(Z\alpha)^2}$ and the apparent principal quantum number $N = \sqrt{(n-|\kappa|)^2 + 2(n-|\kappa|)\gamma + \kappa^2}$.

After describing the method to obtain the hyperfine splitting of the energy levels and separating the nuclear degrees of freedom from the expression, the QED corrections to this result can be derived. Again, the focus is on states with $\ell \geq 2$ and the methods of NRQED detailed in Sec. 4 are employed. Results for S states with $\ell = 0$ have been obtained with NRQED in Refs. [98,121] and with a fully relativistic treatment in Refs. [122–124]. For P states ($\ell = 1$) the calculation with NRQED was carried out in Ref. [120] and numerical results form a fully relativistic evaluation have been obtained in Ref. [124]. All of the results are in excellent agreement.

8.2. LOW-ENERGY PART

8.2.1. Orientation. Following the theoretical method described in Sec. 4, for the low-energy part a nonrelativistic Hamiltonian is required which can be systematically derived through the Foldy-Wouthuysen transformation. The total Hamiltonian H_t to be transformed is given as the sum of the Dirac Hamiltonian without an external field in Eq. (231) and the relativistic hyperfine interaction Hamiltonian in Eq. (620)

$$H_t = H_D + H_{\rm hfs} = \vec{\alpha} \cdot \vec{p} + \beta m_e - \frac{Z\alpha}{r} - e\vec{\alpha} \cdot \vec{A}_{\rm hfs}(\vec{x}) \,. \tag{630}$$

The Foldy-Wouthuysen transformation of this Hamiltonian is carried out as described in Sec. 4.4. The only difference is that the operator $\mathcal{O}$ in Eq. (232) is now

$$\mathcal{O} = \vec{\alpha} \cdot \vec{p} - e\vec{\alpha} \cdot \vec{A}_{\rm hfs}(\vec{x}) \,. \tag{631}$$

In general, the generator of the transformation has to consist of the physical momentum $\vec{p} - e\vec{A}$ if $\vec{A} \neq 0$. The result of the transformation is thus

$$H_t' + UH_tU^{-1} = H_{\rm FW} + H_{\rm HFS}\,, \tag{632}$$

where H_{FW} is the Foldy-Wouthuysen Hamiltonian in Eq. (262) and $H_{\rm HFS}$ is the nonrelativistic hyperfine splitting Hamiltonian which is given as [120, 121]

$$H_{\rm HFS} = \frac{e\,m_e}{4\pi}\vec{\mu}\cdot\vec{h} = \frac{e\,m_e}{4\pi}\vec{\mu}\cdot\left(\vec{h}_S + \vec{h}_D + \vec{h}_L\right)\,, \tag{633}$$

which consists of the terms

$$\vec{h}_S = \frac{4\pi}{3m_e^2}\vec{\sigma}\delta(\vec{x})\,, \tag{634a}$$

$$\vec{h}_D = \frac{3(\vec{\sigma}\cdot\hat{\vec{x}})\hat{\vec{x}} - \vec{\sigma}}{2m_e^2 r^3}\,, \tag{634b}$$

$$\vec{h}_L = \frac{\vec{\ell}}{m_e^2 r^3}\,. \tag{634c}$$

As is seen, in the reduction of the energy splitting only the 0 component in the spherical basis (z component in the Cartesian basis) of this Hamiltonian is important in the calculation. It is denoted as h_0 and given as

$$h_0 = \frac{4\pi}{3m_e^2}\sigma_0\delta(\vec{x}) + \frac{3(\vec{\sigma}\cdot\hat{\vec{x}})\hat{x}_0 - \sigma_0}{2m_e^2 r^3} + \frac{\ell_0}{m_e^2 r^3}\,. \tag{635}$$

With this Hamiltonian also the nonrelativistic expression for the hyperfine splitting can be evaluated

$$\Theta_e^{\rm NR}(n\ell_j) = \left\langle nj\ell\tfrac{1}{2}\left|h_0\right|nj\ell\tfrac{1}{2}\right\rangle = \frac{\kappa}{|\kappa|}\frac{(Z\alpha)^3 m_e}{n^3(2\kappa+1)(\kappa^2-\frac{1}{4})}\,, \tag{636}$$

which is the nonrelativistic limit of the fully relativistic expression for $\Theta_e(j)$ in Eq. (629). Similar to Sec. 6 and in agreement with the notation in Ref. [120] the

QED corrections to the hyperfine structure will be expressed as a multiplicative correction of this nonrelativistic value for $\Theta_e^{\rm NR}(j)$

$$\Theta_e^{\rm NR}(n\ell_j) \to \Theta_e^{\rm NR}(n\ell_j)\left[1+(Z\alpha)^2\left(\frac{12\kappa^2-1}{2\kappa^2(2\kappa-1)(2\kappa+1)}+\frac{3}{2n}\frac{1}{|\kappa|}+\frac{3-8\kappa}{2n^2(2\kappa-1)}\right)+\delta\Theta(n\ell_j)\right]. \tag{637}$$

where the relativistic corrections of order $(Z\alpha)^2$ are obtained by expanding the fully relativistic result in Eq. (629) in $Z\alpha$ up to relative order $(Z\alpha)^2$.

The corresponding energy shift due to the QED corrections can then be obtained by multiplying $\delta\Theta_e(j)$ with the nonrelativistic hyperfine energy splitting

$$\Delta E_{\rm HFS} = \alpha\frac{g_N}{2}\frac{m_e}{m_N}\left[f(f+1)-I(I+1)-j(j+1)\right]\frac{\kappa}{|\kappa|}\frac{(Z\alpha)^3 m_e}{n^3(2\kappa+1)(\kappa^2-\frac{1}{4})} \tag{638}$$

and thus

$$\delta\Delta E_{\rm HFS} = \Delta E_{\rm HFS}\,\delta\Theta(n\ell_j)\,. \tag{639}$$

The nonrelativistic hyperfine splitting of the energy levels $\Delta E_{\rm HFS}$ is sometimes referred to as Fermi energy. For the QED corrections terms up to relative order $\alpha(Z\alpha)^2$ with respect to the nonrelativistic hyperfine splitting will be considered.

The Foldy-Wouthuysen transformation of the relativistic current gives the same result as in Sec. 4.4.1. The right current correction for the hyperfine splitting is found by replacing the momentum operator in the nonrelativistic current by the physical momentum in presence of the vector potential of the hyperfine splitting

$$\frac{p}{m_e} \to \frac{p}{m_e} - \frac{e}{m_e}\vec{A}_{\rm hfs} = \frac{p}{m_e} + \frac{e}{4\pi m_e}\frac{\vec{\mu}\times\vec{x}}{r^3} = \frac{p}{m_e} + \frac{|e|m_e}{4\pi}|\vec{\mu}|\delta\vec{j}_{\rm HFS} \tag{640}$$

This has been found in Ref. [120] and gives the additional current correction after the extraction of the nuclear degrees of freedom

$$\delta\vec{j}_{\rm HFS} = \frac{\hat{\vec{\mu}}\times\vec{x}}{m_e^2 r^3}\,. \tag{641}$$

Again, only the z component is required in the calculations, which is still a vector and given as

$$\delta\vec{j}_{0,\mathrm{HFS}} = \frac{1}{m_e^2 r^3}\left(-y\hat{e}_x + x\hat{e}_y\right) . \tag{642}$$

Now, only the resulting terms, which are different from the terms encountered for the self-energy correction without the hyperfine splitting have to be considered. The effect from the other terms has already been included and only the additional terms due to the hyperfine interaction will give an additional QED correction on top of the already calculated one. The implication is that for the wave function, energy and Hamiltonian correction only the hyperfine splitting Hamiltonian has to be used in the low-energy part.

Because the details on how to obtain the corrections in the low-energy part have been discussed extensively in Sec. 7 the terms here are given without derivation. Likewise, there are four contributions [120] from the correction of the interaction current, from the correction of the Hamiltonian, from the correction of the reference state energy, and finally from the correction of the reference-state wave function. It is important to note that these correction are now due to the hyperfine structure because the levels perturbed by the self-energy are corrected again due to the hyperfine interaction.

