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Correlated two-electron wave functions of any symmetry

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Using a procedure originally due to Hylleraas, a convenient expansion in coupled spherical harmonics which terminates in a very small number of terms is applied to the treatment of fully correlated two-electron wave functions of any symmetry (total angular momentum, parity, and spin). Coupled equations satisfied by these wave functions are derived which are well adapted to computation and which we discretize on a numerical lattice utilizing the basis-spline collocation method. Use of this method which relies on very flexible basis functions is intended to facilitate subsequently the consideration of time-dependent rearrangements such as autoionization, photoionization, and electron-impact excitation and ionization. Here, we describe the underlying theoretical and computational methods concerning our treatment of the two-electron problem, the lattice discretization, and partial eigensolution by damped relaxation. Results of explicit calculations are given regarding the ground state and two low-lying singly excited states of helium.

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I. INTRODUCTION

Though much of present atomic physics is still concerned and productively occupied with the investigation of one-electron or pseudo-one-electron problems, and the use of independent-electron approximations or model interactions to simulate multielectron interactions, an ever growing effort is being devoted to the description and exploration of true fully correlated multielectron systems. However, either approximate or exact numerical solution of the Schrödinger equation for helium, or ions possessing only two electrons, in which the full electron-electron interaction is included in three dimensions, in itself presents a formidable challenge.

Through the present work, we seek to provide a convenient yet exact treatment of the fully correlated two-electron problem, by developing an expansion of the total wave function in a series utilizing coupled spherical harmonics which terminates in a very small number of terms. We may accomplish this task by taking advantage of a procedure originally due to Hylleraas to obtain fully correlated two-electron wave functions for any total angular momentum, spin, and parity. Using standard angular-momentum algebra, coupled differential equations may then be derived variationally from the stationary Schrödinger equation which are satisfied by the coefficients in the expansion. Since in subsequent applications we wish to especially consider time-dependent and rearrangement processes, we choose to discretize the wave function and the action of operators which result from these procedures utilizing a flexible finite element basis and apply the principle of collocation. The derivation of the expansion and of the coupled equations is described below in Secs. II and III, while Secs. IV and V are used to illustrate the important properties of symmetry and hermiticity satisfied by the wave function and Hamiltonian, respectively, and to summarize the discretization scheme. The final sections are used to demonstrate, for the case of helium, the iterative eigensolution on the numerical lattice which results in the ground ($1s^2\,{}^1S$) state and two low-lying excited ($1s2s\,{}^1S$ and $1s2p\,{}^1P$) states, and to draw conclusions. The demonstrations utilize such lattice techniques as damped relaxation and numerical quadrature to produce overlaps and expectation values. Pictorial representations of the states considered are included, illustrating the full radial and angular correlation present in the wave functions. We tabulate the expectation value of the total energy for these states and compare the results to previous accurate values.

Thus, in the present work we attempt to lay the foundation for a number of subsequent investigations, utilizing the procedures developed here, several of which are in progress. For example, doubly excited, autoionizing states have been calculated by Feshbach's projection method, implemented by imposing constraints at each iteration of the damped relaxation which require the state be orthogonal to the ground state, thus preventing its collapse (relaxation) to the ground state. Alternatively, a wave-packet approach has been taken to test the Wannier theory for the breakup (ionization) of atomic hydrogen by electron impact near threshold, and through angular-momentum recoupling we may treat double photoionization (and simultaneous ionization and excitation or double excitation) by computing matrix elements of the dipole operator. Numerous other applications are also possible, including autoionization in external fields, collisions involving fast electrons or ions, and the computation of bound- and continuum-state transition prob-

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abilities.

The lattice-expansion technique we have chosen is extremely well adapted for time-propagation of these processes since it flexibly represents both bound and continuum states, and supports a ready evolution of the wave function as a series of matrix-vector multiplications through such methods as a Taylor expansion of the exponential propagator. In addition, techniques developed previously to facilitate the projection of lattice final states, without explicitly creating a very large basis of continuum states, provide useful adjuncts to the present procedures. We emphasize that all of the foregoing processes are inherently correlated, and their description depends critically on the accurate treatment of the initial fully correlated wave function and the subsequent evolution of the system subject to the full electron-electron interaction. Clearly, many applications in the realm of single and multiple excitation and ionization remain to be explored, and the present approach is intended to provide a useful and powerful tool for these explorations. We note that a very brief description of the present method and of its possible uses was made previously [1].

II. HYLLERAAS EXPANSION

To begin with, consider the stationary Schrödinger equation for the wave function $\Psi(\vec{r}_1,\vec{r}_2)$ describing two electrons, located by the vectors $\vec{r}_1$ and $\vec{r}_2$, in the field of an infinitely massive nucleus of charge C whose position defines the origin of coordinates,

$$(E-H)\Psi(\vec{r}_1,\vec{r}_2)=0. \tag{1}$$

The Hamiltonian, $H=\mathcal{T}+\mathcal{V}$, is given in atomic units by

$$H=-\frac{1}{2}(\nabla_1^2+\nabla_2^2)+\left(\frac{1}{r_{12}}-\frac{C}{r_1}-\frac{C}{r_2}\right). \tag{2}$$

The potential energy $\mathcal{V}$ is a function of only three quantities which constitute the "dynamical variables" (r_1,r_2,ϑ) of the two-electron problem,

$$\mathcal{V}=\mathcal{V}(r_1,r_2,\vartheta)=\left(\frac{1}{r_{12}}-\frac{C}{r_1}-\frac{C}{r_2}\right), \tag{3}$$

where ϑ is the angle between $\vec{r}_1$ and $\vec{r}_2$, obeying the relation $r_{12}=r_1^2+r_2^2-2r_1r_2\cos\vartheta$. Our goal is to reduce the Hamiltonian to the space of these variables rather than treat the problem in the full six-dimensional space $(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$.

The usual approach is to expand the total wave function, using the infinite expansion in terms of coupled spherical harmonics,

$$\Psi_{L\varpi}(\vec{r}_1,\vec{r}_2)=\sum_{l_1,l_2}^{\infty}f_{l_1,l_2}(r_1,r_2)\mathcal{Y}^{LM}_{l_1,l_2}(\hat{r}_1,\hat{r}_2), \tag{4}$$

where

$$\mathcal{Y}^{LM}_{l_1,l_2}(\hat{r}_1,\hat{r}_2)=\sum_{m_1,m_2}(LM|l_1m_1l_2m_2)Y_{l_1m_1}(\hat{r}_1)Y_{l_2m_2}(\hat{r}_2),$$

and $(LM|l_1m_1l_2m_2)$ is a Clebsch-Gordan coefficient, Y_{lm} is a spherical harmonic, and we follow the notation and sign conventions of Edmonds [2]. For the Hamiltonian (2), the good quantum numbers are (i) the total orbital angular momentum $\vec{L}^2=L(L+1)$, (ii) the projection of this angular momentum on the z axis $L_z=M$, and (iii) the parity $\Pi=(-1)^{L+\varpi}=(-1)^{l_1+l_2}$, as well as the total energy. For the moment, we defer all consideration of spin and spatial symmetry to Sec. IV. The dependence on the projection M is trivial, and reference to M is usually omitted for simplicity. The parity is specified by $\varpi=0$ (1) for natural (unnatural) parity, respectively.

