Perturbation Theory of the Hooke's Law Model for the Two-Electron Atom

Ronald White  
*Montana Tech of the University of Montana*

W. Byers Brown  
*University of Wisconsin - Madison*

Follow this and additional works at: [https://digitalcommons.mtech.edu/camp](https://digitalcommons.mtech.edu/camp)  
Part of the Chemistry Commons, and the Physics Commons

**Recommended Citation**  

This Article is brought to you for free and open access by the Faculty Scholarship at Montana Tech. It has been accepted for inclusion in Center for Advanced Mineral and Metallurgical Processing (CAMP) by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact sjuskiewicz@mtech.edu.
Perturbation Theory of the Hooke's Law Model for the Two-Electron Atom

Ronald J. White† and W. Byers Brown‡

Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin

(Received 11 June 1970)

The Hooke model for the two-electron atom replaces the electron-nuclear interaction by a harmonic oscillator potential, but retains the Coulomb repulsion of the electrons. The first-order perturbation equation for the electron repulsion is solved analytically, and the exact first-, second-, and third-order perturbation energies are obtained. A similar $Z^{-1}$ perturbation treatment is carried out for the Hartree-Fock equation and other variational approximations. The $Z^{-1}$ expansion of the correlation energy is compared with that for heliumlike atoms and found to be similar.

The problem of the helium atom has received much attention from the earliest days of quantum mechanics to the present. In spite of strenuous efforts by many eminent theoreticians, the analytical solution of the Schrödinger equation for this system has never been found. As Hylleraas first demonstrated, perturbation theory may be applied to this problem with $Z^{-1}$ providing a natural perturbation parameter but even the simpler inhomogeneous first-order perturbation equation has not been completely solved. The various solutions of the first-order equation would allow the calculation of the energy of any many-electron atom through third order in $Z^{-1}$.

When a problem appears to be too difficult mathematically to yield a frontal attack, it is almost traditional in statistical mechanics and other fields of applied mathematics to divert attention to a model which can be studied analytically. This procedure is not so fashionable in quantum mechanics, but has been used and frequently throws light on the actual problem. In this paper a model will be considered whose first-order equation is exactly soluble. This model retains the Coulomb repulsion term in the potential energy, but traps the two electrons near the origin (nucleus) by means of a Hooke's law force instead of the actual Coulomb force. The unperturbed wavefunction for the model is of Gaussian type instead of the actual exponential Slater type. The most important difference between these wavefunctions is presumably the absence of a cusp in the Gaussian function.

This model has been studied previously by Kestner and Sinanoğlu to throw light on the correlation problem in atoms. They reduced the problem to an ordinary differential equation which they integrated numerically for various values of the analog of the $Z$ (atomic number) parameter. The results for the lowest eigenvalue were then fitted to a $Z^{-1}$-type expansion through third order.

Tuan has applied this model to the actual helium atom by means of double perturbation theory. Her work represents an extension of some of the analytical procedures given in this paper.

The object of the present paper is to show that the first-order wavefunction may be found analytically in closed form, and hence the ground-state energy can be obtained exactly through third order.

**DESCRIPTION OF MODEL: HOOKE'S LAW ATOM**

The model considered, which may be called the **Hooke's law atom**, consists of two electrons attracted independently to an origin (nucleus) by a Hooke law of force, proportional to the distance, and repelling one another by the usual Coulomb law of force. The Hamiltonian for this model is

$$H = -\frac{\hbar^2}{2m}(\nabla^2 + \nabla^2) + \frac{1}{2}m\omega^2(r_1^2 + r_2^2) + \left(\frac{e^2}{r_{12}}\right),$$

where $m$ is the reduced mass of the electron, $\omega$ is the angular frequency of the electron-nucleus oscillator, $r_1$ and $r_2$ are the distances of electrons one and two from the nucleus, and $r_{12}$ is the distance between the electrons.

By introducing $\hbar\omega$ as the unit of energy and $(\hbar/m\omega)^{1/2}$ as the unit of length, the Schrödinger equation for the model can be reduced to the dimensionless form

$$\left[-\frac{1}{2} \left(\nabla^2 + \nabla^2\right) + \frac{1}{2} (r_1^2 + r_2^2) + \left(\lambda/r_{12}\right)\right]\Psi = E\Psi,$$

where $\lambda = \alpha/a$, the ratio of the oscillatory amplitude $\alpha = (\hbar/m\omega)^{1/2}$ to the Bohr radius $a = h^2/m\epsilon$. The Schrödinger equation for the actual two-electron atom in $Z$-reduced atomic units has the form

$$\left[-\frac{1}{2} \left(\nabla^2 + \nabla^2\right) - (r_1^{-1} + r_2^{-1}) + (Zr_{12})^{-1}\right]\Psi = E\Psi.$$

The model parameter $\lambda$ is therefore the analog of $Z^{-1}$, and will be used as the perturbation parameter; it corresponds to taking $\omega = Z^2$ in atomic units.