8.2.2. Hyperfine Correction to the Interaction Current. This correction is given by using the hyperfine correction to the current in the matrix element, which leads to

$$\begin{aligned}\delta\Theta_{L,\delta j}(n\ell_j) = \frac{4\alpha\mathcal{N}}{3\pi}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}} \sum_{n'j'\ell'm'} \left\langle nj\ell\tfrac{1}{2}\left|\frac{p^i}{m_e}\right|n'j'\ell'm'\right\rangle \\ \times \frac{1}{E_n - E_{n'} - \omega_{\vec{k}}}\left\langle n'j'\ell'm'\left|\delta j^i_{0,\mathrm{HFS}}\right|nj\ell\tfrac{1}{2}\right\rangle ,\end{aligned} \tag{643}$$

where the angular integration in $\vec{k}$ has already been carried out. Due to the way the corrections are defined, they have to be multiplied by the normalization factor

$$\mathcal{N} = \frac{1}{\left\langle nj\ell\frac{1}{2}\left|h_0\right|nj\ell\frac{1}{2}\right\rangle} = \frac{1}{\Theta_e^{\mathrm{NR}}(n\ell_j)} . \tag{644}$$

The integration with respect to $\omega_{\vec{k}}$ can then be carried out with the result

$$\delta\Theta_{L,\delta j}(n\ell_j) = \frac{\alpha}{\pi}(Z\alpha)^2\frac{4\mathcal{N}}{3(Z\alpha)^2}\sum_{n'j'\ell'm'}(E_n - E_{n'})\ln\left(\frac{|E_{n'} - E_n|}{m_e(Z\alpha)^2}\right) \times \left\langle nj\ell\tfrac{1}{2}\left|\frac{p^i}{m_e}\right|n'j'\ell'm'\right\rangle \left\langle n'j'\ell'm'\left|\delta j^i_{0,\mathrm{HFS}}\right|nj\ell\tfrac{1}{2}\right\rangle , \tag{645}$$

The term containing the logarithm of ϵ is 0 because it vanishes after angular integration in the matrix element. The structure of the logarithmic term here is very similar to the Bethe logarithm encountered in Sec. 4. Terms of this form will arise for the other corrections in the low-energy part as well. In the following these terms will be denoted as $\beta_{\mathrm{HFS}}(n\ell_j)$ and have to be evaluated numerically with the methods described earlier. Thus, the low-energy correction due to the nuclear-spin dependent current is

$$\delta\Theta_{L,\delta j}(n\ell_j) = \frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS},\delta j}(n\ell_j)\,. \tag{646}$$

8.2.3. Correction to the Hamiltonian, Energy and Wave Function. The next correction is the Hamiltonian correction due to the addition of the hyperfine splitting Hamiltonian, which yields the term

$$\delta\Theta_{L,\delta H}(n\ell_j) = \frac{2\alpha\mathcal{N}}{3\pi}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}} \times \left\langle nj\ell\tfrac{1}{2}\left|\frac{p^i}{m_e}\frac{1}{E_n - H_S - \omega_{\vec{k}}}h_0\frac{1}{E_n - H_S - \omega_{\vec{k}}}\frac{p^i}{m_e}\right|nj\ell\tfrac{1}{2}\right\rangle , \tag{647}$$

Here, and for the remaining terms the intermediate basis set is not written out in order to shorten the notation because the resulting correction is once more of the from of a Bethe logarithm type correction. This term, which is denoted as $\beta_{\mathrm{HFS},\delta H}$, has basically the same structure as $\beta_{\mathrm{SE},\delta H}$, only with δH_S replaced by h_0. Carrying out the integration with respect to $\omega_{\vec{k}}$ thus gives

$$\delta\Theta_{L,\delta H}(n\ell_j) = \frac{2\alpha\mathcal{N}}{3\pi m_e^2}\ln\left[\frac{\epsilon}{m_e(Z\alpha)^2}\right]\left\langle nj\ell\tfrac{1}{2}\left|\left(\frac{1}{2}[p^i,[h_0,p^i]] + p^2h_0\right)\right|nj\ell\tfrac{1}{2}\right\rangle + \frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS},\delta H}(n\ell_j)\,. \tag{648}$$

In the same way the energy correction can be written, which leads to

$$\begin{aligned}\delta\Theta_{L,\delta E}(n\ell_j) &= -\frac{2\alpha\mathcal{N}}{3\pi}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}}\,\langle nj\ell\tfrac{1}{2}\,|h_0|\,nj\ell\tfrac{1}{2}\rangle \\ &\quad\times\left\langle nj\ell\tfrac{1}{2}\left|\frac{p^i}{m_e}\left(\frac{1}{E_n-H_S-\omega_{\vec{k}}}\right)^2\frac{p^i}{m_e}\right|nj\ell\tfrac{1}{2}\right\rangle \\ &= -\frac{2\alpha\mathcal{N}}{3\pi m_e^2}\ln\left[\frac{\epsilon}{m_e(Z\alpha)^2}\right]\langle nj\ell\tfrac{1}{2}\,|p^2|\,nj\ell\tfrac{1}{2}\rangle\,\langle nj\ell\tfrac{1}{2}\,|h_0|\,nj\ell\tfrac{1}{2}\rangle \\ &\quad+\frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS},\delta E}(n\ell_j)\,,\end{aligned} \tag{649}$$

Finally, the correction to the wave function due to the hyperfine splitting Hamiltonian is

$$\begin{aligned}\delta\Theta_{L,\delta\Phi}(n\ell_j) &= \frac{4\alpha\mathcal{N}}{3\pi}\int_0^\epsilon d\omega_{\vec{k}}\,\omega_{\vec{k}} \\ &\quad\times\left\langle nj\ell\tfrac{1}{2}\left|\frac{p^i}{m_e}\frac{1}{E_n-H_S-\omega_{\vec{k}}}\frac{p^i}{m_e}\left(\frac{1}{E_n-H_S}\right)'h_0\right|nj\ell\tfrac{1}{2}\right\rangle \\ &= \frac{4\alpha\mathcal{N}}{3\pi m_e^2}\ln\left[\frac{\epsilon}{m_e(Z\alpha)^2}\right] \\ &\quad\times\left\langle nj\ell\tfrac{1}{2}\left|p^i(H_S-E_n)p^i\left(\frac{1}{E_n-H_S}\right)'h_0\right|nj\ell\tfrac{1}{2}\right\rangle \\ &\quad+\frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS},\delta\Phi}(n\ell_j)\,.\end{aligned} \tag{650}$$

The containing the logarithm of ϵ can be simplified with the relations

$$[p^i,[(H_S-E_n),p^i]]+p^2(H_S-E_n)+(H_S-E_n)p^2 = 2p^i(H_S-E_n)p^i\,, \tag{651a}$$

which basically was already used for the Hamiltonian correction and

$$(H_S-E_n)\left(\frac{1}{E_n-H_S}\right)'h_0\,|nj\ell\tfrac{1}{2}\rangle = \left[-1+|nj\ell\tfrac{1}{2}\rangle\,\langle nj\ell\tfrac{1}{2}|\right]h_0\,|nj\ell\tfrac{1}{2}\rangle\,. \tag{651b}$$

The double commutator $[p^i,[(H_S-E_n),p^i]]$ vanishes for states with $\ell\geq 1$ because of

$$[p^i,[(H_S-E_n),p^i]] = [p^i,[V,p^i]] = \nabla^2\left[-\frac{Z\alpha}{r}\right]\sim\delta(\vec{x})\,. \tag{652}$$

The contribution due to the hyperfine correction to the wave function is thus

$$\delta\Theta_{L,\delta\Phi}(n\ell_j) = \frac{2\alpha\mathcal{N}}{3\pi m_e^2}\ln\left[\frac{\epsilon}{m_e(Z\alpha)^2}\right]\left\{\left\langle nj\ell\tfrac{1}{2}\left|p^2\right|nj\ell\tfrac{1}{2}\right\rangle\left\langle nj\ell\tfrac{1}{2}\left|h_0\right|nj\ell\tfrac{1}{2}\right\rangle + \left\langle nj\ell\tfrac{1}{2}\left|p^2h_0\right|nj\ell\tfrac{1}{2}\right\rangle\right\} + \frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS},\delta\Phi}(n\ell_j)\,. \tag{653}$$