The expansion (4) consists of an infinite number of terms for couplets (l_1,l_2) subject to the constraints imposed by the Clebsch-Gordan coefficients and parity. For a given L and l_1, the Clebsch-Gordan coefficient restricts the value of l_2 according to the following sequence:

$$l_2=l_1-L,\ l_1-L+1,\dots,\ l_1+L.$$

Consequently,

$$l_1+l_2=2l_1-L,\ 2l_1-L+1,\dots,\ 2l_1+L.$$

For a state with natural parity, the minimun value of l_1+l_2 will be L, and for a state with unnatural parity, the minimum value will be $L+1$. Thus, if we define a new quantum number $\Lambda=l_1+l_2$, the terms in (4) can be ordered according to

$$\Lambda=L+\varpi,\ \ L+\varpi+2,\ \dots\ . \tag{5}$$

We are now in a position to derive Hylleraas's theorem. The recursion relations for coupled spherical harmonics connect functions of Λ, $\Lambda+2$, $\Lambda+4$, etc., and having coefficients which depend upon ϑ. Thus, the last term of (4), with the highest angular momentum, can be expressed as a linear combination of harmonics of lower degrees and coefficients depending on ϑ. This process can be continued until $\Lambda=L+\varpi$, at which point (4) has been replaced by the finite sum

$$\Psi_{L\varpi}(\vec{r}_1,\vec{r}_2)=(r_1r_2)^{-1}\sum_{l=\varpi}^{L}\psi_l(r_1,r_2,\vartheta)\mathcal{Y}^{LM}_{l,L+\varpi-l}(\hat{r}_1,\hat{r}_2). \tag{6}$$

The terms in the sum range over all the coupled spherical harmonics for which $l_1+l_2=L+\varpi$ and, anticipating the resulting simplification of the radial equations, the factor of (r_1r_2) has been separated out as is usually done. Owing to this relation, it will henceforth be convenient to use the shorthand $(l_1,l_2)=(l,L+\varpi-l)$ and $(l_1',l_2')=(l',L+\varpi-l')$.

III. COUPLED EQUATIONS

By the familiar variational procedure, we combine (6) and (1), and evaluate

$$\delta\langle\Psi_{L\varpi}|H-E|\Psi_{L\varpi}\rangle=0, \tag{7}$$

under variations in the expansion coefficients ψ_l. It is convenient to introduce a distinct notation, using double brackets to denote integrals over all orientations, with $\{r_1, r_2, \vartheta\}$ fixed,

$$\langle\langle\varphi|W|\psi\rangle\rangle = \int d^2\hat{r}_1 d^2\hat{r}_2 \delta(\cos\vartheta - \hat{r}_1\cdot\hat{r}_2) \times\varphi^*(\vec{r}_1,\vec{r}_2)W\psi(\vec{r}_1,\vec{r}_2), \quad (8)$$

and where the metric in the space of the functions $\psi_l(r_1, r_2, \vartheta)$ is given by

$$\langle\cdots\rangle = \int dr_1 dr_2 d(\cos\vartheta)\cdots,$$

a factor $r_1 r_2$ being incorporated in each radial wave function.

If we insert the expansion (6) into the Schrödinger equation (1), multiply on the left by $\langle l_1 l_2| \equiv \langle\mathcal{Y}^{LM}_{l_1 l_2}(\hat{r}_1\hat{r}_2)|$, and integrate over the elements $d\hat{r}_1 d\hat{r}_2$, keeping the angle $\cos\vartheta \equiv d\hat{r}_1\cdot d\hat{r}_2$ fixed, we obtain a set of coupled equations,

$$\sum_l \langle\langle l'_1 l'_2|H - E|l_1 l_2\rangle\rangle\psi_l = 0, \quad (9)$$

where the sum over l is the sum over all pairs $(l_1, l_2) = (l, L + \varpi - l)$ and

$$\langle\langle l'_1 l'_2|H - E|l_1 l_2\rangle\rangle = \mathcal{Z}^{(0)}_{l'l}(\mathcal{T}_1 + \mathcal{T}_2 + \mathcal{V} - E)\delta_{l'l} + \frac{\mathcal{L}^{(1)}_{l'l}}{2r_1^2} + \frac{\mathcal{L}^{(2)}_{l'l}}{2r_2^2}. \quad (10)$$

We have written $2\mathcal{T}_p = -\partial^2/\partial r_p^2$ for $p = 1, 2$, and the coefficients in (10) are given by

$$\begin{aligned}\mathcal{Z}^{(0)}_{l'l}(\vartheta) &= \langle\langle l'_1 l'_2|l_1 l_2\rangle\rangle,\\ \mathcal{L}^{(1)}_{l'l}(\vartheta) &= \langle\langle l'_1 l'_2|\vec{l}_1{}^2|l_1 l_2\rangle\rangle,\\ \mathcal{L}^{(2)}_{l'l}(\vartheta) &= \langle\langle l'_1 l'_2|\vec{l}_2{}^2|l_1 l_2\rangle\rangle .\end{aligned} \quad (11)$$

The terms $\mathcal{Z}^{(0)}_{l'l}(\vartheta)$ are simple functions of ϑ and can be expanded in Legendre polynomials,

$$\mathcal{Z}^{(0)}_{l'l}(\vartheta) = \sum_K \mathcal{Z}^{(0)}_{KLl'l} P_K(\cos\vartheta). \quad (12)$$

The coefficients in this expansion are expressible as integrals over all $\{\hat{r}_1, \hat{r}_2\}$ obtained by inverting (12) and inserting $\mathcal{Z}^{(0)}_{l'l}(\vartheta) = \langle\langle l'_1 l'_2|l_1 l_2\rangle\rangle$ from (11), and may be evaluated by standard tensor algebra methods,

$$\begin{aligned}\mathcal{Z}^{(0)}_{KLl'l} &= \frac{1}{2}(2K+1)\langle l'_1 l'_2|P_K(\cos\vartheta)|l_1 l_2\rangle\\ &= \frac{1}{2}(-1)^{L+l'_2+l_2}(2K+1)[l'_1, l'_2, l_1, l_2]\\ &\quad\times\begin{pmatrix} l_1 & l'_1 & K\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_2 & l'_2 & K\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} l_1 & l'_1 & K\\ l'_2 & l_2 & L\end{Bmatrix},\end{aligned} \quad (13)$$

where the last terms are Wigner 3-j and 6-j symbols, the range of sums over K is determined by the usual triangle relations, and we use the shorthand that

$$[l'_1, l'_2, l_1, l_2] = [(2l'_1+1)(2l'_2+1)(2l_1+1)(2l_2+1)]^{\frac{1}{2}}.$$

The other coefficients $\mathcal{L}^{(p)}_{l'l}(\vartheta)$ are operators acting on the total wave function and thus on the coupled spherical harmonics multiplied by a function of ϑ, say $f(\cos\vartheta)$. To decompose all the operations, we require two principal relations. First, the action of $\vec{l}_1^{\,2}$ on such products to its right is given by

$$\vec{l}_1^{\,2}[\mathcal{Y}f(\cos\vartheta)] = (\vec{l}_1^{\,2}\mathcal{Y})f + 2(\vec{l}_1\mathcal{Y})\cdot(\vec{l}_1 f) + (\vec{l}_1^{\,2} f)\mathcal{Y}, \quad (14)$$

where we abbreviate $\mathcal{Y}^{LM}_{l_1 l_2}(\hat{r}_1\hat{r}_2)$ by simply $\mathcal{Y}$. Second, the action of $\vec{l}_1$ and $\vec{l}_1^{\,2}$ on $f(\cos\vartheta)$ is found from elementary, but rather lengthy, manipulations to yield

$$\begin{aligned}\vec{l}_1 f &= -i\vec{r}_1\times\nabla_1 f|_{r_1=\kappa} = -i\hat{r}_1\times\hat{r}_2 f',\\ \vec{l}_1^{\,2} f &= -r_1^2\,\nabla_1^2 f\big|_{r_1=\kappa} = -\sin^2\vartheta f'' + 2\cos\vartheta f',\end{aligned} \quad (15)$$

where κ is a constant and the primes denote differentiation with respect to $\cos\vartheta$. We evaluate here the result for the $\vec{l}_1$ operators, from which expressions for the $\vec{l}_2$ case are readily deduced. Writing first and second derivatives with respect to ϑ as

$$\begin{aligned}\mathcal{D}_\vartheta &= \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta},\\ \mathcal{T}_\vartheta &= -\frac{1}{2}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta},\end{aligned} \quad (16)$$

and using (14) and (15), it may be shown that

$$\mathcal{L}^{(1)}_{l'l}(\vartheta) = \mathcal{Z}^{(0)}_{l'l}(\vartheta)[l_1(l_1+1) + 2\mathcal{T}_\vartheta] - 2\mathcal{Z}^{(1)}_{l'l}(\vartheta)\mathcal{D}_\vartheta, \quad (17)$$

where from (15), the coefficient $\mathcal{Z}^{(1)}_{l'l}(\vartheta)$ is given by

$$\mathcal{Z}^{(1)}_{l'l}(\vartheta) = \langle\langle l'_1 l'_2|\vec{\omega}_1\cdot\hat{r}_2|l_1 l_2\rangle\rangle, \quad \vec{\omega}_1 = i\hat{r}_1\times\vec{l}_1. \quad (18)$$