The similarity between the model and the actual atom is best seen from the point of view of perturbation theory. The unperturbed potentials seem very different, but in both cases they serve merely to hold the electrons in the vicinity of the nucleus with unperturbed ground-state wavefunctions $\exp\left[-(r_1^2 + r_2^2)\right]$ and $\exp\left[-(r_1 + r_2)\right]$, which are both monotonically decreasing.

Attention is focussed on the perturbing interaction of the electrons, which is governed by the same pertur-
bation potential. Since the actual Coulomb repulsion between the electrons is present, the usual cusp condition\(^5\) must be satisfied when the two electrons meet, namely
\[
\left[ \frac{\partial \Phi}{\partial r_2} (r_2 = 0) / \partial r_2 \right]_{r_1 + r_2} = \frac{1}{\lambda} \lambda \Phi (r_2 = 0). \tag{4}
\]
On the other hand, since the model potential is finite (zero) when either electron is at the nucleus, the usual electron–nucleus cusp conditions are replaced by
\[
\left[ \frac{\partial \Phi}{\partial r_1} (r_1 = 0) / \partial r_1 \right]_{r_2} = 0, \quad \left[ \frac{\partial \Phi}{\partial r_2} (r_2 = 0) / \partial r_2 \right]_{r_1} = 0, \tag{5}
\]
where \(\Psi\) represents an appropriate angular average of \(\Phi\).

### EXACT FIRST-ORDER TREATMENT

The orthogonal transformation
\[
\mathbf{q} = 2^{1/2}(\mathbf{r}_2 - \mathbf{r}_1), \quad \mathbf{R} = 2^{-1/2} (\mathbf{r}_1 + \mathbf{r}_1) \tag{6}
\]
separates Eq. (2) into the pair of equations
\[
\left[ -\frac{1}{2} \nabla^2 + \frac{1}{2} \mathbf{R}^2 \right] \chi = E \chi \tag{7}
\]
and
\[
\left[ -\frac{1}{2} \nabla^2 + \frac{1}{2} \rho^2 + \Lambda / \rho \right] \psi = E \psi, \tag{8}
\]
where
\[
\psi (r_1, r_2) = \chi (\mathbf{R}) \psi (\mathbf{q}), \quad \Lambda = 2^{-1/2} \lambda, \tag{9}
\]
and
\[
E = E_x + E_\nu. \tag{10}
\]
Equation (7) is simply the three-dimensional harmonic oscillator equation with ground-state solution
\[
\chi = \pi^{-3/4} \exp \left( -\frac{1}{2} \mathbf{R}^2 \right), \quad E_x = \frac{3}{2}. \tag{11}
\]
The potential in Eq. (8) is central and since we are interested in the 1s-type ground-state solution \(\psi\) is only a function of the radial coordinate \(\rho = r_2 / \sqrt{2}\). If the Hamiltonian operator of Eq. (8) is partitioned into an unperturbed part, \(H_0\),
\[
H_0 = -\frac{1}{2} \nabla^2 + \frac{1}{2} \rho^2 \tag{12}
\]
and a perturbation \(V\),
\[
V = 1 / \rho, \tag{13}
\]
then the usual Rayleigh–Schrödinger perturbation theory may be applied to the solution of Eq. (8). To first order the wavefunction is given by
\[
\psi = \psi_0 + \tilde{\Lambda} \psi_1 + O(\Lambda^2) \tag{14}
\]
and the corresponding energy is
\[
E_\nu = E_0 + \Lambda E_1 + \Lambda^2 E_2 + \Lambda^3 E_3 + O(\Lambda^4). \tag{15}
\]
The eigenvalue problem for \(\psi_0\) is identical with Eq. (7). The appropriate solution is therefore
\[
\psi_0 = \pi^{-3/4} \exp \left( -\frac{1}{2} \rho^2 \right), \quad E_0 = \frac{3}{2}. \tag{16}
\]
The inhomogenous equation for \(\psi_1\) is
\[
(H_0 - E_0) \psi_1 = - (V - E_1) \psi_0. \tag{17}
\]
If we require \(\psi_1\) to be orthogonal to \(\psi_0\), the perturbation energies are given by the following well-known expressions:
\[
E_1 = \langle \psi_0, V \psi_0 \rangle, \tag{18}
\]
\[
E_2 = \langle \psi_0, V \psi_1 \rangle, \tag{19}
\]
and
\[
E_3 = \langle \psi_1, (V - E_1) \psi_1 \rangle. \tag{20}
\]
Thus the first-order energy is
\[
E_1 = \langle \psi_0, \rho^{-\psi_0} \rangle = 2 \pi^{-1/2} = 1.12838. \tag{21}
\]
Since Eq. (17) is one-dimensional it can be integrated directly. If the form
\[
\psi_1 = F \psi_0 \tag{22}
\]
is assumed for \(\psi_1\) in Eq. (17), then the equation for \(F\) is
\[
(d/d \rho) [\rho \psi_0 (dF / d \rho)] = 2 \rho \psi_0 (V - E_1). \tag{23}
\]
This equation may immediately be integrated once to yield
\[
\rho \psi_0 (dF / d \rho) = M (\rho), \tag{24}
\]
where
\[
M (\rho) = 2 \int_0^\rho \psi_0^2 (s) \left( \frac{1}{s} - E_1 \right) s^2 ds = (E_1 \rho - 1) \psi_0^2 (\rho) + \pi^{-3/2} \text{erfc} \rho \tag{25}
\]
and where, by definition
\[
\text{erfc} \rho = 2 \pi^{-1/2} \int_\rho^\infty \exp (-s^2) ds. \tag{26}
\]
Let
\[
F = \tilde{F} (\rho) + F_0, \tag{27}
\]
where
\[
\tilde{F} (0) = 0 \tag{28}
\]
and \(F_0\) is an arbitrary constant determined by the orthogonality of \(\psi_1\) and \(\psi_0\),
\[
F_0 = -\langle \psi_0, F \psi_0 \rangle. \tag{29}
\]
Integration of Eq. (24) yields
\[
\tilde{F} = \int_0^\rho \frac{M (s)}{s^2 \dot{\psi}_0^2 (s)} ds = - \frac{M}{\rho \dot{\psi}_0^2} + \int_0^\rho s^{-1} \left( \frac{M}{s \dot{\psi}_0^2} \right) ds \tag{30}
\]
\[
= \rho^{-1} - E_1 - \frac{\exp (\rho^2)}{\rho} \text{erfc} \rho + 2 \int_0^\rho \exp (s^2) \text{erf} \rho \text{ds}. \tag{31}
\]
The function \(\tilde{F}\) may be expanded as the following power series in \(\rho\),
\[
\tilde{F} = \sum_{n=0}^\infty \frac{(-1)^n \pi^{2n} \rho^n}{n! (n+1)} \tag{32}
\]
whose first few terms are
\[
\tilde{F} = \rho - \frac{3}{2} \pi^{-1/2} \rho^2 + \frac{7}{8} \rho^3 - \frac{\pi}{16} \pi^{-1/2} \rho^4 + \cdots. \tag{33}
\]
In terms of $F$ and $\rho = 2^{-1/2}r_{12}$ the cusp conditions, Eqs. (4) and (5), for the first-order wavefunction take the form

