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# Exactly soluble two-electron atomic model

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For the class of "heliumlike" Hamiltonians,  $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V(r_1) + V(r_2) + W(r_{12})$ , there is a fortuitous choice of (attractive)  $V$  and (repulsive)  $W$  potentials such that the system admits of exact analytic solution in both classical and quantum pictures. Specifically, harmonic attraction and inverse-cube repulsion forces result in a soluble three-body problem (with infinite nuclear mass). We derive the general classical electron trajectories and give a complete set of eigenfunctions of the Hamiltonian. We indicate how exact expectation values can be obtained and show that best fits to actual helium data require a nonzero repulsive coupling constant. We exhibit an  $s$ -state basis subset of wave functions, suitable for application to general problems of atomic and chemical physics.

## I. INTRODUCTION

The celebrated unsolved helium problem, which in its simplest form is to find eigenvalues of the two-electron Hamiltonian

$$H = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \quad (1.1)$$

has a vast literature.<sup>1</sup> Unfortunately, the treatments providing most accurate approximation results are patently numerical, and convey little physical intuition. Some investigators have considered lower-dimensional analogs of the helium system in order to reduce the numerical task, but these simple models are often themselves insoluble.<sup>2,3</sup> It is possible to develop a full three-dimensional (that is, six electron coordinates) heliumlike model allowing exact solution. Consider Hamiltonians of the generalized "helium" form

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + W(r_{12}), \quad (1.2)$$

where the potential  $V$  is attractive and the potential  $W$  is repulsive. It is a delightful fact that a fortuitous choice of potentials can be made such that the resulting "atom" admits of exact solution. Specifically, the choice

$$V(r) = \frac{1}{2}m\omega^2 r^2, \quad (1.3)$$

$$W(r_{12}) = \lambda / r_{12}^3; \quad \lambda > 0,$$

corresponding to harmonic electron-nucleus binding force and inverse-cube electron-electron repulsion force, renders the Schrödinger equation for (1.2) exactly soluble. Not surprisingly, the classical picture is also tractable, and is interesting in its own right.

The system (1.2) with the specific choice (1.3) allows us to do various atomic calculations we would surely like to do for real-world atoms. The exact calculations we can perform for the soluble "atom" do convey some intuition about atomic states in general. There is also the possibility, as we discuss in Sec. V, of using the complete solution as an expansion basis for general atomic problems.

## II. THE CLASSICAL SOLUTION

The potentials (1.3) have a mechanical interpretation as shown in Fig. 1. Two electrons are connected to the origin by Hooke springs, but the electrons themselves are connected via a nonlinear device having inverse-cube force

properties. The classical Lagrangian is

$$\mathcal{L} = \frac{1}{2}m(\dot{\mathbf{r}}_1^2 + \dot{\mathbf{r}}_2^2) - \frac{1}{2}m\omega^2(r_1^2 + r_2^2) - \lambda / (r_1 - r_2)^2. \quad (2.1)$$

A certain six-dimensional rotation in the full coordinate space brings this Lagrangian into a separated form. If we define

$$\mathbf{r}_1 = (\mathbf{u} + \mathbf{v})/\sqrt{2} \quad \text{and} \quad (2.2)$$

$$\mathbf{r}_2 = (\mathbf{u} - \mathbf{v})/\sqrt{2},$$

then (2.1) becomes the sum of two independent Lagrangians:

$$\mathcal{L} = \mathcal{L}_u + \mathcal{L}_v = \frac{1}{2}m\dot{\mathbf{u}}^2 - \frac{1}{2}m\omega^2\mathbf{u}^2 + \frac{1}{2}m\dot{\mathbf{v}}^2 - \frac{1}{2}m\omega^2\mathbf{v}^2 - \lambda / 2v^2. \quad (2.3)$$