We absorb the factor i into the spherical tensor so that the matrix elements of $\vec{\omega}$ will be real. If $\mathcal{Z}^{(1)}_{l'l}(\vartheta)$ is now expanded analogously to (12), i.e.,

$$\mathcal{Z}^{(1)}_{l'l}(\vartheta) = \sum_K \mathcal{Z}^{(1)}_{KLl'l} P_K(\cos\vartheta),$$

then the expansion coefficients are given by

$$\begin{aligned}\mathcal{Z}^{(1)}_{KLl'l} &= \frac{1}{2}(2K+1)\langle l'_1 l'_2|P_K(\cos\vartheta)\vec{\omega}_1\cdot\hat{r}_2|l_1 l_2\rangle\\ &= \frac{1}{2}\sum_{j_1,j_2}(-1)^{L+l'_2+j_2}(2K+1)[l'_1, l'_2, j_1, j_2]\\ &\quad\times\begin{pmatrix} j_1 & l'_1 & K\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j_2 & l'_2 & K\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} j_1 & l'_1 & K\\ l'_2 & j_2 & L\end{Bmatrix}\Omega^{(1)}_{Ljl}\\ &= \sum_{j_1,j_2}\mathcal{Z}^{(0)}_{KLl'j}\Omega^{(1)}_{Ljl} ,\end{aligned} \quad (19)$$

where j is short for (j_1, j_2), and

$$\begin{aligned}\Omega^{(1)}_{Ljl} &= \langle j_1 j_2|\vec{\omega}_1\cdot\hat{r}_2|l_1 l_2\rangle\\ &= (-1)^{L+j_1+l_2}\langle l_1|\vec{\omega}|j_1\rangle\langle l_2|\hat{r}|j_2\rangle\begin{Bmatrix} l_1 & l_2 & L\\ j_2 & j_1 & 1\end{Bmatrix} .\end{aligned} \quad (20)$$

The reduced matrix elements of $\vec{\omega}$ and $\hat{r}$ are given by

$$\begin{aligned}\langle l|\vec{\omega}|j\rangle &= \begin{cases}(l+2)\sqrt{l+1} & \text{if } j = l+1\\ (l-1)\sqrt{l} & \text{if } j = l-1\end{cases}\\ \langle l|\hat{r}|j\rangle &= \begin{cases}-\sqrt{l+1} & \text{if } j = l+1\\ \sqrt{l} & \text{if } j = l-1.\end{cases}\end{aligned} \quad (21)$$

A corresponding decomposition [Eqs. (14)–(21)] may be found for the coefficients $\mathcal{L}^{(2)}_{l'l}(\vartheta)$ by replacing the operator $\vec{l}^{\,2}_1$ by $\vec{l}^{\,2}_2$, resulting in an exactly analogous expression for the coefficients $\mathcal{Z}^{(2)}_{l'l}(\vartheta)$. Then, upon substituting these terms into (10), we find that the functions ψ_l satisfy the coupled equations

$$\sum_{l=\varpi}^{L} \mathcal{Z}^{(0)}_{l'l}(\vartheta)\left(h_1 + h_2 + h_\vartheta + \frac{1}{r_{12}} - E\delta_{l'l}\right)\psi_l = \sum_{l=\varpi}^{L}\left[\frac{\mathcal{Z}^{(1)}_{l'l}(\vartheta)}{r_1^2} + \frac{\mathcal{Z}^{(2)}_{l'l}(\vartheta)}{r_2^2}\right]\mathcal{D}_\vartheta\psi_l. \tag{22}$$

where

$$\begin{aligned} h_1 &= \mathcal{T}_1 - \frac{C}{r_1} + \frac{l_1(l_1+1)}{2r_1^2},\\ h_2 &= \mathcal{T}_2 - \frac{C}{r_2} + \frac{l_2(l_2+1)}{2r_2^2},\\ h_\vartheta &= \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\mathcal{T}_\vartheta\,. \end{aligned} \tag{23}$$

Finally, it is convenient to solve (22) for

$$\left(h_1 + h_2 + h_\vartheta + \frac{1}{r_{12}} - E\delta_{l'l}\right)\psi_l$$

by inverting the matrix $[\mathcal{Z}^{(0)}(\vartheta)]$ in the space (l', l), and defining a new coefficient, $\mathcal{X}^{(p)}(\vartheta)$, by

$$[\mathcal{X}^{(p)}(\vartheta)] = [\mathcal{Z}^{(0)}(\vartheta)]^{-1}[\mathcal{Z}^{(p)}(\vartheta)], \tag{24}$$

for $p = 1, 2$. Thus, the particularly simple form

$$\left(h_1 + h_2 + h_\vartheta + \frac{1}{r_{12}} - E\right)\psi_l + \sum_{l=\varpi}^{L}(\mathcal{U}^{(1)}_{l'l} + \mathcal{U}^{(2)}_{l'l})\psi_l = 0 \tag{25}$$

is obtained, where the coupling terms are given by

$$\mathcal{U}^{(p)}_{l'l} = -\frac{\mathcal{X}^{(p)}_{l'l}}{r_p^2}\mathcal{D}_\vartheta. \tag{26}$$

IV. SYMMETRY PROPERTIES AND HERMITICITY

If the spatial wave function (6) is associated with a spin eigenfunction of singlet ($S = 0$) or triplet ($S = 1$) symmetry, the criterion of overall antisymmetry requires that the dynamical wave functions ψ_l must satisfy

$$\psi_l(r_2, r_1, \vartheta) = (-1)^{S+\varpi}\psi_{L+\varpi-l}(r_1, r_2, \vartheta). \tag{27}$$

It may be shown that if the functions ψ_l are laid out on a line, the first and last pair, the second and next to last pair, and so on, are related by symmetry. Also, if $L + \varpi$ is even, indicating that there is an odd total number of terms in the expansion (6), then the "middle" function $\psi_{l=(L+\varpi)/2}$ is symmetric or antisymmetric following the parity of $S + \varpi$.

Next we consider the hermiticity of the effective Hamiltonian in the space of the ψ_l wave functions. From (22), this Hamiltonian can be written as

$$\begin{aligned} \mathcal{H}(l'l) &= \mathcal{Z}^{(0)}_{l'l}(\vartheta)\left(h_1 + h_2 + h_\vartheta + \frac{1}{r_{12}}\right)\\ &\quad - [\nu_1\mathcal{Z}^{(1)}_{l'l}(\vartheta) + \nu_2\mathcal{Z}^{(2)}_{l'l}(\vartheta)]\mathcal{D}_\vartheta\,, \end{aligned} \tag{28}$$

where $\nu_p = 1/r_p^2$. From the hermiticity of the original Hamiltonian (2), it must follow that

$$\langle\Phi|H|\Psi\rangle = \langle\Psi|H|\Phi\rangle \tag{29}$$

for a pair of wave functions

$$\begin{aligned} \Phi &= \sum_{l'} \varphi_{l'}\mathcal{Y}^{LM}_{l',L+\varpi-l'}(\hat{r}_1, \hat{r}_2),\\ \Psi &= \sum_{l} \psi_l\mathcal{Y}^{LM}_{l,L+\varpi-l}(\hat{r}_1, \hat{r}_2). \end{aligned} \tag{30}$$

Thus,

$$\langle\varphi_{l'}|\mathcal{H}(l'l)|\psi_l\rangle = \langle\psi_l|\mathcal{H}(ll')|\varphi_{l'}\rangle. \tag{31}$$