8.2.4. Summary of Corrections in the Low-Energy Part. Summing up all four corrections in the low-energy part yields

$$\begin{aligned}\delta\Theta_L(n\ell_j) &= \delta\Theta_{L,\delta j}(n\ell_j) + \delta\Theta_{L,\delta H}(n\ell_j) + \delta\Theta_{L,\delta E}(n\ell_j) + \delta\Theta_{L,\delta\Phi}(n\ell_j)\\ &= \frac{\alpha\mathcal{N}}{3\pi m_e^2}\ln\left[\frac{\epsilon}{m_e(Z\alpha)^2}\right]\left\langle nj\ell\tfrac{1}{2}\left|[p^i,[h_0,p^i]]\right|nj\ell\tfrac{1}{2}\right\rangle + \frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS}}(n\ell_j)\,,\end{aligned} \tag{654}$$

where $\beta_{\mathrm{HFS}}(n\ell_j)$ is the sum

$$\beta_{\mathrm{HFS}}(n\ell_j) = \beta_{\mathrm{HFS},\delta j}(n\ell_j) + \beta_{\mathrm{HFS},\delta H}(n\ell_j) + \beta_{\mathrm{HFS},\delta E}(n\ell_j) + \beta_{\mathrm{HFS},\delta\Phi}(n\ell_j)\,. \tag{655}$$

The double commutator

$$\left\langle nj\ell\tfrac{1}{2}\left|[p^i,[h_0,p^i]]\right|nj\ell\tfrac{1}{2}\right\rangle = \left\langle nj\ell\tfrac{1}{2}\left|\nabla^2 h_0\right|nj\ell\tfrac{1}{2}\right\rangle \tag{656}$$

has been evaluated for S states in Ref. [98] and for P states in Ref. [120]. For higher excited states it vanishes which can be seen by writing $\nabla^2 h_0$ in the form

$$\nabla^2 h_0 = \frac{4\pi}{3m_e^2}\nabla^2\delta(\vec{x})\sigma_0 - \frac{4\pi}{6m_e^2}\left[3\nabla_0\vec{\nabla}\delta(\vec{x})\cdot\vec{\sigma} - \nabla^2\delta(\vec{x})\sigma_0\right] - \frac{4\pi}{m_e^2}\mathrm{i}\varepsilon_{0jk}\nabla_j\delta(\vec{x})\nabla_k\,. \tag{657}$$

Each of the terms is basically a second derivative of the absolute square of the wave function at the origin, which is 0 for states with $\ell \geq 2$.

Hence, the complete low-energy part up to including order $\alpha(Z\alpha)^2\Delta E_{\mathrm{HFS}}$ for states with $\ell \geq 2$ takes the very simple form

$$\delta\Theta_L(n\ell_j) = \frac{\alpha}{\pi}(Z\alpha)^2\beta_{\mathrm{HFS}}(n\ell_j)\,. \tag{658}$$

8.3. HIGH-ENERGY PART

8.3.1. Orientation. For the high-energy part again a graphical expansion is used. Only the self-energy correction to order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$ is considered. It is therefore enough to treat only the diagram with one interaction with the binding potential in Fig. 4.2. Following the derivation in Sec. 4.6, this can be calculated by employing the modified Dirac Hamiltonian from Eq. (321)

$$H_D^{(m)} = \vec{\alpha}\left[\vec{p} - eF_1(\nabla^2)\vec{A}\right] + \beta m_e + F_1(\nabla^2)V + F_2(\nabla^2)\frac{e}{2m_e}\left(i\vec{\gamma}\cdot\vec{E} - \beta\vec{\Sigma}\cdot\vec{B}\right) . \quad (659)$$

Compared to the high-energy part of the self-energy calculation in Sec. 4.6, the magnetic field and the vector potential are not zero anymore but given by Eqs. (618) and (619). Only the additional correction terms compared to those already included in Sec. 4.6 are relevant [98]. The discussion goes through the terms from left to right in the modified Hamiltonian.

8.3.2. F_1 Form-Factor Correction to the Hyperfine Interaction. Consequently, the first term is the correction to the interaction with hyperfine vector potential due to the form-factor F_1

$$-eF_1'(0)\nabla^2\vec{\alpha}\cdot\vec{A}_{\rm hfs} = \frac{\alpha}{3\pi}\left[\ln\left(\frac{m_e}{2\epsilon}\right) + \frac{11}{24}\right]\nabla^2 H_{\rm hfs} . \quad (660)$$

The lowest order term with $F_1(0)$ is the hyperfine splitting Hamiltonian due to $F_1(0) = 1$. For the evaluation of this term it is very helpful to analyze the order of the correction. In this case $F_1'(0)$ is of order α and ∇^2 of order $(Z\alpha)^2$ because it corresponds to p^2. Hence, the whole expression is already of order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$. To obtain the QED correction of order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$, it is thus enough to evaluate this on the nonrelativistic wave function, which is the term of order 1 in the $Z\alpha$ expansion of the fully relativistic wave function. When the correction is scaled in the same way as in the low-energy part, this yields for the first term

$$\delta\Theta_{H,1}(n\ell_j) = \frac{\alpha\mathcal{N}}{3\pi m_e^2}\left[\ln\left(\frac{m_e}{2\epsilon}\right) + \frac{11}{24}\right]\left\langle nj\ell\tfrac{1}{2}\left|\nabla^2 h_0\right|nj\ell\tfrac{1}{2}\right\rangle . \quad (661)$$

The operator acting on the nonrelativistic wave function in this matrix element has already been evaluated in Eq. (657) in the last section and it is shown that it vanishes

for states with $\ell \geq 2$. For $\delta\Theta_{H,1}$ this implies

$$\delta\Theta_{H,1}(n\ell_j) = 0 \tag{662}$$

for $\ell \geq 2$.

8.3.3. F_1 Form-Factor Correction to the Potential. The next correction is due to form factor F_1 correction to the potential. This term was already included in Sec. 4.6, so now the correction is given by having this operator act on the through the hyperfine splitting perturbed wave function. In general, new terms arising because of $\vec{A}_{\rm hfs}$ are evaluated on the unperturbed wave function, whereas corrections already present in Sec. 7 have to be evaluated on the perturbed wave function. The actual calculation as carried out in Ref. [120] employs a Foldy-Wouthuysen transformation acting on the matrix element. The correction term to the result in Sec. 4.6 is then [120]

$$\delta\Theta_{H,2}(n\ell_j) = \frac{2\alpha\mathcal{N}}{3\pi m_e^2}\left[\ln\left(\frac{m_e}{2\epsilon}\right) + \frac{11}{24}\right]\left\langle nj\ell\tfrac{1}{2}\left|\nabla^2 V\left(\frac{1}{E_n - H_S}\right)' h_0\right|nj\ell\tfrac{1}{2}\right\rangle . \tag{663}$$

Again, $\nabla^2 V$ is proportional to the Dirac δ and therefore only gives a contribution for S states ($\ell = 0$). Accordingly, for the states with $\ell \geq 2$ it is found

$$\delta\Theta_{H,2}(n\ell_j) = 0\,. \tag{664}$$

8.3.4. F_2 Form-Factor Correction to the Electric Interaction. Also, the correction due to the form factor F_2 interaction with the electric field is already present in the self-energy calculation in Sec. 4.6. Therefore it has to be applied to the perturbed wave function. In Ref. [120] this term was found to be

$$\delta\Theta_{H,3}(n\ell_j) = 2\mathcal{N}F_2(0)\left\langle\psi^\dagger\left|\frac{-\mathrm{i}}{2m_e}\vec{\gamma}\cdot\vec{\nabla}V\left(\frac{1}{E_\psi - H_D}\right)' H_{\rm hfs}\right|\psi\right\rangle , \tag{665}$$

where F_2 is the magnetic form factor. For $F_2(0)$, the Schwinger value $F_2(0) = \frac{\alpha}{2\pi}$ is used. Order counting reveals that this has to be evaluated on the relativistic wave function, which is denoted as ψ. It has been shown in Ref. [120] that the calculation of this matrix element can be greatly simplified when it is transformed with the Foldy-Wouthuysen transformation from Sec. 4 without the hyperfine splitting Hamiltonian.