$$ (dF/d\rho)_{\rho=0} = 1 $$

(31)

which agrees with Eq. (30).

The evaluation of $F_0$ involves an integral of a type also encountered in $E_2$ and $E_0$, but not evaluated in the literature and therefore it will be treated in detail. The orthogonality integral can be reduced to the form

$$ F_0 = -2\int_0^\infty \exp(x^2) \text{erfc} x dx. $$

(32)

This is a special case ($\alpha = \beta = 1$) of the more general integral

$$ I(\alpha, \beta) = \int_0^\infty \exp(x^2) \text{erfc}(\alpha x) \text{erfc}(\beta x) dx. $$

(33)

By introducing the definition of erfcx and substituting $t = x$ and $u = x^2$, this integral becomes

$$ I = 4\pi^{-1/2} \int_0^\infty s^2 \exp(s^2) ds \int_0^\infty \exp(-x^2 s^2) dx \times \int_0^\infty \exp(-y^2 s^2) dy. $$

(34)

Interchanging the order of integration and performing the integration with respect to $s$ yields

$$ I = 8\pi^{-1/2} \int_0^\infty dy (y^2+1)^{-1} \text{erfc}(y). $$

(35)

This integral can be evaluated by integrating first with respect to $y$ and then making the substitution $z = y^2+1$, which leads to the final result

$$ I(\alpha, \beta) = \frac{4}{\sqrt{\pi}} \text{log} \{ (\alpha+1) (\beta+1) / \log(\alpha+1)^{\alpha+1} (\beta+1)^{\beta+1} \}. $$

(36)

The orthogonality integral $F_0$, Eq. (32), thus has the value

$$ F_0 = -2\pi^{-1/2} \text{log} 2. $$

(37)

The asymptotic form of $\tilde{F}$ for large $\rho$ is not apparent either from the closed form, Eq. (28), or the power series, Eq. (29). However, after lengthy manipulations of the integral in Eq. (28), $\tilde{F}$ may be written in the alternative form

$$ \tilde{F} = 2\pi^{-1/2} \text{log} \rho + \pi^{-1/2} (\gamma + 2 \text{log} 2 - 2) + \rho^{-1} - \int_0^\infty \exp(x^2) \text{erfc} x s^2 ds, $$

(38)

where $\gamma = 0.5772157\ldots$ is Euler's constant. Since $\text{erfc} x \sim e^{-x^2} [\exp(-x^2)/s]^{-1} + O(x^{-3})$ for large $x$ the integral in Eq. (38) behaves like $x^{-1}$ and the asymptotic behavior of $\tilde{F}$ may be obtained directly:

$$ \tilde{F}(\rho) \sim 2\pi^{-1/2} \text{log} \rho + \pi^{-1/2} (\gamma + 2 \text{log} 2 - 2) + \rho^{-1} + O(\rho^{-3}). $$

(39)

Note that $\tilde{F}$ is dominated by $\text{log} \rho$ when $\rho$ is large.