The trajectories  $\mathbf{u}(t)$  and  $\mathbf{v}(t)$  solve independent central-force problems: There will be two planes of motion on which  $\mathbf{u}$ ,  $\mathbf{v}$  will trace orbits that conserve respective angular momenta. Let  $(u, \phi)$  and  $(v, \theta)$  denote planar polar coordinates for the respective orbit problems. Denoting the conserved angular momenta by  $L_u, L_v$ , we obtain equations of motion from (2.3) as

$$\dot{\phi} = L_u / mu^2; \quad \ddot{u} = -\omega^2 u + L_u^2 / m^2 u^3, \quad (2.4)$$

$$\dot{\theta} = L_v / mv^2; \quad \ddot{v} = -\omega^2 v + (L_v^2 + m\lambda) / m^2 v^3. \quad (2.5)$$

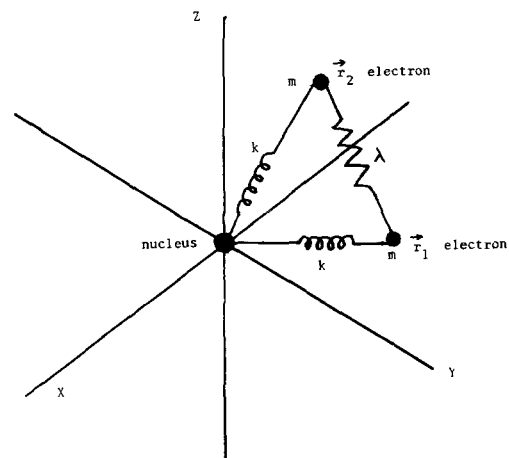


Fig. 1. Schematic for exactly soluble atomic model. Two electrons are connected to an infinite-mass nucleus by Hooke springs, but repel each other via an inverse-cube-force device.

The  $\mathbf{u}(t)$  motion is standard, two-dimensional simple-harmonic motion so that  $\mathbf{u}(t)$  describes an ellipse centered at the origin. The general  $u$  orbit may be expressed in terms of the semiaxes  $a, b$  and reference angle  $\phi_0$ :

$$u(\phi) = \frac{ab}{[b^2 \cos^2(\phi - \phi_0) + a^2 \sin^2(\phi - \phi_0)]^{1/2}}. \quad (2.6)$$

The orbit has angular momentum

$$L_u = m\omega ab \quad (2.7)$$

and total energy (with respect to the Lagrangian  $\mathcal{L}_u$ )

$$E_u = \frac{1}{2}m\omega^2(a^2 + b^2). \quad (2.8)$$

Thus, the orbital shape may be parametrized in an equivalent manner by the constants  $(E_u, L_u)$ . It is easy to show that  $2\pi/\omega$  is the temporal period of the orbital motion (2.6).

It is interesting that the preceding brief review of the two-dimensional oscillator is enough to allow immediate solution of the motion for the Lagrangian  $\mathcal{L}_v$ . The key observation is that under *angular dilation* of the  $v$  orbit's polar angle

$$\theta \rightarrow \theta' = \theta \sqrt{1 + m\lambda/L_v^2}, \quad (2.9)$$

the system (2.5) is formally identical to the oscillator (2.4), but with the angular momentum constant of the latter system modified to the number  $\sqrt{L_v^2 + m\lambda}$ . It is to be stressed that this new number is a formal device: The true angular momentum of the  $v$  orbit is just  $L_v$ . We infer that the general  $v$  orbit is described, for some  $A, B, \theta'_0$ , by

$$V(\theta') = \frac{AB}{[B^2 \cos^2(\theta' - \theta'_0) + A^2 \sin^2(\theta' - \theta'_0)]^{1/2}} \quad (2.10)$$

together with angular momentum and energy relations

$$L_v = \sqrt{m^2\omega^2 A^2 B^2 - m\lambda}, \quad (2.11)$$

$$E_v = \frac{1}{2}m\omega^2(A^2 + B^2).$$

The orbit (2.10) is a precessing ellipse because of the dila-

tion (2.9). It can be shown that the temporal behavior of the angle  $\theta$  is

$$\theta(t) - \theta(t_0) = (1 + m\lambda/L_v^2)^{-1/2} \times \tan^{-1}[(L_v/m\omega A^2) \tan \omega t], \quad (2.12)$$

implying that in one temporal period,  $t - t_0 = 2\pi/\omega$ , the  $v$  orbit precesses by the amount

$$\Delta\theta = 2\pi \left( \frac{1}{\sqrt{1 + m\lambda/L_v^2}} - 1 \right). \quad (2.13)$$