Applying the transformation the correction term takes the form

$$\begin{aligned}\delta\Theta_{H,3}(n\ell_j) &= \frac{2\alpha\mathcal{N}}{\pi}\left\langle\psi^\dagger\middle|U^\dagger U\left(\frac{-\mathrm{i}}{4m_e}\vec{\gamma}\cdot\vec{\nabla}V\right)U^\dagger\left(\frac{1}{U(E_\psi-H_D)U^\dagger}\right)'UH_{\mathrm{hfs}}U^\dagger U\middle|\psi\right\rangle \\ &= \frac{2\alpha\mathcal{N}}{\pi}\left\langle(U\psi)^\dagger\middle|U\left(\frac{-\mathrm{i}}{4m_e}\vec{\gamma}\cdot\vec{\nabla}V\right)U^\dagger\left(\frac{1}{U(E_\psi-H_D)U^\dagger}\right)'UH_{\mathrm{hfs}}U^\dagger\middle|U\psi\right\rangle .\end{aligned} \tag{666}$$

The transformation applied on the relativistic wave function gives the nonrelativistic wave function including the spin i.e.

$$|U\psi\rangle = |\Phi\rangle = |nj\ell m\rangle \ . \tag{667}$$

For the Foldy-Wouthuysen transformed potential term and the hyperfine splitting Hamiltonian, Ref. [120] found

$$U\left(\frac{-\mathrm{i}}{4m_e}\vec{\gamma}\cdot\vec{\nabla}V\right)U^\dagger = \frac{-\mathrm{i}}{4m_e}\vec{\gamma}\cdot\vec{\nabla}V + \frac{1}{8m_e^2}\nabla^2V + \frac{Z\alpha}{4m_e^2r^3}\vec{\sigma}\cdot\vec{\ell}+\ldots \tag{668}$$

$$UH_{\mathrm{hfs}}U^\dagger = H_{\mathrm{hfs}} + H_{\mathrm{HFS}} + \ldots . \tag{669}$$

It is important to note that the relativistic hyperfine splitting Hamiltonian remains after the transformation because the Foldy-Wouthuysen transformation used here only diagonalizes the Dirac Hamiltonian. In Sec. 4.6, the remaining mixing terms are neglected, which is not possible here up to the required order. But, through the transformation, the operators have been separated into mixing and non mixing operators. The non-mixing part is considered first, which gives the first correction

$$\delta\Theta_{H,3n}(n\ell_j) = \frac{\alpha\mathcal{N}}{2\pi m_e^2}\left\langle nj\ell\tfrac{1}{2}\middle|\frac{Z\alpha}{r^3}\vec{\sigma}\cdot\vec{\ell}\left(\frac{1}{E_n-H_S}\right)'H_{\mathrm{HFS}}\middle|nj\ell\tfrac{1}{2}\right\rangle . \tag{670}$$

To the required order, it is enough to only take terms of H_{FW} up to including order $m_e(Z\alpha)^2$, which is just the Schrödinger Hamiltonian, into account. The term $\nabla^2V/8m_e^2$ is proportional to the Dirac δ and does not contribute for states with $\ell \geq 1$.

There are now basically two ways to determine the contribution $\delta\Theta_{H,3n}$ from the non-mixing part. The first approach employs the numerical lattice method [78], which is usually used to evaluate the contributions in the low-energy part (see Sec. 6.5). The

resulting numerical value is first fitted to a fraction, before being fitted to a function of the type $a + b/n + c/n^2$.

The second way to determine the coefficient is, to find the first order perturbation of the wave function explicitly and use it to determine the matrix element. Both methods just evaluate the radial part and the angular algebra is dealt with already using Wigner-Eckhart theorem [23]. The perturbed wave function is determined based on

$$\begin{aligned} |\delta\Phi\rangle &= \left(\frac{1}{E-H}\right)' \delta V\,|\Phi\rangle \\ \Rightarrow (E-H)\,|\delta\Phi\rangle &= \delta V\,|\Phi\rangle - |\Phi\rangle\,\langle\Phi\,|\delta V|\,\Phi\rangle\ . \end{aligned} \tag{671}$$

For the perturbed wave function an ansatz of the structure

$$|\delta\Phi\rangle = \exp\left[-\frac{Z\,r}{n\,a_0}\right] \sum_i \left[\,c_i\,r^i + d_i\,r^i \ln(r)\,\right] \tag{672}$$

is made and the coefficients determined by the above equation. This allows to obtain all but one coefficient which is determined by the condition that the perturbed wave function has to be orthogonal to the unperturbed wave function i.e.

$$\langle\Phi\,|\,\delta\Phi\rangle = 0\,. \tag{673}$$

Both methods are used, which allows to check both results for consistency. In this way the coefficient $\delta\Theta_{H,3n}$ is obtained. For states with $\ell \geq 2$ the result can be formulated as

$$\begin{aligned} \delta\Theta_{H,3n}(n\ell_j) = \frac{\alpha}{\pi}(Z\alpha)^2 \Bigg(& \frac{1}{2\ell\kappa}\,\frac{60\ell^4+120\ell^3+55\ell^2-5\ell-3}{(2\ell+1)^2\,(4\ell^3+8\ell^2+\ell-3)} \\ & + \frac{3}{2n}\,\frac{1}{\kappa(2\ell+1)} - \frac{3}{8n^2}\,\frac{\ell(\ell+1)}{\kappa(\ell+\frac{3}{2})(\ell-\frac{1}{2})}\Bigg)\ , \end{aligned} \tag{674}$$

where $\kappa = (-1)^{j+\ell+\frac{1}{2}}(j+\frac{1}{2})$ is the Dirac quantum number.

The mixing part now has to be treated very carefully. For its evaluation, it is instructive to consider how the relativistic hyperfine splitting Hamiltonian $H_{\rm hfs}$, given in Eq. (620), acts on the nonrelativistic wave function. With the notation of

Eq. (230) this can be written as

$$H_{\rm hfs}\,|\Phi\rangle \sim \frac{[\vec{x}\times\vec{\alpha}]_0}{r^3}\,|\Phi\rangle = \frac{1}{r^3}\begin{pmatrix} 0 & [\vec{x}\times\vec{\sigma}]_0 \\ [\vec{x}\times\vec{\sigma}]_0 & 0 \end{pmatrix}\begin{pmatrix}\Phi\\ 0\end{pmatrix} = \frac{1}{r^3}\begin{pmatrix} 0 \\ [\vec{x}\times\vec{\sigma}]_0\Phi \end{pmatrix} . \quad (675)$$

This shows that the upper component of the bispinor couples only to the lower component in the intermediate state and therefore only its lower component has to be different from zero. As outlined in Ref. [120], this allows to approximate the energy of the state by its leading term the electron mass m_e. The lowest order term of H^l_{FW} for the lower components in Eq. (264) is $-m_e$. With $\vec{\nabla}V = Z\alpha\vec{x}/r^3$ the correction term is

$$\delta\Theta_{H,3m}(n\ell_j) = -\mathrm{i}\frac{\alpha\mathcal{N}}{2\pi m_e}\left\langle nj\ell\tfrac{1}{2}\left|\frac{Z\alpha}{r^3}\,(\vec{\gamma}\cdot\vec{x})\,\frac{1}{2m_e}H_{\rm hfs}\right|nj\ell\tfrac{1}{2}\right\rangle . \quad (676)$$

In Ref. [120] the complete contribution $\delta\Theta_{H,3}(n\ell_j)$ was also calculated within a fully relativistic framework and the result was found to be in agreement with the approach used here.

Following the explanation of the spinor structure of $\delta\Theta_{H,3m}$, it is possible to simplify the matrix element and evaluate part of its structure for arbitrary angular momentum. The result can be expressed as

$$\delta\Theta_{H,3m}(n\ell_j) = \frac{\alpha\mathcal{N}}{\pi}\frac{-\kappa}{8j(j+1)}\left\langle nj\ell\tfrac{1}{2}\left|\frac{Z\alpha}{m_e^3r^4}\right|nj\ell\tfrac{1}{2}\right\rangle , \quad (677)$$

in from of a radial matrix element to be evaluated. This radial matrix element was already encountered in the high-energy part in Sec. 4.6 and can be evaluated using known identities mentioned therein. The general form of the correction $\delta\Theta_{H,3m}$ is thus

$$\delta\Theta_{H,3m}(n\ell_j) = \frac{\alpha}{\pi}(Z\alpha)^2\frac{|\kappa|}{4j(j+1)}\frac{(2\kappa+1)(\kappa^2-\frac{1}{4})}{(2\ell-1)(2\ell+3)(\ell+\frac{1}{2})}\left(\frac{1}{n^2}-\frac{3}{\ell(\ell+1)}\right) . \quad (678)$$

8.3.5. F_2 Form-Factor Correction to the Magnetic Interaction. The last corrections in the high-energy part now arise from the form factor correction to the magnetic interaction

$$-F_2(\nabla^2)\frac{e}{2m_e}\beta\vec{\Sigma}\cdot\vec{B}_{\rm hfs} = F_2(\nabla^2)\left[\frac{em_e}{4\pi}\beta\vec{\mu}\cdot\left(\vec{h}_s+\vec{h}_d\right)\right]. \tag{679}$$