To verify this relation, we pick out the terms in (28), $\tilde{\mathcal{H}}$, which are not explicitly symmetric,

$$\begin{aligned} \tilde{\mathcal{H}}(l'l) &= \frac{1}{2}(\nu_1 + \nu_2)(1-\mu^2)\frac{d}{d\mu}\mathcal{Z}^{(0)}_{l'l}\frac{d}{d\mu}\\ &\quad + (\nu_1\mathcal{Z}^{(1)}_{l'l} + \nu_2\mathcal{Z}^{(2)}_{l'l})\frac{d}{d\mu}\\ &\quad + \frac{1}{2}[l_1(l_1+1)\nu_1 + l_2(l_2+1)\nu_2]\mathcal{Z}^{(0)}_{l'l}, \end{aligned} \tag{32}$$

where we have written $\mu = \cos\vartheta$, and integrated by parts the term in $\mathcal{T}_\vartheta$. Grouping like terms, this becomes

$$\tilde{\mathcal{H}}(l'l) = (\nu_1\mathcal{A}^{(1)} + \nu_2\mathcal{A}^{(2)})\frac{d}{d\mu} + (\nu_1\mathcal{B}^{(1)} + \nu_2\mathcal{B}^{(2)}), \tag{33}$$

where for $p = 1, 2$

$$\begin{aligned} \mathcal{A}^{(p)}(l'l) &= \sum_K [\tfrac{1}{2}\mathcal{Z}^{(0)}_K(1-\mu^2)P'_K(\mu) + \mathcal{Z}^{(p)}_K P_K(\mu)]\\ \mathcal{B}^{(p)}(l'l) &= \sum_K \tfrac{1}{2}l_p(l_p+1)\mathcal{Z}^{(0)}_K P_K(\mu), \end{aligned} \tag{34}$$

using the shorthand notations $\mathcal{Z}^{(p)}_{KLl'l} = \mathcal{Z}^{(p)}_K$ and $dP_K(\mu)/d\mu = P'_K(\mu)$.

If we now take the matrix elements of (33) and integrate by parts, (31) requires that

$$\begin{aligned} \mathcal{A}^{(p)}(l'l) &= -\mathcal{A}^{(p)}(ll')\,,\\ \frac{d}{d\mu}\mathcal{A}^{(p)}(l'l) &= \mathcal{B}^{(p)}(ll') - \mathcal{B}^{(p)}(l'l). \end{aligned} \tag{35}$$

These identities may be readily verified for particular cases of interest by expanding $\mathcal{A}^{(p)}$ and $d\mathcal{A}^{(p)}/d\mu$ in Legendre polynomials. In addition, we note that the coefficients $\mathcal{Z}^{(2)}$ and $\mathcal{A}^{(2)}$ may be inferred from symmetry once $\mathcal{Z}^{(1)}$ and $\mathcal{A}^{(1)}$ have been computed, since

$$\begin{aligned} \mathcal{Z}^{(1)}(l_1'l_2', l_1l_2) &= \mathcal{Z}^{(2)}(l_2'l_1', l_2l_1), \\ \mathcal{A}^{(1)}(l_1'l_2', l_1l_2) &= \mathcal{A}^{(2)}(l_2'l_1', l_2l_1). \end{aligned} \tag{36}$$

V. DISCRETIZATION ON A NUMERICAL LATTICE

We choose to represent Eqs. (25) on a discrete lattice of points in the space defined by the coordinates $\{r_1, r_2, \vartheta\}$ by means of the basis-spline collocation method (BSCM). This technique has been applied with success to the solution of the Schrödinger [3, 4] and Dirac [5, 6] equations in three Cartesian coordinates in the context of ion-atom and relativistic ion-ion collisions, so its application to a similar equation in another three-dimensional space is straightforward. Experience has also been gained previously [7]–[9] in treatments of two-electron systems utilizing the traditional finite-element method and the time-dependent wave-packet approach. Since the theory and use of the BSCM has been described comprehensively in several papers [10–12], for completeness in the present discussion we only state the underlying postulates and final working equations here.

If we consider a function of a single variable, say x, then in a collocation method, an operator equation $\mathcal{O}(F(x)) = 0$ is discretized by expanding the continuous function $F(x)$ in a finite basis $u_k(x), k = 1, 2, \ldots, K$, i.e.,

$$F(x) \approx f(x) = \sum_k u_k c^k. \tag{37}$$

The coefficients c^k in this approximate solution are determined by setting $\mathcal{O}(\sum_k u_k c^k) = 0$ at N so-called collocation points ξ_α, $\alpha = 1, 2, \ldots, N$. That is, we require the residual, defined by

$$\begin{aligned} R(x) &= \mathcal{O}\left(\sum_k u_k(x) c^k\right) \\ &= \sum_k (\mathcal{O} u_k(x)) c^k, \end{aligned} \tag{38}$$

to be zero at the set of points $\{\xi_\alpha\}$ (see, e.g., [12]). In practice, each function is localized around a small subset of these points, and the coefficients are eliminated in favor of the values of the solution at the points ξ_α, $f(\xi_\alpha)$.

To do this, we define a matrix $\mathbf{B}$ whose rows are the vectors composed of the basis functions evaluated at the collocation points,

$$B_{k\alpha} = u_k(\xi_\alpha), \tag{39}$$

and its inverse

$$B^{\alpha k} = [\mathbf{B}^{-1}]_{\alpha k}. \tag{40}$$

Then, we may solve for the coefficients,

$$c^k = \sum_\alpha B^{\alpha k} f(\xi_\alpha), \tag{41}$$

and define

$$\tilde{B}_{k\beta} = \mathcal{O} u_k(x)|_{x=\xi_\beta}. \tag{42}$$

Thus we may replace the operator $\mathcal{O}$ by a matrix $\mathbf{O}$ whose elements are

$$[\mathbf{O}]_\alpha^\beta = \tilde{B}_{\alpha k} B^{k\beta} \tag{43}$$

with a summation implied over the repeated index.

For example, a local operator, say $L = V(x)$, becomes a diagonal matrix

$$[L]_\alpha^\beta = V(\xi_\alpha) \delta_\alpha^\beta, \tag{44}$$

and the first spatial derivative takes the form

$$[D]_\alpha^\beta = B'_{\alpha k} B^{k\beta} \tag{45}$$

where

$$B'_{\alpha k} = \frac{d}{dx} u_k(x)|_{x=\xi_\alpha}. \tag{46}$$

The spline basis, and hence the matrix $\mathbf{O}$, incorporates the boundary conditions which are usually linear relations between $F(x)$ and its derivatives. The resulting equations have the structure of finite difference algorithms, but employ flexible interpolating functions. We choose localized piecewise continuous polynomials, known as *basis splines*, as the most suitable functions with which to carry out these expansions, and hence the name BSCM.

Applying this method to the problem at hand, the solutions of (25) are thus expanded in products of splines,

$$\psi_l(r_1, r_2, \vartheta) = \sum_{i,j,k} c_{ijkl} u_i(r_1) u_j(r_2) w_k(\vartheta). \tag{47}$$

The same splines u_i and collocation points ξ_α are used for the dependence on r_1 and r_2 since these coordinates always stand on the same footing. However, different splines w_k and points η_γ are required for the dependence on ϑ. In addition, each set of splines is constructed so as to incorporate appropriate boundary conditions. The radial functions $u_i(r) \sim r - Cr^2$ as $r \to 0$ and thus we arrange that u_i satisfies

$$u_i(0) = 0, \quad u_i'(0) \neq 0. \tag{48}$$

Regarding the dependence on ϑ, we note that near $\vartheta = 0$, the expansion $\psi \sim a + b\vartheta + \cdots$ fits the two-body cusp $\psi \sim c(1 + \frac{1}{2} r_{12})$. Near $\vartheta = \pi$, the correct expansion is $\psi \sim a' + b'(\pi - \vartheta)^2$. These conditions are satisfied if $w_k(\vartheta)$ is a polynomial in the variable ϑ, as opposed to $\cos\vartheta$, such that

$$\begin{aligned} &w_k(0) \neq 0, \quad w_k'(0) \neq 0, \\ &w_k(\pi) \neq 0, \quad w_k'(\pi) = 0. \end{aligned} \tag{49}$$

The collocation principle is applied as described to obtain the equations satisfied by the vector of $\psi_{\alpha\beta\gamma l} = \psi_l(r_1 = \xi_\alpha, r_2 = \xi_\beta, \vartheta = \eta_\gamma)$ on the collocation lattice. Operators become matrices in this space in accordance with (43). The potential energy, and indeed any local function of r_1, r_2, ϑ, is diagonal in the indices α, β, γ. Each term in the kinetic energy is a sparse block matrix. For example, $\mathcal{T}_1$ has the structure $t_{\alpha\alpha'}\delta_{\beta\beta'}\delta_{\gamma\gamma'}$. This extreme sparseness gives the collocation method an advantage, particularly in three dimensions, over other formulations, such as that of Galerkin. That is, in regard to computer memory requirements, since we do not wish to store its full matrix representation, it is preferable that the Hamiltonian be sparse. Thus, all algorithms are broken down into canonical operations of the form "(matrix)×(vector) ⟶vector," where the matrix need only be represented implicitly by its nonzero blocks.