The complete solution for the classical "atom" defined by the assignment (1.3) is to be obtained from the inverse transformation

$$\mathbf{u} = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}, \quad (2.14)$$

$$\mathbf{v} = (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2},$$

together with the preceding orbit equations. It is to be remembered that the  $u$  plane, on which  $\mathbf{u}(t)$  describes its ellipse, is completely independent from the  $v$  plane, on which a precessing ellipse occurs. The total angular momentum

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2 = m\mathbf{r}_1 \times \dot{\mathbf{r}}_1 + m\mathbf{r}_2 \times \dot{\mathbf{r}}_2 = \mathbf{L}_u + \mathbf{L}_v \quad (2.15)$$

is conserved, as is the total energy

$$E = E_1 + E_2 = E_u + E_v. \quad (2.16)$$

An interesting phenomenon occurs for  $L_v = 0$ , in which case the precession (2.13) is  $-2\pi$  per temporal period; that is,  $\mathbf{r}_1 - \mathbf{r}_2$  has fixed direction. Indeed, a subcase of this anomaly is the situation in which the two electrons are stationary and diametrically opposed, having the nonlinear repulsion exactly balanced by the Hooke springs.

Figure 2 shows the typical complex motion of  $\mathbf{r}_1$  and  $\mathbf{r}_2$  electron positions. Figure 3 shows the same motion, but in terms of the  $\mathbf{u}, \mathbf{v}$  vectors. Evidently, the  $u, v$  picture greatly simplifies the approach to exact solutions. This will also be true for the quantum-mechanical case, to which we now turn.

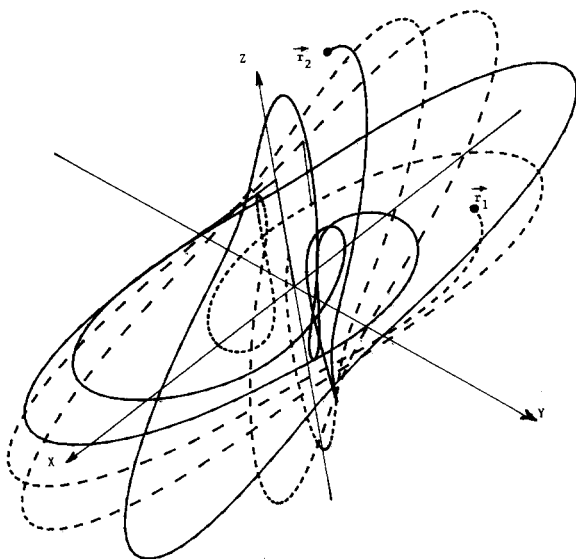


Fig. 2. Typical classical trajectories  $\mathbf{r}_1$  and  $\mathbf{r}_2$  for the electrons. Motion is complicated in appearance, as the electrons tend to avoid close encounters.

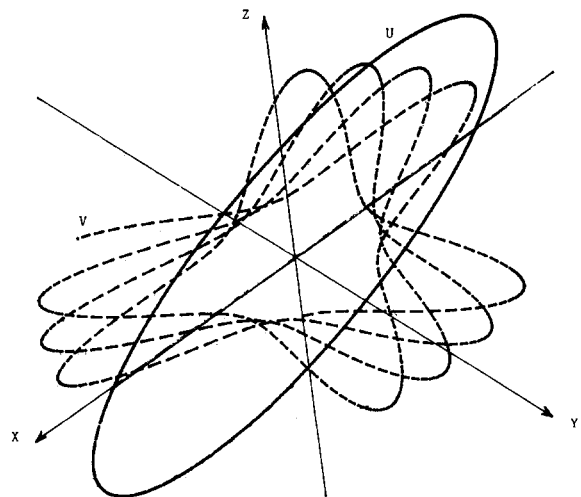


Fig. 3. Classical motion of Fig. 2, but plotted in  $u-v$  space. The  $u$  motion is always a planar ellipse, while the  $v$  motion is always a precessing planar ellipse. The inherent simplicity of the  $u-v$  dynamics makes possible exact classical and quantum solutions.