$\vec{h}_s$ and $\vec{h}_d$ can be seen as the generalizations of $\vec{h}_S$ and $\vec{h}_D$ to 4×4 matrices. They are in fact the two terms from $\vec{B}_{\rm hfs}$ in Eq. (619) when swapping $\vec{\mu}$ and $\vec{\Sigma}$ and taking out a factor of $2\pi m_e^2$ as was done in the equation above. So they are

$$\vec{h}_s = \frac{4\pi}{3m_e^2}\vec{\Sigma}\,\delta(\vec{x}), \tag{680}$$

$$\vec{h}_d = \frac{3\,(\vec{\Sigma}\cdot\hat{\vec{x}})\,\hat{\vec{x}}-\vec{\Sigma}}{2\,m_e^2\,r^3}. \tag{681}$$

Up to the considered order, $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$, the first two terms in the expansion of $F_2(\nabla^2)$ have to be included. The first term is thus

$$\delta\Theta_{H,4}(n\ell_j) = \mathcal{N}F_2(0)\,\langle\psi\,|\beta\,(h_{s,0}+h_{d,0})|\,\psi\rangle = \frac{\alpha\mathcal{N}}{2\pi}\,\langle\psi\,|\beta\,(h_{s,0}+h_{d,0})|\,\psi\rangle\,. \tag{682}$$

Because the term $F_2(0)=\alpha/2\pi$ itself is just of order α, this matrix element has to be evaluated on the relativistic wave function expanded up to order $(Z\alpha)^2$ so that the correction includes all corrections up to order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$. Through such an expansion also divergences are avoided, which would arise otherwise when working with the fully relativistic wave function. The δ part in the matrix element is 0 for states with $\ell\le 2$ for the relativistic wave function and therefore only $h_{s,0}$ has to be considered for these states. The term in order $\alpha\Delta E_{\rm HFS}$ for arbitrary angular momentum and principal quantum number is given as $1/4\kappa$. This has been published in Ref. [85] and can be found by generalizing the known expressions [120, 121] to general κ. By explicit integration for reference states with from $\ell=2$ to $\ell=16$ a generalized expression for the contribution in order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$ can be obtained,

which reads

$$\delta\Theta_{H,4}(n\ell_j) = \frac{\alpha}{\pi}\left[\frac{1}{4\kappa} + (Z\alpha)^2\left(\frac{1}{8\kappa^3}\,\frac{24\kappa^3+18\kappa^2-\kappa-1}{4\kappa^3+4\kappa^2-\kappa-1} + \frac{3}{8n}\frac{1}{|\kappa|\kappa} + \frac{1}{n^2}\frac{1}{2\kappa}\frac{1-3\kappa}{2\kappa-1}\right)\right] \tag{683}$$

in terms of the Dirac quantum number $\kappa = (-1)^{j+\ell+\frac{1}{2}}(j+\frac{1}{2})$.

The last term is given by the next term in the expansion of $F_2(\nabla^2)$ and is

$$F_2'(0)\frac{e}{2m_e}\beta\,\nabla^2\,\vec{\Sigma}\cdot\vec{B}_{\rm hfs} = \frac{\alpha}{12\pi}\left[\frac{em_e}{4\pi}\beta\vec{\mu}\cdot\left\{\nabla^2\left(\vec{h}_s+\vec{h}_d\right)\right\}\right]\,, \tag{684}$$

with $F_2'(0) = \alpha/12\pi$. As $F_2'(0)\nabla^2$ already is of order $\alpha(Z\alpha)^2$, this operator only has to be applied to the nonrelativistic wave function. Thus, β can be replaced by unity and $\vec{\Sigma}$ by $\vec{\sigma}$. This converts the relativistic operators $\vec{h}_s$ and $\vec{h}_d$ into their nonrelativistic counterparts $\vec{h}_S$ and $\vec{h}_D$ and leads to the correction term

$$\delta\Theta_{H,5}(n\ell_j) = \frac{\alpha\mathcal{N}}{12\pi}\left\langle nj\ell\tfrac{1}{2}\left|\nabla^2\left(h_{S,0}+h_{D,0}\right)\right|nj\ell\tfrac{1}{2}\right\rangle\,. \tag{685}$$

Recalling the earlier discussion in Eq. (657), it can be seen that for states with $\ell \geq 2$ one finds

$$\delta\Theta_{H,5}(n\ell_j) = 0\,. \tag{686}$$

8.3.6. Summary of Corrections in the High-Energy Part. This completes the discussion of the various correction terms in the high-energy part. The complete high-energy part of the self-energy correction is then the sum of all discussed corrections

$$\begin{aligned}\delta\Theta_H(n\ell_j) = {}& \delta\Theta_{H,1}(n\ell_j) + \delta\Theta_{H,2}(n\ell_j) + \delta\Theta_{H,3n}(n\ell_j) \\ & + \delta\Theta_{H,3m}(n\ell_j) + \delta\Theta_{H,4}(n\ell_j) + \delta\Theta_{H,5}(n\ell_j)\,.\end{aligned} \tag{687}$$

As the discussed for states with $\ell \geq 2$ shows, fortunately, only three terms give a non-zero contribution. So the high-energy part reduces to

$$\delta\Theta_H(n\ell_j) = \delta\Theta_{H,3n}(n\ell_j) + \delta\Theta_{H,3m}(n\ell_j) + \delta\Theta_{H,4}(n\ell_j) \tag{688}$$

because all other correction terms vanish for the states with $\ell \geq 2$ considered in this work. With the results from the previous section, the complete high-energy part of the self-energy correction is then given as

$$\begin{aligned}\delta\Theta_H(n\ell_j) = \frac{\alpha}{\pi}\Bigg\{\frac{1}{4\kappa} + (Z\alpha)^2\Bigg[&\frac{1}{8\kappa^3}\,\frac{24\kappa^3+18\kappa^2-\kappa-1}{4\kappa^3+4\kappa^2-\kappa-1} \\ &+\frac{1}{2\ell\kappa}\,\frac{60\ell^4+120\ell^3+55\ell^2-5\ell-3}{(2\ell+1)^2\,(4\ell^3+8\ell^2+\ell-3)} \\ &-\frac{3}{\ell(\ell+1)}\,\frac{j+\frac{1}{2}}{4j(j+1)}\,\frac{(2\kappa+1)(\kappa^2-\frac{1}{4})}{(2\ell-1)(2\ell+3)(\ell+\frac{1}{2})} \\ &+\frac{1}{n}\,\frac{3}{8\kappa}\,\frac{4(j+\frac{1}{2})+(2\ell+1)}{(2\ell+1)(j+\frac{1}{2})} + \frac{1}{8n^2}\left(\frac{4}{1-2\kappa}-\frac{4}{\kappa}\right. \\ &\left.+\frac{(2j+1)(2\kappa-1)(2\kappa+1)^2}{2j(j+1)(2\ell+3)\,(4\ell^2-1)} - \frac{3\ell(\ell+1)}{\kappa(\ell+\frac{3}{2})(\ell-\frac{1}{2})}\right)\Bigg]\Bigg\}\,.\end{aligned} \tag{689}$$

This can be simplified into a formula depending on the Dirac quantum number $\kappa = (-1)^{j-\ell+\frac{1}{2}}(j+\frac{1}{2})$ exclusively. Thus, the result for the high-energy part is

$$\begin{aligned}\delta\Theta_H(n\ell_j) = \frac{\alpha}{\pi}\Bigg\{\frac{1}{4\kappa} + (Z\alpha)^2\Bigg[&\frac{1}{8\kappa^3}\,\frac{(4\kappa+1)(6\kappa+1)(6\kappa^2+3\kappa-1)}{(2\kappa+1)^2(2\kappa-1)(\kappa+1)} \\ &+\frac{1}{n}\,\frac{3}{8}\,\frac{\kappa}{|\kappa|}\,\frac{6\kappa+1}{\kappa^2(2\kappa+1)} + \frac{1}{n^2}\,\frac{4\kappa-1}{2\kappa(1-2\kappa)}\Bigg]\Bigg\}\,.\end{aligned} \tag{690}$$

8.4. RESULTS

It is important to note in this problem that even though both the low-energy as well as the high-energy part are finite separately for states with $\ell \geq 2$, it is still required to consider both parts in order to obtain all relevant correction terms.