In the evaluation of the second-order energy it is more convenient to use the equation

$$ E_2 = -\frac{1}{2} \langle \psi_0, (dF/d\rho)^2 \psi_0 \rangle $$

(40)

than the previous definition, Eq. (19). Substitution of $dF/d\rho$ from Eq. (24) gives the result

$$ E_2 = -2\pi \int_0^\infty \langle \frac{M}{\langle \psi_0, \psi_0 \rangle} \rangle d\rho, $$

(41)

and performing the integration after substitution of $M$ from Eq. (25) yields

$$ E_2 = -4\pi^{-1} (1 - \frac{1}{2} \text{log} 2) = -0.155782. $$

(42)

If in addition to the energy through third order the norm of $\psi_1$ is known, an upper bound to the energy may be obtained. The norm of $\psi_1$ is therefore of interest and will now be derived. Note that

$$ \langle \psi_i, \psi_i \rangle = \langle \psi, \tilde{F}_0 \psi_0 \rangle - F_\sigma, $$

(43)

which may be manipulated to yield

$$ \langle \psi_i, \psi_i \rangle = E_1 + E_2 + 8\pi^{-1/2} \int_0^\infty d\rho \exp(-\rho^2) \times \int_0^\infty \exp(s^2) \text{erfc} x ds \int_0^\infty \exp(x^2) \text{erfc} x dt. $$

(44)

The integral in Eq. (44) is a special case ($\alpha = \beta = 1$) of the more general integral

$$ J(\alpha, \beta) = \int_0^\infty \exp(-t^2) dt \int_0^\infty \exp(s^2) \text{erfc}(\alpha s) ds \times \int_0^\infty \exp(s^2) \text{erfc}(\beta s) dt $$

(45)

which is evaluated in the Appendix. By using the result found in the Appendix,

$$ J(1, 1) = 2\pi^{-1/2} (\gamma \pi^2 + \log^2 2), $$

as well as Eq. (42) for $E_2$ and Eq. (37) for $F_0$, the square norm of $\psi_i$ may be seen to be

$$ \langle \psi_i, \psi_i \rangle = (2/\pi) (\gamma \pi^2 + \pi - 2 - 2 \text{log} 2 - \log^2 2) = 0.0619809. $$

(46)

After manipulation, the expression for the third-order energy, Eq. (2) may be reduced to

$$ E_3 = \langle \psi_0, \tilde{F}_3 V \psi_0 \rangle - E_1 \langle \psi_1, \psi_1 \rangle - F_\sigma E_4 + 2F_\sigma E_2. $$

(47)
The integrals required in the evaluation of this expression are given in the Appendix. Substitution of the values of these integrals and of the other previously calculated quantities into Eq. (47) yields

\[
E_3 = 8\pi^{-3/2} \left[ 2(1 - C) - \frac{3}{2}\pi + (\pi + 3)\log 2 \right] + \frac{3}{2} \log^2 2 - \left(\pi^2/24\right) 
\]

\[= 0.0318278, \]  
(48)

where \( C \) denotes Catalan’s constant

\[
C = \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)^2} = 0.915965\ldots
\]

The final expression for the total energy through third order in \( \lambda \) is

\[
E = 3 + 1.12838\lambda - 0.15578\lambda^2 + 0.031828\lambda^3 + O(\lambda^4),
\]

or in terms of the original perturbation parameter \( \lambda = 2^{1/3}\Delta \),

\[
E = 3 + 0.797884\lambda - 0.0778909\lambda^2 + 0.0112528\lambda^3 + O(\lambda^4). \]  
(49)

**HARTREE–FOCK APPROXIMATION**

The Hartree–Fock approximation will be considered for the Hooke’s law atom in order to obtain the correlation energy and, perhaps more importantly, to examine in some detail the solution obtained by a method which is often used for actual atoms and molecules.