### III. THE QUANTUM-MECHANICAL SOLUTION

The Hamiltonian (1.2) for the specific potentials (1.3) yields, in units where  $\hbar = m = 1$ , the dimensionless Schrödinger equation

$$E\psi = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2)\psi + \frac{1}{2}\omega^2(r_1^2 + r_2^2)\psi + \frac{\lambda\psi}{(\mathbf{r}_1 - \mathbf{r}_2)^2} \quad (3.1)$$

for the wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$ .

The equation (3.1) is separable by the same technique as used for the classical approach. The transformation

$$\mathbf{u} = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}, \quad (3.2)$$

$$\mathbf{v} = (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2},$$

allows us to assume  $\psi = U(\mathbf{u})V(\mathbf{v})$  and obtain two Schrödinger equations,

$$FU = (-\frac{1}{2}\nabla_u^2 + \frac{1}{2}\omega^2 u^2)U, \quad (3.3)$$

$$GV = \left(-\frac{1}{2}\nabla_v^2 + \frac{1}{2}\omega^2 v^2 + \frac{\lambda}{2v^2}\right)V,$$

with total eigenvalue  $E = F + G$ . As in the classical approach, we shall be able to solve the  $v$  system by inspecting the standard analysis for the well-known simple harmonic  $u$  system.

Denote spherical coordinates  $(u, \theta_u, \phi_u)$  and  $(v, \theta_v, \phi_v)$  for the separated systems (3.3). The  $u$  system admits of the well-known three-dimensional eigenfunction solutions<sup>4</sup>

$$U_{n'l'm'}(\mathbf{u}) = e^{-\omega u^2/2} L_n^{l'+1/2}(\omega u^2) Y_{l'm'}(\theta_u, \phi_u), \quad (3.4)$$

where the  $Y_{l'm'}$  are spherical harmonics,  $L_n^a$  is the associated Laguerre polynomial, and the quantum numbers take on values

$$n', l' = 0, 1, 2, 3, \dots, \quad (3.5)$$

$$m' = -l', \dots, +l'.$$

It is to be stressed that there is no constraint, in the representation (3.4), between  $l'$  and  $n'$ : both can take on non-negative integer values independently. The eigenvalues for the state  $U_{n'l'm'}$  are  $m'$  independent:

$$F_{n'l'} = (\omega/2)(4n' + 2l' + 3), \quad (3.6)$$

showing the energy degeneracy standard to the three-dimensional oscillator. The spherical-coordinate eigenfunctions together with the eigenvalues (3.6) completely solve the  $u$  system, so we now turn to the  $v$  system.

Recall that in the classical picture, the  $v$  system was solved quickly by formal replacement of centrifugal acceleration terms in (2.4). That is, we took the closed-ellipse orbit solution for the  $u$  system and made the replacement [Eq. (2.9) and discussion following]:

$$L_u^2 \rightarrow L_v^2 + m\lambda. \quad (3.7)$$

In the quantum picture, the correct procedure is to use the oscillator eigenfunctions (3.4) but with the replacement

$$l'(l' + 1) \rightarrow l(l + 1) + \lambda \quad (3.8)$$

for the *radial* part of these functions. The index  $l'$  for the spherical harmonic in (3.4) will, however, become just an integer  $l$ . This is all analogous to the classical situation for which  $L_v$  is still the physical angular momentum even though the formal replacement (3.7) solves the radial motion problem. All of these remarks take on more meaning