The only contribution form the low-energy part is given by $\beta_{\mathrm{HFS}}(n\ell_j)$, which has a similar structure as the Bethe logarithm. It can only be evaluated numerically for each specific states, using the lattice method of Ref. [78], described in Sec. 6.5

and Ref. [42]. Results obtained for D states with principal quantum number between $n = 3$ and $n = 12$ are found in Table 8.1. For states with angular momentum $\ell = 3$ and $\ell = 4$ calculations are carried out for principal quantum number up to $n = 10$, the resulting values are given in Tables 8.2 and 8.3. In order to prevent an uncertainty arising in the prediction of transition frequencies for nuclei with non zero nuclear spin, β_{HFS} is also determined for Rydberg states. The results are given in Table 8.4.

Table 8.1. Low-energy contribution β_{HFS} of the QED self-energy correction for the hyperfine splitting for D states ($\ell = 2$) for principal quantum numbers n between 3 and 12. The numbers in parentheses are standard uncertainties in the last figure.

n	$\beta_{\mathrm{HFS}}(nD_{3/2})$	$\beta_{\mathrm{HFS}}(nD_{5/2})$
3	$-2.068\,39(5) \times 10^{-2}$	$-3.455\,22(5) \times 10^{-2}$
4	$-1.302\,99(5) \times 10^{-2}$	$-3.793\,94(5) \times 10^{-2}$
5	$-1.025\,92(5) \times 10^{-2}$	$-3.965\,95(5) \times 10^{-2}$
6	$-0.943\,28(5) \times 10^{-2}$	$-4.084\,82(5) \times 10^{-2}$
7	$-0.938\,17(5) \times 10^{-2}$	$-4.174\,23(5) \times 10^{-2}$
8	$-0.963\,40(5) \times 10^{-2}$	$-4.243\,45(5) \times 10^{-2}$
9	$-0.999\,20(5) \times 10^{-2}$	$-4.297\,92(5) \times 10^{-2}$
10	$-1.037\,11(5) \times 10^{-2}$	$-4.341\,30(5) \times 10^{-2}$
11	$-1.073\,55(5) \times 10^{-2}$	$-4.376\,27(5) \times 10^{-2}$
12	$-1.110\,71(5) \times 10^{-2}$	$-4.404\,75(5) \times 10^{-2}$

The total QED self-energy correction to the hyperfine splitting is then given by adding the contribution $\beta_{\mathrm{HFS}}(n\ell_j)$ from the low-energy part to the high-energy part in Eq. (690), which yields

$$\delta\Theta(n\ell_j) = \frac{\alpha}{\pi}\left\{\frac{1}{4\kappa} + (Z\alpha)^2\left[\frac{1}{8\kappa^3}\,\frac{(4\kappa+1)(6\kappa+1)(6\kappa^2+3\kappa-1)}{(2\kappa+1)^2(2\kappa-1)(\kappa+1)} + \frac{1}{n}\,\frac{3}{8}\,\frac{\kappa}{|\kappa|}\,\frac{6\kappa+1}{\kappa^2(2\kappa+1)} + \frac{1}{n^2}\,\frac{4\kappa-1}{2\kappa(1-2\kappa)} + \beta_{\mathrm{HFS}}(n\ell_j)\right]\right\}. \tag{691}$$

The total frequency shift due to the hyperfine splitting can then be found by combining this result with Eq. (604). Here, the nonrelativistic expansion of the fully relativistic hyperfine splitting energy is used and, thus, a relativistic and QED expansion in $Z\alpha$ and α simultaneously is obtained. In SI units, it is found to be

$$\begin{aligned}\nu_{\rm hfs}(n\ell_j) = & \frac{R_\infty c}{1+r(\mathcal{N})}\frac{Z^3\alpha^2}{n^3}\frac{r(\mathcal{N})}{1+r(\mathcal{N})}\frac{\kappa}{|\kappa|} \\ & \times \frac{g_N}{(2\kappa+1)(\kappa^2-\frac{1}{4})}\left[f(f+1)-I(I+1)-j(j+1)\right] \\ & \times \left\{1+(Z\alpha)^2\left[\frac{12\kappa^2-1}{2\kappa^2(2\kappa-1)(2\kappa+1)}+\frac{3}{2n}\frac{1}{|\kappa|}+\frac{3-8\kappa}{2n^2(2\kappa-1)}\right]\right. \\ & +\frac{\alpha}{\pi}\frac{1}{4\kappa}+\frac{\alpha}{\pi}(Z\alpha)^2\left[\frac{1}{8\kappa^3}\frac{(4\kappa+1)(6\kappa+1)(6\kappa^2+3\kappa-1)}{(2\kappa+1)^2(2\kappa-1)(\kappa+1)}\right. \\ & \left.\left.+\frac{1}{n}\frac{3}{8}\frac{\kappa}{|\kappa|}\frac{6\kappa+1}{\kappa^2(2\kappa+1)}+\frac{1}{n^2}\frac{4\kappa-1}{2\kappa(1-2\kappa)}+\beta_{\rm HFS}(n\ell_j)\right]\right\}.\end{aligned} \tag{692}$$

Table 8.2. Low-energy contribution $\beta_{\rm HFS}$ of the QED self-energy correction for the hyperfine splitting for F states ($\ell = 3$) for principal quantum numbers n between 4 and 10. The numbers in parentheses are standard uncertainties in the last figure.

n	$\beta_{\rm HFS}(nF_{5/2})$	$\beta_{\rm HFS}(nF_{7/2})$
4	$-1.021\,46(5)\times10^{-2}$	$-0.953\,04(5)\times10^{-2}$
5	$-0.683\,94(5)\times10^{-2}$	$-1.077\,62(5)\times10^{-2}$
6	$-0.504\,64(5)\times10^{-2}$	$-1.141\,28(5)\times10^{-2}$
7	$-0.407\,32(5)\times10^{-2}$	$-1.182\,43(5)\times10^{-2}$
8	$-0.353\,63(5)\times10^{-2}$	$-1.212\,34(5)\times10^{-2}$
9	$-0.324\,00(5)\times10^{-2}$	$-1.235\,41(5)\times10^{-2}$
10	$-0.308\,07(5)\times10^{-2}$	$-1.253\,79(5)\times10^{-2}$

The hyperfine shift is considered for one particular example. The state $n = 16$, $\ell = 15$, and $j = 31/2$ in atomic hydrogen, which has a nuclear spin of $I = \frac{1}{2}$. If the total angular momentum j of state $|2\rangle$ couples with I to the total angular momentum

of the hydrogen atom $f = 16$, the energy of state $|2\rangle$ gets shifted by

$$\begin{aligned}\nu_{\rm hfs}(16\,15_{31/2}) &= \frac{R_\infty c}{[1+r(\mathcal{N})]^2} Z^3\alpha^2 r(\mathcal{N}) g_N \\ &\quad \times 4.7730327 \times 10^{-7} \left\{1 + (Z\alpha)^2\,[5.632635] \right. \\ &\quad \left. + \frac{\alpha}{\pi}\,(-0.015625) + \frac{\alpha}{\pi}(Z\alpha)^2\,\left[-6.323744 \times 10^{-4}\right]\right\} \qquad (693) \\ &= 254.094\,691\,40\,\text{Hz} + 0.076\,214\,54\,\text{Hz} \\ &\quad - 0.009\,222\,13\,\text{Hz} - 0.000\,000\,02\,\text{Hz} = 254.161\,683\,80\,\text{Hz}\,.\end{aligned}$$

Table 8.3. Low-energy contribution $\beta_{\rm HFS}$ of the QED self-energy correction for the hyperfine splitting for G states ($\ell = 4$) for principal quantum numbers n between 5 and 10. The numbers in parentheses are standard uncertainties in the last figure.

n	$\beta_{\rm HFS}(nG_{7/2})$	$\beta_{\rm HFS}(nG_{9/2})$
5	$-0.368\,23(5) \times 10^{-2}$	$-0.341\,76(5) \times 10^{-2}$
6	$-0.147\,39(5) \times 10^{-2}$	$-0.388\,58(5) \times 10^{-2}$
7	$-0.012\,93(5) \times 10^{-2}$	$-0.414\,24(5) \times 10^{-2}$
8	$0.072\,16(5) \times 10^{-2}$	$-0.430\,98(5) \times 10^{-2}$
9	$0.127\,85(5) \times 10^{-2}$	$-0.443\,13(5) \times 10^{-2}$
10	$0.165\,33(5) \times 10^{-2}$	$-0.452\,55(5) \times 10^{-2}$

Including uncertainties for the transition from Sec. 7, $|1\rangle \leftrightarrow |2\rangle$, in hydrogen with the nuclear spin added, the additional hyperfine transition frequency is thus found as

$$|1\rangle = |n = 15, \ell = 14, j = 29/2, f = 15\rangle\,, \qquad (694a)$$

$$|2\rangle = |n = 16, \ell = 15, j = 31/2, f = 16\rangle\,, \qquad (694b)$$

$$\Delta\nu_{\rm hfs,1\to2} = 254.161\,684(2)\,\text{Hz} - 351.002\,805(3)\,\text{Hz}\,, \qquad (694c)$$

$$\Delta\nu_{\rm hfs,1\to2} = -96.841\,121\,3(8)\,\text{Hz}\,, \qquad (694d)$$

where the CODATA 2006 value [22]

$$g_P = 5.585\,694\,713(46) \tag{695}$$

is used for the g factor of the proton.