In order to derive and display the explicit representation of (27) in addition to the matrices $B_{k\alpha}$ and $B'_{k\alpha}$, we introduce the matrices

$$\begin{aligned} B''_{k\alpha} &= u''_k(\xi_\alpha), \quad D_{j\gamma} = w_j(\eta_\gamma), \\ D'_{j\gamma} &= w'_j(\eta_\gamma), \quad D''_{j\gamma} = w''_j(\eta_\gamma), \end{aligned} \tag{50}$$

where the primes denote derivatives with respect to the argument. Then the required terms in (23) and (26) are given by

$$\begin{aligned} [h_1]_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} &= [\mathcal{T}_1]_{\alpha\alpha'}\delta_{\beta\gamma l,\beta'\gamma' l'} \\ &\quad + \left[-\frac{C}{\xi_\alpha} + \frac{l_1(l_1+1)}{2\xi_\alpha^2}\right]\delta_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} \\ [h_2]_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} &= [\mathcal{T}_2]_{\beta\beta'}\delta_{\alpha\gamma l,\alpha'\gamma' l'} \\ &\quad + \left[-\frac{C}{\xi_\beta} + \frac{l_1(l_1+1)}{2\xi_\beta^2}\right]\delta_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} \\ [h_\vartheta]_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} &= (\xi_\alpha^{-2} + \xi_\beta^{-2})[\mathcal{T}_\vartheta]_{\gamma\gamma'}\delta_{\alpha\beta l,\alpha'\beta' l'} \\ [\mathcal{U}^{(1)}]_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} &= -\frac{\mathcal{X}_{ll'}^{(1)}}{\xi_\alpha}[\mathcal{D}_\vartheta]_{\gamma\gamma'}\delta_{\alpha\beta,\alpha'\beta'} \\ [\mathcal{U}^{(2)}]_{\alpha\beta\gamma l,\alpha'\beta'\gamma' l'} &= -\frac{\mathcal{X}_{ll'}^{(2)}}{\xi_\beta}[\mathcal{D}_\vartheta]_{\gamma\gamma'}\delta_{\alpha\beta,\alpha'\beta'}, \end{aligned} \tag{51}$$

where the kinetic-energy matrices are

$$\begin{aligned} [\mathcal{T}_1]_{\alpha\alpha'} = [\mathcal{T}_2]_{\alpha\alpha'} &= -\frac{1}{2}B^{k\alpha}B''_{k\alpha'}, \\ [\mathcal{T}_\vartheta]_{\gamma\gamma'} &= -\frac{1}{2}D^{j\gamma}[D''_{j\gamma'} + \cot\eta_\gamma D'_{j\gamma'}], \\ [\mathcal{D}_\vartheta]_{\gamma\gamma'} &= D^{j\gamma}D'_{j\gamma'}. \end{aligned} \tag{52}$$

We note that the collocation representation of the Hamiltonian is not always self-adjoint (i.e., the kinetic-energy matrices are not symmetric), since the grid spacing on the numerical lattice may be chosen to be nonuniform. Such nonuniform spacing is particularly useful for situations like ionization, which, of necessity, involve the long-ranged aspect of the Coulomb interaction. In these cases, there is more than one natural length scale in the problem, and we require the fidelity of representation of the wave function and the forces over these varying scales. However, this must be balanced against the practical need to reduce the density of interpolating functions in the asymptotic regions. Another practical consequence of the Hamiltonian not being self-adjoint is that both the normal and adjoint solutions must be carried along together so that norms and inner products may be properly defined.

To do this, we have opted to compute both these wave functions, that is, to solve both

$$(\mathbf{H} - E)\mathbf{\Psi} = \mathbf{0} \tag{53}$$

and

$$(\mathbf{H}^T - E)\mathbf{\Phi} = \mathbf{0} \tag{54}$$

so that the vectors $\mathbf{\Psi}$ and $\mathbf{\Phi}$ are biorthogonal. Therefore,

$$\langle \mathbf{\Phi}^T | \mathbf{\Psi} \rangle = 1 \tag{55}$$

and expectation values of local operators are given by

$$\langle L \rangle = \langle \mathbf{\Phi}^T | L | \mathbf{\Psi} \rangle. \tag{56}$$

Though this procedure is implemented in our computer codes, we are presently pursuing the use of a unitary transformation technique which makes the problem self-adjoint. This alternate method would have the great practical benefit of eliminating the need to store the adjoint wave function and to solve both (53) and (54), reducing the memory requirements by a factor of 2 and the number of floating-point operations similarly by a factor of 2.

VI. PARTIAL LATTICE EIGENSOLUTION

Even with the significant (typically one to two orders of magnitude) reduction in the rank of the Hamiltonian made possible by using a basis spline approach rather than the technique of finite differences, direct complete eigensolution of the Hamiltonian matrix for realistic three-dimensional problems is not presently tractable. For low-lying bound states of helium, for example, where we typically require 50 to 100 basis splines in each coordinate, the rank of this matrix is typically on the order of 10^5 to 10^6 (i.e., $\mathcal{N} = N_{r_1}N_{r_2}N_\vartheta$). Consideration of higher bound states or rearrangements such as photoionization which result in the need to follow the evolution of one or both of the electrons in the continuum, necessitates larger spatial lattices and therefore presents matrices of even larger rank. Thus, traditional methods of diagonalizing a matrix which require on the order of $\mathcal{N}^2$ storage locations and $\mathcal{N}^3$ operations are not feasible.

We circumvent this situation by performing a partial eigensolution for particular states of interest, using the damped relaxation method, the details of which have been given previously [13], using the same underlying basis-spline expansion. In this case, we replace diagonalization with the repeated application of sparse matrix-vector multiplications whose computational effort is on the order of $\mathcal{N}$ operations on each iteration. Specifically, the ground-state eigenvector is found as the limit of the iterates Ψ_i, generated by

$$\Psi_{i+1} = \Psi_i - \nu\mathbf{D}(\mathbf{H} - E_0)\Psi_i, \tag{57}$$

where $\mathbf{D}$ is a damping operator and ν a constant. As described in Ref. [13], the basic form of $\mathbf{D}$ is a product of terms, one for each spatial dimension, of the basic form

$$D_n = \left(1 + \frac{\mathcal{T}_n}{\mu}\right)^{-1}, \quad n = 1,2,3, \tag{58}$$

where μ is another constant. Convergence of the processes is judged by the approach to zero of the fluctuation η, defined by

$$\eta^2 = \langle\Psi|(\mathbf{H} - \langle\mathbf{H}\rangle)^2|\Psi\rangle. \tag{59}$$

Typically, we require fluctuations to be at least as small as 10^{-6}. Thus, our procedure consists of first determining an appropriate trial state, usually a linear combination of product hydrogenic states, then iteratively applying the damping operator as in (57) until the fluctuation is below a certain preset limit. At each iteration the symmetry described in Sec. IV is enforced. Excited states may be computed by requiring orthogonality to previously determined lower-lying states.