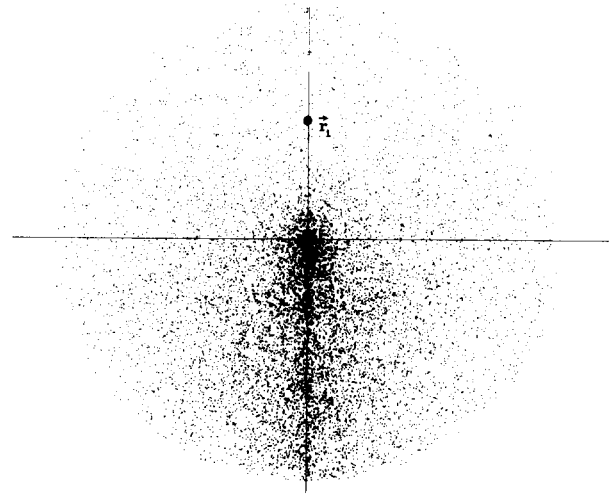


Fig. 4. Plot of the ground-state probability density  $|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$  for electron 2, with electron 1 fixed as indicated. The repulsion tendency is evident.

when one traces through the standard textbook argument for the derivation of (3.4) and at the appropriate juncture makes the replacement (3.8) in the centrifugal term of the radial equation for the  $v$  system.

The eigenfunctions for the  $v$  system can now be written down immediately, using the definition

$$a = \frac{1}{2}[\sqrt{1 + 4\lambda + 4l(l + 1)} - 1], \quad (3.9)$$

obtained by solving (3.8) for  $l'$  and calling this solution  $a$ . The functions are<sup>4</sup>

$$V_{nlm}(\mathbf{v}) = e^{-\omega v^2/2} L_n^a L_n^{a+1/2}(\omega v^2) Y_{lm}(\theta_v, \phi_v) \quad (3.10)$$

with quantum number constraints identical to (3.5) with primes removed. The eigenvalues appropriate to (3.10) are

$$G_{nl} = (\omega/2)(4n + 2a + 3), \quad (3.11)$$

so that except for very special values of  $\lambda$ , the harmonic oscillator degeneracy is removed by the repulsive coupling.

The Schrödinger equation (3.1) is completely solved by the wave functions

$$\psi_{nlm}^{n'l'm'}(\mathbf{r}_1, \mathbf{r}_2) = U_{n'l'm'}\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{\sqrt{2}}\right) V_{nlm}\left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{\sqrt{2}}\right), \quad (3.12)$$

possessing associated eigenvalues

$$E_{nl}^{n'l'} = (\omega/2)\{5 + 4n + 4n' + 2l' + [1 + 4\lambda + 4l(l + 1)]^{1/2}\}. \quad (3.13)$$

It is instructive to write out the ground state and its energy with units recovered. We have for some constant  $C$

$$\psi_{000}^{000}(\mathbf{r}_1, \mathbf{r}_2) = C e^{-m\omega r_1^2/2\hbar^2} e^{-m\omega r_2^2/2\hbar^2} r_{12}^{[(1 + 4\lambda m/\hbar^2)^{1/2} - 1]/2} \quad (3.14)$$

and energy

$$E_{00}^{00} = \frac{1}{2}\hbar\omega [5 + (1 + 4\lambda m/\hbar^2)^{1/2}]. \quad (3.15)$$

As expected, there is nontrivial  $r_{12}$  dependence on the ground-state wave function when  $\lambda$  is positive. Figure 4 shows the ground-state distribution for electron 2 if electron 1 is at the indicated fixed position of the plot, and  $a = 1$ . There is a clear tendency for electron 2 to lie opposite electron 1.

#### IV. EXACT ATOMIC CALCULATIONS

A positive feature of the soluble model is that various atomic calculations, such as those we would very much like to perform for real, physical atoms, are tractable. In particular, many expectation values can be obtained in closed form. We indicate in this section some simple examples of such calculations.