If the variational approximation

\[
\Psi_{HF}(r_1, r_2) = \phi(r_1)\phi(r_2)
\]

(50)

is made for \( \Psi \), then the equation which determines \( \phi \) is the well-known Hartree or Hartree–Fock equation

\[
\left(-\frac{1}{2}\nabla^2 + \frac{3}{2}r^2 + \lambda r \right)\phi = \epsilon\phi,
\]

(51)

where \( \epsilon \) is the Hartree–Fock orbital energy and \( r \) is the Hartree–Fock potential

\[
v(r) = \langle \phi, r_{12}^{-1}\phi \rangle = \int [\phi^2(r_2)/r_{12}]d^3r_2.
\]

(52)

Equation (51) is a nonlinear integrodifferential equation for \( \phi \) whose exact solution is not known. A perturbation treatment may be used to obtain the approximate solution of this equation. For the ground state \( \phi \) has no angular dependence and thus depends only on \( r \).

To apply perturbation theory to Eq. (51) expand \( \phi, \epsilon, \) and \( v \) in powers of \( \lambda \), as Dalgarno\(^{31} \) has done for the corresponding equation for the actual two-electron atom:

\[
\phi = \phi_0 + \lambda \phi_1 + \cdots, \]

(53)

\[
\epsilon = \epsilon_0 + \lambda \epsilon_1 + \lambda^2 \epsilon_2 + \lambda \epsilon_3 + \cdots, \]

(54)

\[
v = v_1 + \lambda v_2 + \cdots. \]

(55)

Defining \( n_0 \) as

\[
n_0 = -\frac{1}{2}\nabla^2 + \frac{3}{2}r^2
\]

(56)

leads to the unperturbed eigenvalue problem

\[
\hbar \phi_0 = \epsilon_0 \phi_0
\]

(57)

for \( \phi_0 \) and to the inhomogeneous equation

\[
(h_0 - \epsilon_0) \phi_1 = - (\epsilon - \epsilon_1) \phi_0
\]

(58)

for \( \phi_1 \).

The necessary \( \nu_1 \)'s are easily seen to be

\[
\nu_1(r) = \int [\phi_0^2(r_2)/r_{12}]d^3r_2,
\]

(59)

\[
\nu_2(r) = \int [\phi_0(r_2)\phi(r_2)/r_{12}]d^3r_2,
\]

(60)

and the required orbital perturbation energies are

\[
\epsilon_0 = \langle \phi_0, \nu \phi_0 \rangle,
\]

(61)

\[
\epsilon_1 = \langle \phi_0, \nu \phi_1 \rangle = \langle \phi_0(1)\phi_0(2), r_{12}^{-1}\phi_0(1)\phi_0(2) \rangle,
\]

(62)

\[
\epsilon_2 = \langle \phi_0, \nu \phi_2 \rangle = \langle \phi_0(1)\phi_0(2), r_{12}^{-1}\phi_0(1)\phi_0(2) \rangle,
\]

(63)

and

\[
\epsilon_3 = \langle \phi_0, \nu \phi_3 \rangle + 4\langle \phi_1, (\nu - \epsilon_1) \phi_1 \rangle
\]

(64)

where \( \phi_1 \) has been chosen orthogonal to \( \phi_0 \),

\[
\langle \phi_0, \phi_1 \rangle = 0.
\]

The total Hartree–Fock energy is given by the expression

\[
E_{HF} = 2\epsilon - \lambda \langle \phi, v \phi \rangle,
\]

(65)

and may be expanded in powers of \( \lambda \):

\[
E_{HF} = E_{HF}^{(0)} + \lambda E_{HF}^{(1)} + \lambda^2 E_{HF}^{(2)} + \lambda^3 E_{HF}^{(3)} + \cdots.
\]

(66)

It has been shown\(^{11} \) that the relationship between the orbital energies and the total energies is

\[
E_{HF} = [2/((n+1))\epsilon_n \quad (n = 0, 1, 2, \cdots).
\]

(67)

Equation (57) for \( \phi_0 \) is the equation for a threedimensional harmonic oscillator. For the ground state the solution is

\[
\phi_0 = \pi^{-3/4} \exp(- \frac{1}{2}r^2), \quad \epsilon_0 = \frac{3}{4}.
\]

(68)

The explicit form of \( \nu_1 \) [Eq. (59)] is thus seen to be

\[
\nu_1 = \frac{\exp(r)}{r} = 2\pi^{-1/2} - 1 \int_0^r \exp(-s^2)ds.
\]

(69)

(70)

\( \epsilon_1 \) may be calculated from Eq. (62) and is

\[
\epsilon_1 = (2/\pi)^{1/2} = 0.797884\ldots.
\]

(71)

To determine \( \phi_0 \) a technique may be employed which exactly parallels the determination of \( \psi_1 \) in a previous section. Only the result will be given here\(^3 \) which is

\[
\phi_1 = \left[ \tilde{f}(r) + \tilde{f}_0 \right] \phi_0(r).
\]