For example, the expectation value of total energy for the ground state of helium as a function of damped relaxation iteration is shown in Fig. 1. The trial state in this case was a simple product of hydrogenic ground-state wave functions in r_1 and r_2. We see that the convergence is roughly exponential in the iteration and that it is towards the accurate value given by Pekeris [14]. The spatial mesh extended from 0 to 6 a.u. and 78, fifth-order basis splines were used in r_1, r_2, and ϑ, the calculation requiring approximately 100 min on a Cray-C90 computer. We are presently investigating a number of ways in which to improve the result further. For example, recent work has shown [12] that the use of higher-order splines can significantly improve the momentum spectrum on the lattice and therefore the representation of the wave function, with no additional increase in computational effort. Further, as we briefly described above, by eliminating the need to produce and carry the adjoint solution, a savings of one-half the total computational effort may be made, and therefore the number of mesh points could be doubled for the same computational cost as in the present case. Finally, improved calculation of the ground-state wave function or of other states can be accelerated greatly by using the present result as the new starting estimate.

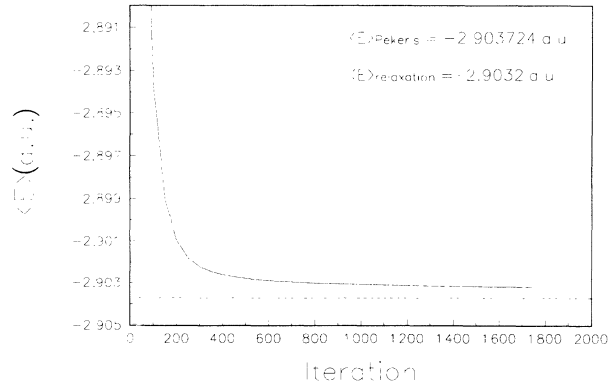

FIG. 1. The expectation value of total energy as a function of the iteration number for the relaxation of the trial wave function to the ground state of helium. The legend indicates the value obtained at the last iteration performed as well as the exact value due to Pekeris [14], which is also illustrated by the dashed horizontal line. The numerical mesh used to obtain this result is described in the text.

VII. EXAMPLES: He($1s^2\,{}^1S$, $1s2s\,{}^1S$, $1s2p\,{}^1P$)

To demonstrate the use of the present technique for other cases, we have also computed two singly excited states, He($1s2s\,{}^1S$) and He($1s2p\,{}^1P$). For each of these states we have used somewhat fewer basis functions (i.e., $58\times58\times58$) and extended the lattice to 12 a.u. to accommodate the larger spatial extent of these wave functions. Calculation of the $1s2s$ state proceeds by orthogonalizing the trial function to the lattice ground-state wave function at each iteration of the relaxation. For the $1s2p$ state, since it is the lowest state of ${}^1P$ symmetry, there are no states of like symmetry below it and there is no need to orthogonalize. To judge the reliability of the present method, we have compared in Table I the computed expectation value of total energy for these three states with well-known accurate values. One sees that the present results are accurate to between 0.2% to 0.5% relative error, while significant improvement should be fairly readily obtainable.

Plots of the probability density for the three states are shown in Figs. 2–4 and are instructive in that they illustrate some of the consequences of the correlation in these wave functions. These probability densities have been computed using the coefficients ψ_l in (6), for simplicity, and the full result would be obtained by first performing the sum including the appropriate coupled spherical harmonics. To do so would then necessitate a four-dimensional plot to illustrate the result, and it suffices here to illustrate the nature of the wave functions by displaying only the coefficients. For example, Fig. 2 shows for the ground state that the electrons are most likely to be found at equal radial distances, since the density is mostly peaked along the line $r_1 = r_2$, while the greatest probability is for the electrons to have an angle between their position vectors near π, owing to their mutual repulsion. In addition, for small values of ϑ, the density peaks on either side of this line $r_1 = r_2$, indicating that at small angular separations, one or the other electron

TABLE I. For each state of He considered here, the table lists the computed expectation value of total energy along with accurate reference values. The accurate values for the $1s^2$, $1s2s$, and $1s2p$ states are from Refs. [14], [15], and [16], respectively, as quoted in Ref. [17]. The expectation value of either radial coordinate is also tabulated. All quantities are in atomic units.

State	$\langle E\rangle_{\text{reference}}$	$\langle E\rangle$	$\langle r_{p=1,2}\rangle$
He($1s^2$) ${}^1S$	−2.903 72	−2.903 2	0.930
He($1s2s$) ${}^1S$	−2.145 97	−2.144 8	2.84
He($1s2p$) ${}^1P$	−2.123 84	−2.123 4	2.72

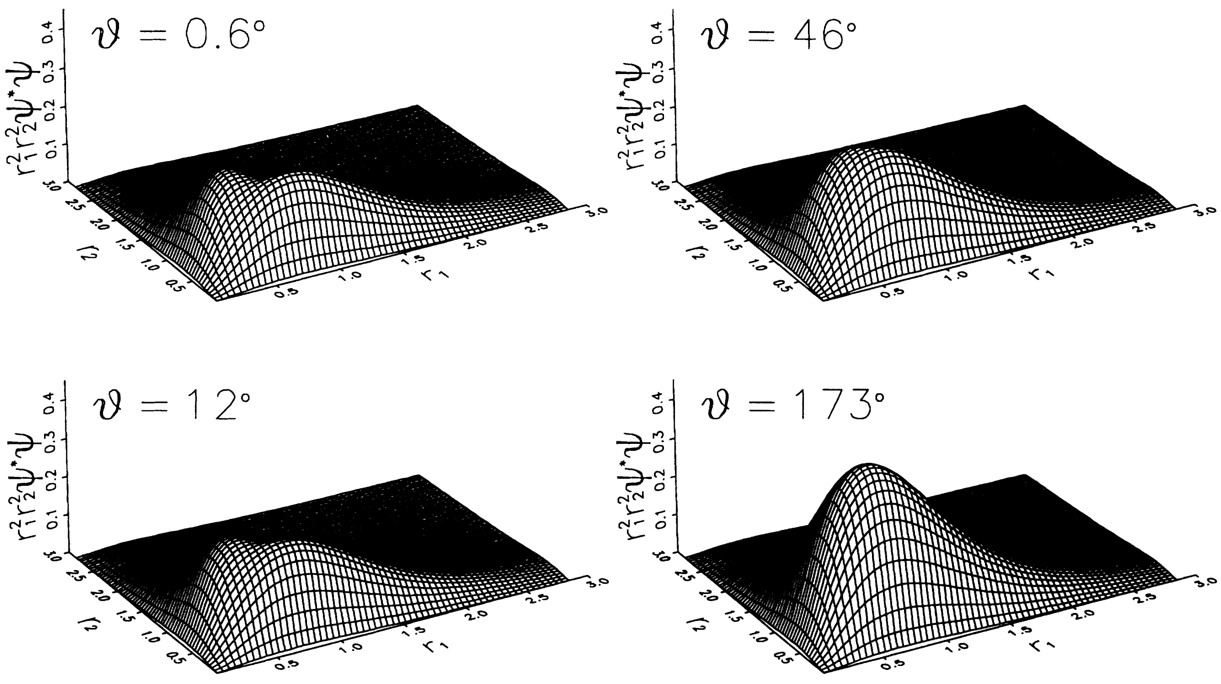

FIG. 2. The probability density for the ground state of helium computed using the expansion coefficient $\psi_0(r_1, r_2, \vartheta)$, for several values of ϑ. For this, or any, ^1S state, there is only one term in the expansion (6) and thus the quantity displayed need only be multiplied by the appropriate coupled spherical harmonic, in this case a constant, to obtain the probability density for the full wave function. All quantities are in atomic units.

is pushed inward (outward) from the other due to the repulsion.