For wave functions depending only on  $u, v$ , and the relative angle  $\theta_{uv}$ , it suffices to perform expectation integrals with volume element  $u^2 du v^2 dv d \cos \theta_{uv}$ , since this element is proportional to  $d^3\mathbf{u} d^3\mathbf{v}$  which in turn equals  $d^3\mathbf{r}_1 d^3\mathbf{r}_2$  on the basis of the transformation (3.2). For such states the expectation of an operator  $O$  can be written

$$\langle O \rangle_\phi = \frac{\int \Phi^* O \Phi u^2 v^2 du dv d \cos \theta_{uv}}{\int \Phi^* \Phi u^2 v^2 du dv d \cos \theta_{uv}}. \quad (4.1)$$

What is the size of the soluble "atom?" This is measured in a certain sense by the square root of the following expectation value in the ground state:

$$\begin{aligned} \langle r_1^2 \rangle &= \langle r_2^2 \rangle = \left| \frac{(\mathbf{u} + \mathbf{v})^2}{2} \right| \\ &= \frac{M(4,2 + 2a) + M(2,4 + 2a)}{2M(2,2 + 2a)}, \end{aligned} \quad (4.2)$$

where we have used the ground-state wave function (3.14) in the form

$$\Phi(u, v) = e^{-\omega u^2/2} e^{-\omega v^2/2} v^a \quad (\hbar = m = 1) \quad (4.3)$$

and defined the integral

$$\begin{aligned} M(j, k) &= \int_0^\infty \int_0^\infty u^j v^k e^{-\omega u^2} e^{-\omega v^2} du dv \\ &= \frac{1}{4} \Gamma\left(\frac{j+1}{2}\right) \Gamma\left(\frac{k+1}{2}\right) \omega^{-(j+k)/2}. \end{aligned} \quad (4.4)$$

The result for the size of the ground state is

$$\sqrt{\langle r_1^2 \rangle} = \sqrt{(a+3)/2\omega}. \quad (4.5)$$

It is interesting that for large repulsion coupling constant  $\lambda$  we have

$$\text{atomic size} \sim \lambda^{1/4}. \quad (4.6)$$

In a similar manner, it is straightforward to compute additional expectations in the ground state:

$$\langle r_{12} \rangle = \sqrt{2} \langle v \rangle = \sqrt{\frac{2}{\omega}} \frac{\Gamma(a+2)}{\Gamma(a+3/2)}, \quad (4.7)$$

$$\langle r_{12}^2 \rangle = 2 \langle v^2 \rangle = (2a+3)/\omega.$$

The expectations (4.5) and (4.7) have been computed numerically for helium itself, to considerable accuracy.<sup>1(b)</sup> Using such helium data affords a method for "best approximation" using the soluble model. For example, taking the optimized values

$$a = 0.097, \quad (4.8)$$

$$1/\omega = 0.849,$$

we can construct a table (see Table I). The match of each expectation is within 10%. The soluble "atom" can, in this way, be made to approximate the helium system. It is to be stressed that some features of the helium atom can never be adequately approximated by the model. For one thing, the spectrum of energies for the soluble model is that charac-

Table I. Comparison of helium [Ref. 1(b)] and soluble model expectations.

Ground expectation	Helium	Soluble model with Eqs. (4.8)
$\langle r_1^2 \rangle$	1.1935	1.146
$\langle r_{12} \rangle$	1.4221	1.391
$\langle r_{12}^2 \rangle$	2.5164	2.712

teristic of a perturbed harmonic oscillator—for example, there are no continuum states in the soluble model. The interesting possibility remains, however, of treating the soluble model wave functions (3.12) as a basis set useful in variational calculations involving helium or more general systems. As a first approximation, we can ask, to what extent does the assignment (4.8) give a good trial function for the helium ground state energy? In order to answer the question, we must first obtain several more expectation values.

In particular, we require the expectations

$$\langle r_1^{-1} \rangle = \sqrt{2} \langle |\mathbf{u} + \mathbf{v}|^{-1} \rangle, \quad (4.9)$$

$$\langle r_{12}^{-1} \rangle = \frac{1}{\sqrt{2}} \langle v^{-1} \rangle = \sqrt{\frac{\omega}{2}} \frac{\Gamma(a+1)}{\Gamma(a+3/2)}.$$