Table 8.4. Low-energy contribution $\beta_{\rm HFS}$ of the QED self-energy correction for the hyperfine splitting for highly excited states. The numbers in parentheses are standard uncertainties in the last figure.

n	ℓ	$2j$	κ	$\beta_{\rm HFS}$	$2j$	κ	$\beta_{\rm HFS}$
16	15	29	15	$0.006\,310(5) \times 10^{-2}$	31	-16	$-0.002\,130(5) \times 10^{-2}$
16	14	27	14	$0.016\,397(5) \times 10^{-2}$	29	-15	$-0.003\,041(5) \times 10^{-2}$
15	14	27	14	$0.006\,888(5) \times 10^{-2}$	29	-15	$-0.002\,795(5) \times 10^{-2}$
15	13	25	13	$0.019\,372(5) \times 10^{-2}$	27	-14	$-0.004\,086(5) \times 10^{-2}$
14	13	25	13	$0.007\,420(5) \times 10^{-2}$	27	-14	$-0.003\,741(5) \times 10^{-2}$
14	12	23	12	$0.023\,029(5) \times 10^{-2}$	25	-13	$-0.005\,617(5) \times 10^{-2}$
13	12	23	12	$0.007\,794(5) \times 10^{-2}$	25	-13	$-0.005\,122(5) \times 10^{-2}$

9. CONCLUSIONS

The fundamental interactions of nature are basically described by the standard model. It contains the elementary particles and provides a set of rules of how these interact but it also contains a number of free parameters, the fundamental constants, which have to be fixed by a comparison of this model and actual experiments. These fundamental constants cannot be explained by the standard model and imply that the standard model is only an effective low energy limit of a more fundamental theory.

Consequently, the standard model is intensively studied at high energies in order to find hints at this more fundamental theory. At high energies, even the more exotic and heavy particles can be observed and not only arise as loop effects as for low-energy processes. Hence, their characteristics can be measured and compared to the predictions of the standard model. These investigations have lead to build experiments, which allow to achieve higher and higher energies. Unfortunately, in order to reach the required energy scales as well as minimize energy loss due to synchrotron radiation, these experiments have reached a scale, at which they can only be realized by global efforts.

Due to the unprecedented precision, which has been achieved in the study of the low energy regime of quantum electrodynamics, it has become possible to use these systems as an alternative for the investigation of the fundamental structure of interactions. While the effect from highly energetic particles may be very small in these systems, the accuracy of the measurements and theoretical predictions is so high that even these high energy effects have to be included. In fact, the most accurately known fundamental constants, are determined by a comparison of theory in experiment in this low-energy regime.

In this work, one of the most prominent low-energy systems of quantum electrodynamics is investigated, the atom. Here, the focus is set on one-electron ions because these can approximately be treated as an effective one particle systems when recoil corrections are included. Moreover, no electron-electron interactions are present, making one-electron ions ideal study objects for the study of quantum electrodynamics and a possible determination of fundamental constants.

Compared to the theoretical study of free particles though, for bound states a severe problem has to be overcome. For free particles QED perturbation theory has a natural expansion in the fine-structure constant α and therefore, every diagram contributes on a specific order in α. Due to the presence of the interaction with the core in addition to the interaction with the quantized radiation field, this is no longer the case in bound states. There, a diagram with a certain order α for the interaction with the quantized radiation field receives contributions from all orders in $Z\alpha$ for the interaction with the binding potential, thus destroying the possibility to order the contributions in α. Therefore, a very careful study of QED theory for bound states is carried out in this work. For this the work is organized as follows. The theory is described in Secs. 3, 4 and 5. In Secs. 6, 7 and 8 the theory is then applied to a number of problems namely, the two-photon decay and the self-energy correction to the Lamb shift as well as self-energy corrections to the hyperfine structure for highly excited states. Especially the later two are of great interest for reducing theoretical uncertainties and enable a determination of fundamental constants in highly excited Rydberg states.

In Sec. 3, the fully relativistic QED approach is investigated. Based on the methods developed by Mohr in Ref. [7,8], it is explained how this problem can be dealt with. An expression for the shift of the bound-state energies is derived based upon a integral with respect to the energy of the virtual photon. First of all, the integral has to be separated into a low- and a high-energy part. In the low-energy part only the interaction with a virtual photon from the radiation field with energy up to the bound state energy are considered. Because the photon energies are low, the electron can be described by the bound Dirac equation and the corresponding Coulomb-Dirac Green's function. The resulting integral can then evaluated numerically. For the high-energy part, the electron is basically scattered into free intermediate states as the virtual photon energy is much larger than the strength of the binding potential. Thus, it becomes possible to extract problematic terms by making use of a re-summed perturbative expansion. The resulting integrals are then finite and can be evaluated again numerically. The final result is then given as the sum of the low- and the high-energy part. Both parts receive contributions, which are, in fact, of lower order than the resulting correction. While these lower order terms cancel in the final result,

they still necessitate high precision arithmetic for the numerical evaluation. With this approach the energy shift in order α due to the interaction with the radiation field, but in all orders in the interaction with the binding potential is calculated.

The second theoretical approach discussed in Sec. 4, also makes use of the separation of the integral over the energy of the virtual photon into a low- and a high-energy part. Instead of a finite overlapping parameter, an infinitesimal one is used. Consequently, it becomes possible in the low-energy part to expand the fully relativistic theory around its nonrelativistic limit because now both the electron as well as the virtual photon are mainly described by nonrelativistic theory. This nonrelativistic expansion can be achieved by the Foldy-Wouthuysen transformation of the Dirac equation which gives the nonrelativistic Schrödinger equation plus corrections in orders of the nonrelativistic expansion parameter $v/c = Z\alpha$. This expansion allows to uniquely identify the physical origin of the correction terms and provides them with a face. Even though, for example, the spin-orbit coupling is naturally contained in the Dirac theory, it is much more apparent in the Foldy-Wouthuysen Hamiltonian in Eq. (262), where it can directly be identified as the term $[(Z\alpha)/4m_e r^3]\,\vec{\Sigma}\cdot\vec{\ell}$. Likewise, corrections due to the relativistic energy momentum relation are spotted while these are intertwined with the spin corrections in the Dirac equation.

In the high-energy part another expansion in $Z\alpha$ is employed. As described high-photon energies scatter the electron into basically free intermediate states. Hence, the natural expansion for the high-energy part is in powers of the binding potential, which also constitutes a $Z\alpha$ expansion. The lowest order term without interaction with the binding potential cancels the mass renormalization and the term with one interaction with binding potential can be described by an effective Dirac Hamiltonian. Finally, the two-interaction term is given by a separate Hamiltonian. In turn, both in the low- and the high-energy part an expansion in powers of $Z\alpha$ is obtained, which is matched together order by order at the end of the calculation to cancel the dependence on the overlapping parameter. In this way additionally to the series in α from the interaction with the radiation field also a series in $Z\alpha$ for interactions with the binding potential is obtained and a natural ordering of contributions in powers of α and $Z\alpha$ is recovered.

In Sec. 5, the application of the overlapping parameter both finite as well as infinitesimal is elucidated in a model problem. It is also illustrated that an infinitesimal overlapping parameter can be useful for the evaluation of integral with poles at the boundaries of the integration interval. For this purpose the vacuum polarization correction to the Coulomb potential, the so-called Uehling potential is calculated with the help of an infinitesimal overlapping parameter. After the theory has been explained and discussed in Secs. 3 to 5, it is evaluated for the two-photon decay in Sec. 6, for QED corrections to the Lamb shift in Sec. 7 and finally for the QED corrections to the hyperfine structure in Sec. 8.