For 1*snl* states, the manifestations of angular correlation are not as pronounced as when both electrons occupy the 1*s* orbital. This may be seen in Fig. 3 where the result for the 1*s*2*s* state is displayed. Here the radial correlation present results in the most probable configuration to be one in which one electron is close to the nucleus and one is relatively far away. For the 1*s*2*s* wave function, the magnitude of the peak near the nucleus for

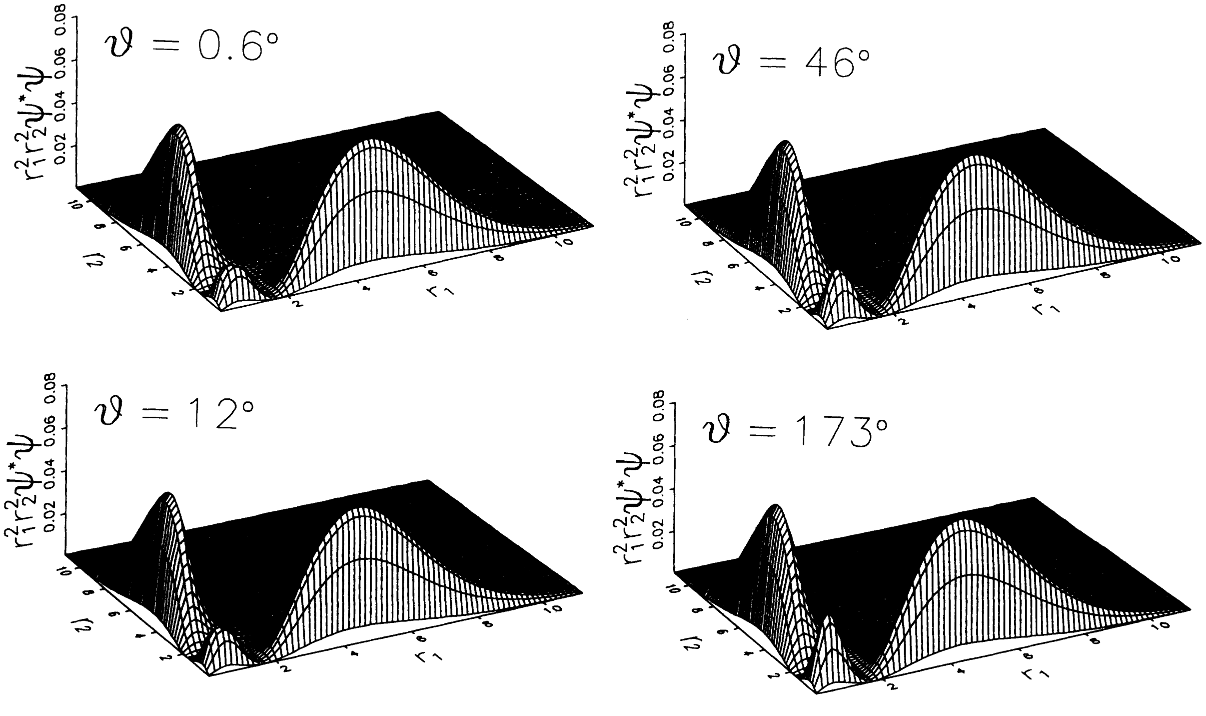

FIG. 3. The same as in Fig. 2 but for He(1*s*2*s* ^1S).

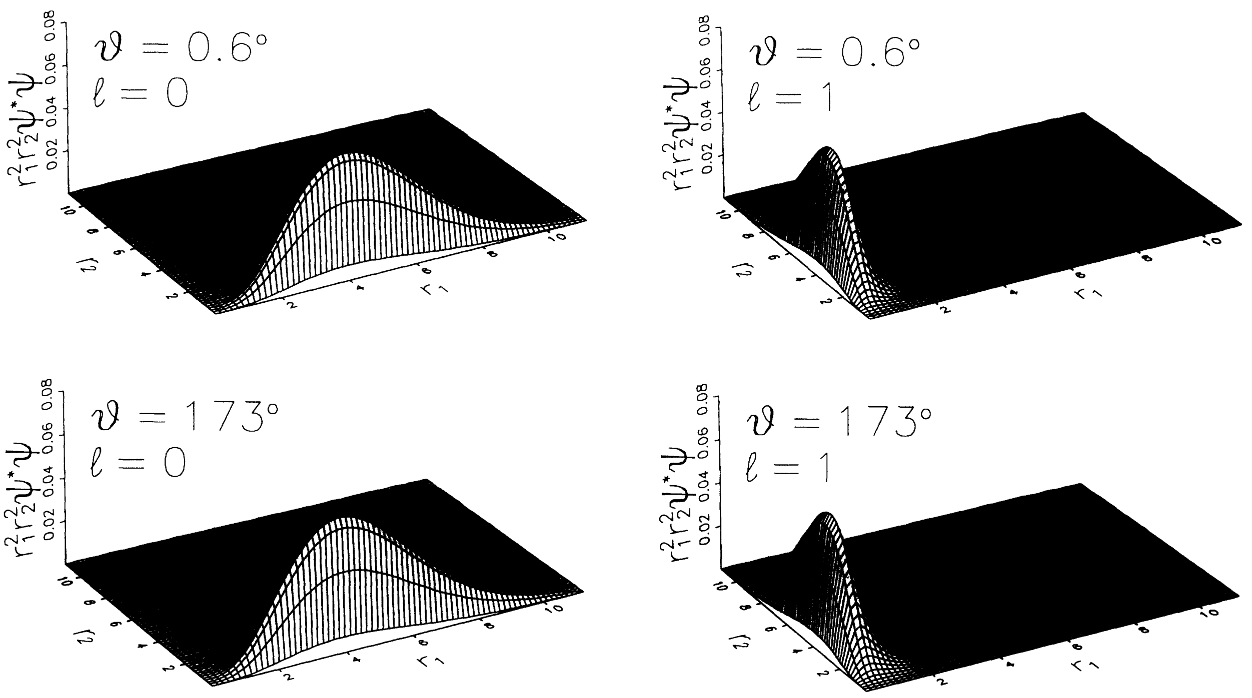

FIG. 4. The same as in Fig. 2 but for He($1s2p\,^1P$). In this case the expansion (6) has two terms, $l = 0, 1$.

$r_1 = r_2$ decreases with angular separation, as one would expect.

Whereas both the $1s^2\,^1S$ and $1s2s\,^1S$ wave functions require only a single term in the expansion (6); the $1s2p\,^1P$ requires two terms. These are displayed in Fig. 4. By examining the structures in this figure, one can see that along, say, r_1 the peak is narrow, while along the other coordinate it is quite broad. This reflects the relatively small spatial extent of the $1s$ part of the wave function and the larger extent of the $2p$ portion. The sum in coupled spherical harmonics then provides the proper combination of these features to represent the $1s2p\,^1P$ wave function. All these simple observations are clearly in accord with our intuitive picture of the consequences of the electron-electron interaction on the low-lying states of helium.

VIII. CONCLUSIONS

In order to treat a wide class of problems which depend crucially on the electron-electron interaction, including such phenomena as autoionization, double photoionization, and electron impact, we have developed a treatment which numerically solves the Schrödinger equation exactly for fully correlated two-electron wave functions of any symmetry. This has been accomplished by deriving an expansion in coupled spherical harmonics which terminates quickly and the corresponding coupled equations which determine the expansion coefficients. In addition, the discretization of the problem utilizing the basis-spline collocation method has been described, as well as the relaxation technique used for partial eigensolution on the lattice. The resulting three-dimensional representation of the Hamiltonian is sparse, which makes tractable operations such as this partial eigensolution and time propagation, which require repeated action of this matrix on wave functions. The accuracy of the procedure has been demonstrated for the ground state and two singly excited states of helium, and several other applications are presently in progress.