The second of these is obtained in the style of (4.2), but the first is somewhat problematic. These more difficult expectations can be obtained as a consequence of the particular form for the soluble model eigenfunctions. Using (4.1) and performing the  $\theta_{uv}$  integrations, we have

$$\begin{aligned} \langle r_1^{-1} \rangle &= \frac{1}{\sqrt{2}M(2,2+2a)} \int_0^\infty \int_0^\infty uve^{-u^2} e^{-v^2} v^{2a} \\ &\quad \times (|u+v| - |u-v|) du dv. \end{aligned} \quad (4.10)$$

The term  $|u-v|$  is typical of Coulombic expectations and normally presents considerable difficulties for completion of the calculation. For the soluble model ground state, a powerful substitution in such problems is the choice

$$u = q \cos x, \quad (4.11)$$

$$v = q \sin x.$$

In other words, the first quadrant of the  $u-v$  plane is parametrized with polar coordinates, the variable  $x$  running from 0 to  $\pi/2$ . In this way the exact Coulombic expectation can be evaluated as

$$\langle r_1^{-1} \rangle = 2 \sqrt{\frac{2\omega}{\pi}} \frac{1}{2^{a+3/2}} [1 + (2a+3)2^{a+3/2} D(a)], \quad (4.12)$$

where the  $D$  function is given by

$$D(a) = \int_0^1 \frac{u^2 du}{(1+u^2)^{a+5/2}}. \quad (4.12')$$

It is easy to show that  $\langle r_1^{-1} \rangle \rightarrow 0$  as the repulsion coupling  $\lambda \rightarrow \infty$ . This is reasonable, since the electron separation must, by any appropriate measure, diverge in this limit. A more direct way to see this phenomenon is to note that

$$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle = \frac{1}{2} \langle u^2 - v^2 \rangle = -a/2\omega, \quad (4.13)$$

showing that the cosine of the mutual electron angle tends to be negative, as implied by Fig. 4.

The expectation calculations of this section can be used with the  $u-v$  form of the helium Hamiltonian (1.1),

$$H = -\frac{\hbar^2}{2m}(\nabla_u^2 + \nabla_v^2) - \frac{e^2\sqrt{8}}{|\mathbf{u} - \mathbf{v}|} - \frac{e^2\sqrt{8}}{|\mathbf{u} + \mathbf{v}|} + \frac{e^2}{v\sqrt{2}}, \quad (4.14)$$

to obtain the expectation of  $H$  in the soluble model ground state. In atomic units ( $\hbar = m = e = 1$ ),

$$\langle H \rangle = \frac{\omega}{2} \frac{5a+3}{2a+1} - 2^{2-a} \sqrt{\frac{\omega}{\pi}} - 8 \frac{2\omega}{\pi} (2a+3) D(a) + \frac{\Gamma(a+1)}{\Gamma(a+3/2)} \sqrt{\frac{\omega}{2}}. \quad (4.15)$$

The assignment (4.8), which gives a best fit for the helium expectation values, results in  $\langle H \rangle = -2.21$  a.u. ( $-61$  eV). The variational minimum of (4.15) is obtained with  $a \approx 0.092$  and  $\omega \approx 1.58$  giving

$$E_{\text{helium}} \leq -2.30 \text{ a.u. } (-62.8 \text{ eV}). \quad (4.16)$$

This is in error by about 20% of the accepted helium value,  $-2.90$  a.u. ( $-79$  eV).<sup>1(b)</sup> Though much simpler variational formulas, for example, those arising from products of hydrogenic functions, give much better results, there is an interesting feature of the soluble model calculation. The repulsion as measured by the parameter  $a$  is nontrivial in that there is a definite "best"  $a$  for the helium ground-state problem. It is evident that whether we attempt to match helium expectation values or to minimize  $\langle H \rangle$ , the repulsion parameter is to be nonzero. Apparently the most "heliumlike" soluble ground state is, in atomic units,

$$\psi_{000}^{000} \sim e^{-0.6(v_1^2 + v_2^2)} r_{12}^{0.09}. \quad (4.17)$$

It would be fruitful to determine how well variational bounds converge for the Hamiltonian (4.14) as more soluble model eigenfunctions are included in a trial expansion. We have not performed any calculations beyond the ones indicated above.