(72)
where

\[
\frac{f}{r} = \frac{\text{erf}(r)}{r} - \delta_1 + \frac{2^{-1/2} \exp(r^2)}{r} \left[ \text{erfc}(2^{1/2}r) - \text{erfc}(r) \right] \\
+ 2^{1/2} \int_0^\infty \exp(s^2) \left[ \text{erfc}(s) - \text{erfc}(2^{1/2}s) \right] ds 
\]

(73)

and

\[
f_\lambda = - \langle \phi_\lambda | \tilde{j}_{\phi_\lambda} \rangle = - \left( \frac{2}{\pi} \right)^{1/2} \left[ \frac{3}{2} \log(1 + 2^{1/2}) - \log(1 + 2^{-1/2}) \right]. 
\]

(74)

A power series expansion of \( f \) in even powers of \( r \) may be made, but it is not particularly useful and will not be given here. The asymptotic form of \( f \) may be obtained from

\[
f = \left( \frac{2}{\pi} \right)^{1/2} \log r + \left( \frac{2}{\pi} \right)^{1/2} \left[ \frac{3}{2} \log(1 + 2^{1/2}) - 1 \right] + r^{-1} \\
- 2^{-1/2} \int_0^\infty \frac{\exp(s^2)}{s^2} \left[ \text{erfc}(s) - \text{erfc}(2^{1/2}s) \right] ds \\
- \int_0^\infty \frac{\text{erfc}(s)}{s^2} ds 
\]

(75)

since the integrals in Eq. (75) behave like \( r^{-s} \). Thus for large \( r \) the asymptotic form of \( f \) is

\[
f \sim \left( \frac{2}{\pi} \right)^{1/2} \log r + \left( \frac{2}{\pi} \right)^{1/2} \left[ \frac{3}{2} \log(1 + 2^{1/2}) - 1 \right] \\
+ r^{-1} + O(r^{-3}). 
\]

(76)

The evaluation of the orbital energy \( \delta_1 \) is lengthy but straightforward. The result is

\[
\delta_1 = - \left( \frac{12}{\pi} \right)^{1/2} \left[ - \frac{1}{4} \log(1 + 2^{1/2}) + \frac{3}{2} \log(2 - 3^{1/2}) \right] \\
= -0.0422822. 
\]

(77)

The norm of \( \phi \) may also be calculated. Note, however,

\[
\langle \psi_{\text{HF}} | \psi_{\text{HF}} \rangle = 1 + 2 \langle \phi_1 \phi_1 \rangle \lambda^2 + O(\lambda^3). 
\]

(78)

The result for the square norm is

\[
\langle \phi_1 \phi_1 \rangle = \pi^{-1} \left[ \frac{1}{2} \pi^2 - L_b \frac{1}{2} \left( 3 + 2^{1/2} \right) - \frac{3}{2} \log(1 + 2^{1/2}) + 2 \log(2 + 3^{1/2}) \right] = 0.006832, 
\]

where

\[
L_b(x) = - \int_0^x \log(1 - t) \frac{dt}{t}, \\
= \sum_{k=1}^{\infty} \frac{\lambda^k}{k \lambda^2} 
\]

(80)

is the dilogarithm function.

The third-order orbital energy appears to be rather complicated when expressed analytically, and was therefore evaluated numerically using Gaussian quadratures with the result

\[
\delta_1 = 0.003767. 
\]

The total Hartree–Fock energy through third order in \( \lambda \) is thus

\[
E_{\text{HF}} = 3 + 0.79788\lambda - 0.028188\lambda^2 + 9.001884\lambda^3 + O(\lambda^4). 
\]

(81)

The unperturbed and first-order energies are, of course, the same as those in the exact expansion [Eq. (49)] in powers of \( \lambda \). The second-order Hartree–Fock energy is only 37% of the exact value. The third-order energy is positive like the exact value, but over six times smaller.

**SCALING APPROXIMATION TO HARTREE–FOCK SOLUTION**

One of the earliest approximate treatments of the actual two-electron atom consisted in assuming the wavefunction to be a scaled zero-order function and then requiring the energy to be stationary with respect to variations in the scale parameter. This scaling procedure is a simple and useful approximation to the Hartree–Fock wavefunction. In this section, the corresponding approximation will be made for the model atom, and the result expanded in a perturbation series in \( \lambda \).

The scaled trial function for the Hartree–Fock orbital \( \phi \) is

\[
\phi(x) = \xi^{\alpha} \phi_\lambda(x) = \xi^{\alpha} \exp(-\frac{1}{2} \xi^2 x^2), 
\]

(82)

where \( \xi \) is the scale parameter.