ACKNOWLEDGMENTS

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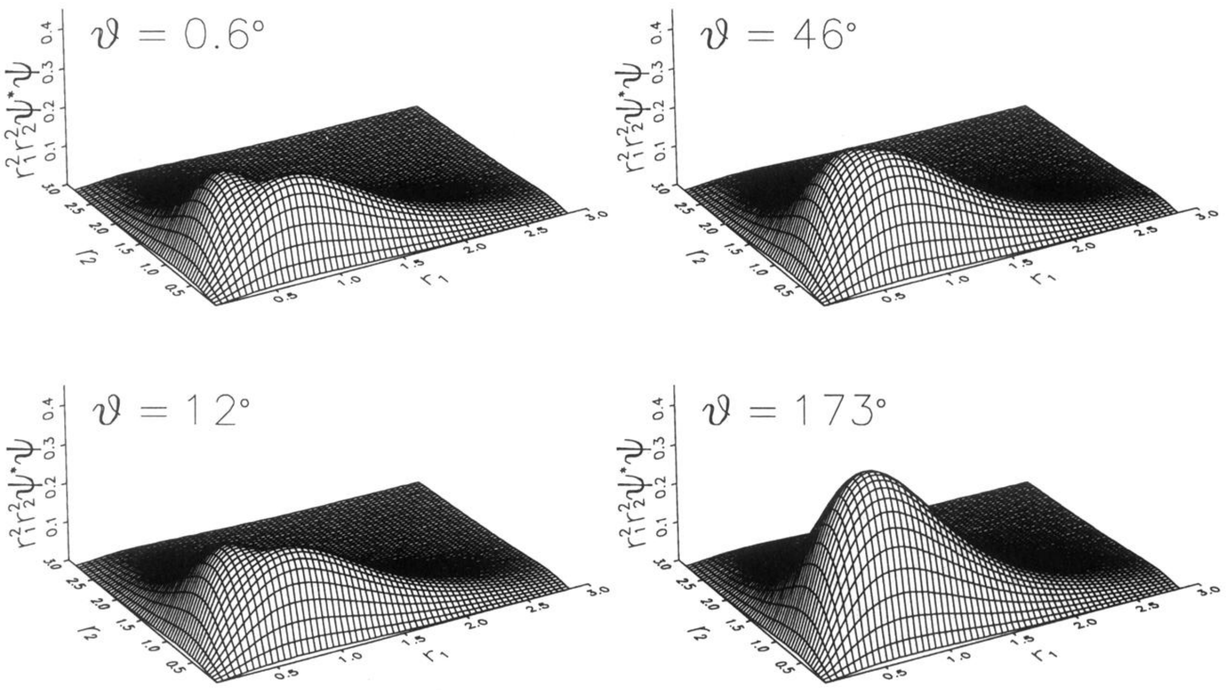


$\vartheta = 0.6°$

$\vartheta = 46°$

$\vartheta = 12°$

$\vartheta = 173°$

FIG. 2. The probability density for the ground state of helium computed using the expansion coefficient $\psi_0(r_1, r_2, \vartheta)$, for several values of ϑ. For this, or any, ^1S state, there is only one term in the expansion (6) and thus the quantity displayed need only be multiplied by the appropriate coupled spherical harmonic, in this case a constant, to obtain the probability density for the full wave function. All quantities are in atomic units.

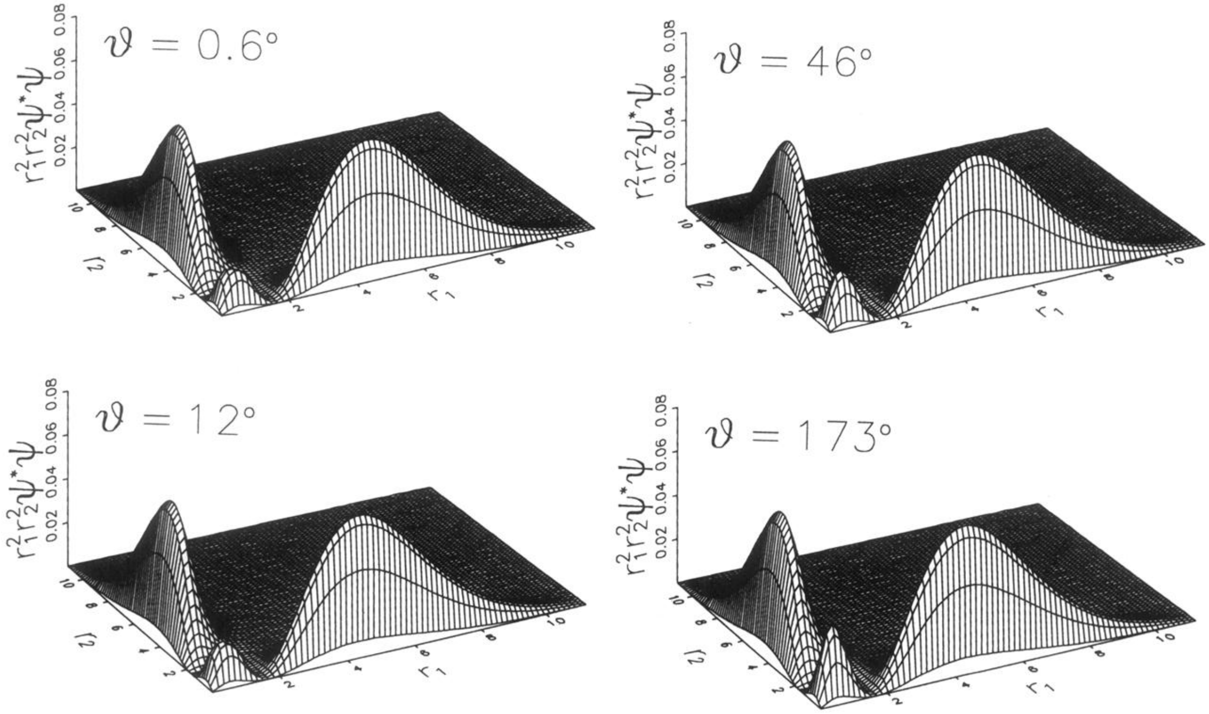
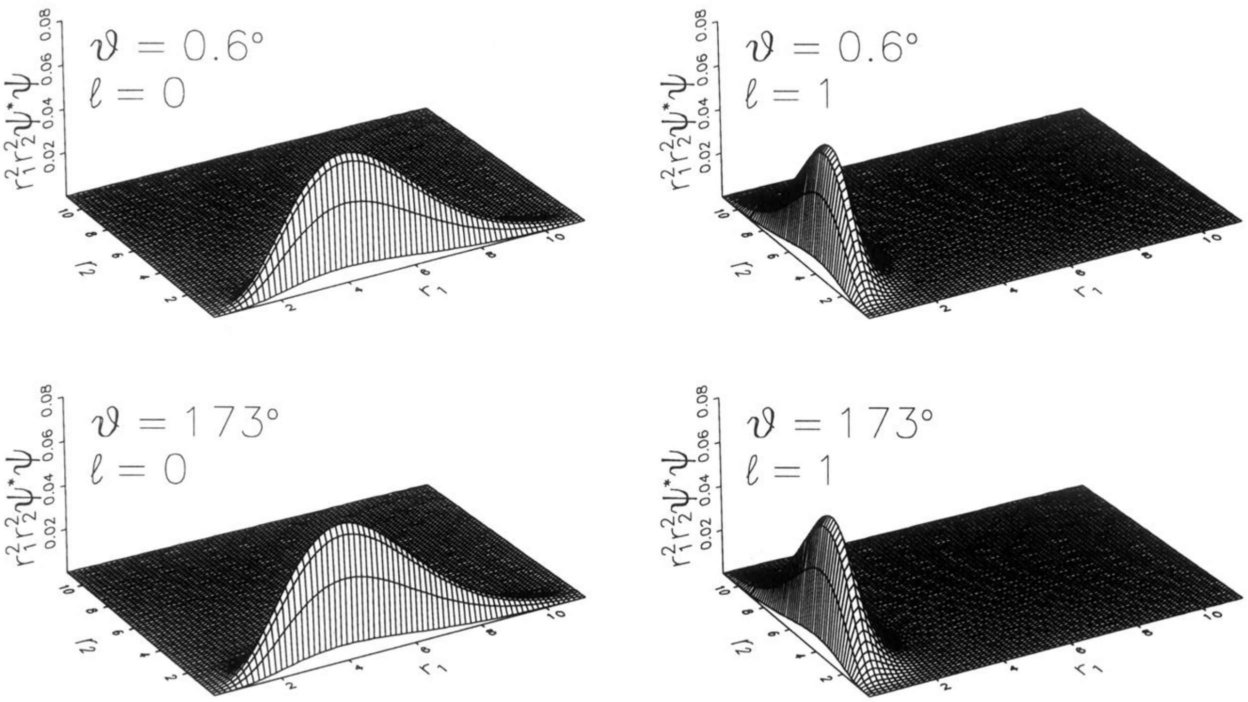


FIG. 3. The same as in Fig. 2 but for He($1s2s\,^1S$).



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