Another interesting feature of this model is that the transition moments can be calculated quite easily. For a two-electron system, the transition moment is given by the appropriate matrix element of<sup>5</sup>

$$\mathbf{r}_1 + \mathbf{r}_2 = \sqrt{2}\mathbf{u}. \quad (4.18)$$

However, since the states given by (3.10) are orthonormal, the matrix element (4.18) can be nonzero only when there is no change in the set of quantum numbers  $nlm$ ; i.e., there can be no transitions between different  $V$  states. Since the  $U$  states are simply the eigenstates for the three-dimensional isotropic harmonic oscillator, the selection rules for the model are the same as those for the oscillator, namely,

$$\begin{aligned} \Delta n' &= \pm 1, \\ \Delta l' &= \pm 1, \\ \Delta m &= 0, \pm 1. \end{aligned} \quad (4.19)$$

The transition moments can then be calculated easily using the properties of Laguerre polynomials.

## V. SOLUBLE MODEL BASIS SET

For the purpose of application to general atomic problems, it is useful to consider a subset of the complete eigenfunctions (3.12) that comprises an  $S$ -state basis. This will be a basis of functions  $\Phi_{n'l}^{n'}(u, v, \theta_{uv})$  that will allow expansion of arbitrary atomic  $S$  states in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \sum_{n,l,n'} A_{n'l}^{n'} \phi_{n'l}^{n'}. \quad (5.1)$$

A class of  $S$ -state basis functions can be constructed using the standard sum rule for spherical harmonics<sup>6</sup>:

$$P_l(\cos\theta_{uv}) = \frac{4\pi}{2l+1} \sum_{|m| \leq l} Y_{lm}^*(\theta_u, \phi_u) Y_{lm}(\theta_v, \phi_v). \quad (5.2)$$

We sum over the states of (3.12) having  $l = l'$  and  $m' = m$ , demanding that a normalization condition be satisfied:

$$\int \phi_{n_1 l_1}^{n_1'} \phi_{n_2 l_2}^{n_2'} u^2 v^2 du dv d \cos \theta_{uv} = \delta_{n_1}^{n_1'} \delta_{l_1}^{l_1'} \delta_{n_2}^{n_2'}. \quad (5.3)$$

Using the integral<sup>7</sup>

$$\begin{aligned} & \int_0^\infty t^2 e^{-t^2} t^{2a} L_n^{a+1/2}(t^2) L_n^{a+1/2}(t^2) dt \\ &= \frac{1}{2} \frac{\Gamma(a+n+3/2)}{\Gamma(n+1)} \end{aligned} \quad (5.4)$$

we arrive at an orthonormal  $S$ -state basis:

$$\begin{aligned} & \phi_{n'l}^{n'}(u, v, \theta_{uv}) \\ &= \frac{1}{\omega^{a+l+3}} \left( \frac{(4l+2)n!n!}{\Gamma(a+n+3/2)\Gamma(l+n+3/2)} \right)^{1/2} \\ & \quad \times u^l v^a e^{-\omega/2(u^2+v^2)} L_n^{a+1/2}(\omega v^2) L_n^{l+1/2}(\omega u^2) P_l(\cos \theta_{uv}). \end{aligned} \quad (5.5)$$

The set (5.5) may be used in calculations previously performed using, for example, the discrete Laguerre basis set.<sup>8</sup> As stated in the introduction, we anticipate certain advantages arising from the fact that  $\lambda$ , which is embedded in the number  $a$ , is an extra variational parameter. This supposition is borne out by the rudimentary calculations of Sec. IV. It would certainly be interesting to discover precisely to what extent the repulsive coupling has practical importance in the basis set (5.5).

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<sup>5</sup>H. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), p. 249.

<sup>6</sup>E. Jahmke and F. Emde, *Tables of Functions* (Dover, New York, 1945), p. 115.

<sup>7</sup>I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic, New York, 1965), Eq. 7.414.3.

<sup>8</sup>H. Shull and P. O. Löwdin, *J. Chem. Phys.* **30**, 617 (1959).