From Eqs. (51) and (66), it follows that

\[
\frac{dE}{d\xi} = \xi^2 + \frac{3}{2} \xi^4 + \delta_1 \lambda, 
\]

(83)

where \( \delta_1 (2/\pi)^{1/2} \). The optimum value of \( \xi \) is given by

\[
\frac{dE}{d\xi} = 3 (\xi - \xi^3) + \delta_1 \lambda = 0; 
\]

(84)

if it is assumed that for \( \lambda \) small

\[
\xi = 1 + \alpha \lambda + \beta \lambda^2 + \gamma \lambda^3 + \cdots, 
\]

(85)

it is simple to show that

\[
\alpha = -\delta_1 / 12 = -2^{1/2} / 12^{1/2}, 
\]

(86)

\[
\beta = \delta_1 / 96 = 1 / 48 \pi, 
\]

(87)

and

\[
\gamma = -\delta_1 / 864 = -2^{1/2} / 432 \pi^{1/2}. 
\]

(88)

Substitution of these results into Eq. (83) yields

\[
E_{\text{HF}} = 3 + 0.79788\lambda - 0.028188\lambda^2 + 9.001884\lambda^3 + \cdots. 
\]

(89)

We note that the unperturbed and first-order energies agree with those in the correct Hartree–Fock expansion, Eq. (81), as they must, and that the second- and third-order energies are similar. The approximate second-order energy in (89) is less than that in (81), in accordance with the variational principle.
The trial function itself may be written in the form
\[ \phi = \phi_0 + \lambda \phi_1 + \cdots, \] (90)
where
\[ \phi_0 = \exp(-\gamma r^2) \] (91)
and
\[ \phi_1 = \frac{1}{2} \alpha(3 - 2r^2) \phi_0. \] (92)
Note that the square norm of \( \phi_1 \) is
\[ \langle \phi_1, \phi_1 \rangle = \frac{3}{2} \gamma^2 = 1/48\gamma = 0.0066315 \] (93)
which is close to the exact value of Eq. (79).

**HYLLERAAS-TYPE APPROXIMATION**

An important step in the variational treatment of the helium atom was the introduction of the interelectron distance \( r_{12} \) into a trial wavefunction by Hylleraas,\(^4\) which produces a more marked improvement in the energy than any pair of one-electron terms. The exact solution must have a term linear in \( \alpha r_{12} \) in order to satisfy the interelectron cusp condition (4); as we have seen from Eqs. (30) and (31), the exact solution for the Hooke model has such a term. In this section we investigate the perturbation theory of a trial function of the form
\[ \tilde{\Psi} = (1 + \alpha r_{12}) \Psi_0 \] (94)
for the Hooke model. Kestner and Sinanoglu\(^5\) have already considered functions of this form. Our contribution is to obtain the second- and third-order perturbation energies implied by (94), and to compare them with the exact values.

Since the Hooke equation is separable in the coordinates \( \rho = 2^{-1/2} \tau r_1 \) and \( R \) of Eq. (6), we revert to the notation of the separated problem with perturbation parameter \( \lambda \), and seek an approximate variational solution \( \Psi_1 \) of Eq. (17), of the form
\[ \tilde{\Psi}_1 = F \Psi_0 \] (95)
with \( F = C \rho \),
where \( C \) is a variational constant. The best \( F \) is that which minimizes the Hylleraas second-order function \( \tilde{E}_2 = \frac{\langle \Psi_0, F(V - E_1) \Psi_0 \rangle}{\langle \Psi_0, \nabla F \rangle \Psi_0} \).

This "Dirichlet" form is convenient because it is optimized with respect to \( C \), and therefore independent of \( \rho \); it is also independent of an additive constant in \( F \). By substituting \( F = \rho \) in (96) and noting that \( \langle \rho \rangle = E_1 \), we obtain
\[ \tilde{E}_2 = -2 (E_2 - 1)^2 = -2 [\frac{8}{3} - 1] = -0.14932. \] (96)

The coefficient \( \tilde{E}_2 \) of \( \lambda^2 \) in the energy expansion is therefore
\[ \tilde{E}_2 = \frac{1}{3} \tilde{E}_2 = -0.07466, \] (97)
which is only about 5% less than the exact value \(-0.07789\), and dramatically better than the Hartree-Fock value \(-0.02819\).

The third-order energy in the \( \Lambda \) series is given by
\[ E_3 = \langle \Psi_0, F(V - E_1) \tilde{F} \Psi_0 \rangle - 2 \tilde{E}_2 \Psi_0 \tilde{F} \Psi_0, \]
\[ = \frac{\pi^2}{16} \left[ \frac{4}{\pi} - 1 \right] \left[ 16 \pi - 5 \right] = 0.003916. \] (98)

For the \( \lambda \) series,
\[ \tilde{E}^{(0)} = +0.001384. \] (99)
This is positive like the exact value (0.01125), but too small by a factor of about 8.