The nonrelativistic $Z\alpha$ expansion of the fully relativistic theory is useful for many calculations. As in the two-photon decay the photon energy is bounded by the energy difference of the initial to the final state, the integral over the photon energy is constraint to nonrelativistic photon energy. This makes it very well suited for an investigation with the $Z\alpha$ expansion. With this, the relativistic corrections in order $(Z\alpha)^2$ as well as the leading logarithmic QED corrections of order $\alpha(Z\alpha)^2 \ln[(Z\alpha)^{-2}]$ are determined in Sec. 6. Furthermore, the nonrelativistic theory can also be formulated in different gauge and the formulation in length gauge [29,45] for the two-photon decay is also studied. It is shown that gauge invariance holds holds within the framework of a "hybrid" gauge transformation, in which the gauge transformation of the wave function is ignored. Again, the nonrelativistic theory is able to illustrate the physical origin of the corrections and able to reveal interesting correlations between the terms in the gauge transformation. The relativistic corrections to the two-photon decay rate are given in the form

$$\Gamma = \Gamma_0 \left[1 + \gamma_2 (Z\alpha)^2 + \dots\right] . \tag{696}$$

For the $2S$–$1S$ two photon decay the coefficient in order $(Z\alpha)^2$ correcting the nonrelativistic result of Göppert-Mayer in Ref. [70] reads

$$\gamma_2 = -0.6636 . \tag{697}$$

QED self-energy corrections with the $Z\alpha$ expansion are then considered in Sec. 7. Here, a special focus is set on Rydberg states. These are highly excited states with

high angular momentum and offer the advantage that not only the general magnitude of the corrections are relatively small but also that they are free of nuclear size effects. This study is supplemented by an overview over all additional correction terms, which have to be considered in order to theoretically predict transition frequencies in one-electron ions. These additional terms are due to the finite nuclear mass and included reduced mass effects of the electron as well as recoil terms. In this way, very accurate theoretical predictions for the transition frequencies between Rydberg states in one-electron ions can be obtained. For one such transition $|1\rangle \leftrightarrow |2\rangle$ between highly excited Rydberg states, where $|1\rangle$ is the state with quantum numbers $n = 15$, $\ell = 14$ and $j = 29/2$, and $|2\rangle$ has quantum numbers $n = 16$, $\ell = 15$, and $j = 31/2$, the transition frequency including all know corrections for $\mathcal{N} = {}^4\mathrm{Ne}^+$ is found to be

$$\nu_{1\leftrightarrow 2} = 7.081\ 331\ 009\ 805\ 59(4736)\,\mathrm{THz}\,, \tag{698}$$

where the frequency shift due to QED self-energy corrections alone is

$$\nu_{\mathrm{QED}} = -0.000\ 000\ 001\ 261\ 66\,\mathrm{THz}\,. \tag{699}$$

With the availability of high precision spectroscopy for optical transitions using frequency combs, these theoretical predictions can be very interesting for numerous projects. Of special importance here is the possibility of determining a more accurate value for the Rydberg constants in Rydberg states which is described in Sec. 7.5.3 and currently being pursued at NIST. The reason is the following, for lower-lying states the theory contains basically two parameters which limit the accuracy of the theoretical prediction, namely, the Rydberg constant and the RMS charge radius of the nucleus. For a determination of either of these out of a comparison of high precision spectroscopy and the theoretical prediction, one of them has to be known from another source. However, both of these parameters are highly intertwined, which implies that if one changes the other changes as well. This makes Rydberg states so interesting because in them only the Rydberg constant is contained as a free parameter. Another possible use of Rydberg states for the determination of nuclear masses is explored in Sec. 7.5.4.

A possible additional uncertainty in such a determination of the Rydberg constant for nuclei with a non zero nuclear spin could arise from the hyperfine structure. Therefore, in Sec. 8 QED self-energy corrections to the hyperfine structure up to order $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$ are calculated for the highly excited Rydberg states considered in Refs. [83–85, 88] within the $Z\alpha$ expansion. The result is a beautiful example of the power of the nonrelativistic expansion as the resulting frequency shift can be expressed as the leading nonrelativistic term times a factor, which contains the relativistic and QED corrections in a structured expansion, where each correction can be uniquely identified. It reads

$$\begin{aligned}
\nu_{\rm hfs} = {} & \frac{R_\infty c}{1+r(\mathcal{N})}\frac{Z^3\alpha^2}{n^3}\frac{r(\mathcal{N})}{1+r(\mathcal{N})}\frac{\kappa}{|\kappa|} \\
& \times \frac{g_N}{(2\kappa+1)(\kappa^2-\frac{1}{4})}\left[f(f+1)-I(I+1)-j(j+1)\right] \\
& \times \left\{1+(Z\alpha)^2\left[\frac{12\kappa^2-1}{2\kappa^2(2\kappa-1)(2\kappa+1)}+\frac{3}{2n}\frac{1}{|\kappa|}+\frac{3-8\kappa}{2n^2(2\kappa-1)}\right]\right. \\
& + \frac{\alpha}{\pi}\frac{1}{4\kappa}+\frac{\alpha}{\pi}(Z\alpha)^2\left[\frac{1}{8\kappa^3}\frac{(4\kappa+1)(6\kappa+1)(6\kappa^2+3\kappa-1)}{(2\kappa+1)^2(2\kappa-1)(\kappa+1)}\right. \\
& \left.\left. +\frac{1}{n}\frac{3}{8}\frac{\kappa}{|\kappa|}\frac{6\kappa+1}{\kappa^2(2\kappa+1)}+\frac{1}{n^2}\frac{4\kappa-1}{2\kappa(1-2\kappa)}+\beta_{\rm HFS}(n\ell_j)\right]\right\}.
\end{aligned} \tag{700}$$

The first term is due to the relativistic corrections of the nonrelativistic result, obtained by expanding the fully relativistic result in $Z\alpha$, the terms in order $\alpha\Delta E_{\rm HFS}$ and $\alpha(Z\alpha)^2\Delta E_{\rm HFS}$ are due to QED corrections. With this result also the additional hyperfine splitting for the transition considered before for a nucleus with non zero nuclear spin can be determined. For hydrogen with nuclear spin $I=\frac{1}{2}$ for the transition $|1\rangle \leftrightarrow |2\rangle$, it is found with

$$|1\rangle = |n=15, \ell=14, j=29/2, f=15\rangle\,, \tag{701a}$$

$$|2\rangle = |n=16, \ell=15, j=31/2, f=16\rangle\,, \tag{701b}$$

$$\Delta\nu_{{\rm hfs},1\to2} = 254.161\,684(2)\,{\rm Hz} - 351.002\,805(3)\,{\rm Hz}\,, \tag{701c}$$

$$\Delta\nu_{{\rm hfs},1\to2} = -96.841\,121\,3(8)\,{\rm Hz}\,, \tag{701d}$$

In the end, it is important to stress once again that Rydberg states offer unique opportunities because they constitute a nearly pure QED system. Through the determination of the Rydberg constant free of nuclear size effects, they can help the investigation of the recent discrepancy of the RMS charge radius of the proton. In muonic hydrogen, where a muon instead of an electron is bound by the proton, the radius has been found as [100]

$$r_p = 0.84184(67)\ \text{fm}\,, \tag{702}$$

which deviates from the 2006 CODATA value of [22]

$$r_p = 0.8768(69)\ \text{fm} \tag{703}$$

as well as with other values from scattering experiments [101] by 5.0σ. Because the nuclear size correction and the Rydberg constant are so intertwined, using the 2006 CODATA proton RMS charge radius [22] in the muonic hydrogen measurement would lead to a determination of the Rydberg constant with a value, which reads [100, 125]

$$R_\infty c = 3\,289\,841\,960\,251(5)\ \text{kHz}\,. \tag{704}$$

Naturally, this is in disagreement with the 2006 CODATA value for the Rydberg constant [22]

$$R_\infty c = 3\,289\,841\,960\,361(22)\ \text{kHz}\,. \tag{705}$$

The Rydberg constant determined in Rydberg states would now be independent of nuclear size effects and therefore ideally suited to clear up these disagreements because the effects not related to the nuclear size could be quantified exactly.

Partial results from this work have been communicated to the scientific community in Refs. [47, 59, 83–85].

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Talks about these published results were held at various conferences.