The value of \( C \) is
\[ C = 2 \frac{\left( \frac{8}{3} - 1 \right)}{0.5465}, \] (100)
and the total first-order wavefunction, orthogonalized to \( \Psi_0 \), is
\[ \tilde{\Psi}^{(1)} = (0.3864) \left( 1.595 \right) \Psi_0. \] (101)
The ratio \( \tilde{\Psi}^{(1)}/\Psi_0 \) is plotted against \( r_{12} \) in Fig. 2, and compared with the exact ratio from Eq. (28).

The results for similar treatments of the actual two-electron atom and the delta model\(^6\) are given in Table I. In all three cases, the errors in the second-order energy are about 10% or less.

**LEGENDRE EXPANSION**

One of the popular techniques used in the two-electron atom has been the method of superposition of configurations.\(^1\) A superposition of configurations calculation for the Hooke's law atom, correct to first order in the parameter \( \lambda \), can be carried out by writing the total wavefunction in the form
\[ \Psi(r_1, r_2, \cos \theta_{12}) = \sum_{i=0}^{\infty} \Psi_i^{(1)}(r_1, r_2) P_i(\cos \theta_{12}). \] (102)
The second-order energy [second order in \( \lambda \), not \( \Lambda \) as in Eq. (19)]
\[ E^{(2)} = \langle \Psi_0, V \Psi^{(1)} \rangle \] (103)
may similarly be expanded as
\[ E^{(2)} = \sum_{i=0}^{\infty} E_i^{(2)}, \] (105)
where
\[ E_i^{(2)} = \left( 2i + 1 \right)^{-1} \langle \Psi_0, r_i \Psi_i^{(1)} \rangle. \] (106)

If the wavefunction \( \Psi^{(1)} \) is divided into even and odd parts,
\[ \Psi^{(1)} = \Psi_{e}^{(1)} + \Psi_{o}^{(1)}, \] (108)
Perturbation Theory of Two-Electron Atom

Table I. Perturbation energy coefficients of powers of \( \lambda \) for the ground states of the Hooke model, the actual Coulomb atom, and the delta model (atomic units).

| System          | Calculation | \( E^{(0)} \) | \( E^{(1)} \) | \( E^{(2)} \) | \( E^{(3)} \) | \( \langle \Psi^{(2)} | \Psi^{(0)} \rangle \) |
|-----------------|-------------|---------------|---------------|---------------|---------------|---------------------------------|
| Hooke           | Exact       | 0.797884      | 0.078909      | 0.0112528     | 0.0399755     |
|                 | Hylleraas   | 0.797884      | 0.074660      | 0.0013843     | 0.038860      |
|                 | Hartree–Fock| 0.797884      | 0.0281881     | 0.001884      | 0.013664      |
|                 | Scaling     | 0.797884      | 0.0265258     | 0.001764      | 0.013262      |
|                 | Numerical*  | 0.7974        | 0.075888      | 0.00853       | ...           |
| Coulomb         | Exact       | -1            | 0.625         | 0.157666      | 0.00869868    | 0.244435                       |
|                 | Hylleraas   | -1            | 0.625         | -0.134827     | -0.005925     | 0.163794                       |
|                 | Hartree–Fock| -1            | 0.625         | -0.111003     | -0.00103525   | 0.218296                       |
|                 | Scaling     | -1            | 0.625         | -0.0976563    | 0             | 0.146484                       |
| Delta           | Exact       | -1            | 0.5           | -0.162793     | 0.0139891     | 0.082773                       |
|                 | Hylleraas   | -1            | 0.5           | -0.140625     | 0.0087891     | 0.061523                       |
|                 | Hartree–Fock| -1            | 0.5           | -0.083333     | 0             | 0.072916                       |
|                 | Scaling     | -1            | 0.5           | -0.0625       | 0             | 0.0625                         |

*See Ref. 3.

where

\[
\Psi_{s}^{(1)} = \sum_{l=0}^{m} \Psi_{s1}^{(1)} P_{s1}(\cos \theta_{12}),
\]

and

\[
\Psi_{s}^{(2)} = \sum_{l=0}^{m} \Psi_{s2}^{(1)} P_{s2} \cos \theta_{12},
\]

and if the second-order energy is similarly divided into two parts

\[
E_{2}^{(2)} = E_{2}^{(0)} + E_{2}^{(3)},
\]

then it is easily shown that for this model

\[
E_{2}^{(3)} = E_{2}^{(2)} - \frac{1}{2} E_{2}^{(0)}.
\]

The proof consists of writing

\[
\Psi_{s}^{(1)} = \frac{1}{2} (1 + \beta) \Psi_{s}^{(0)},
\]

where \( \beta \) is the operator which inverts one of the electrons and takes \( \cos \theta_{12} \) into \( -\cos \theta_{12} \). The effect of \( \beta \) is to interchange the roles of \( R \) and \( \rho \) [defined by Eq. (6)] in \( \Psi^{(0)} \), so that

\[
E_{2}^{(2)} = \frac{1}{2} \langle \Psi_{s}^{(0)}, V(1 + \beta) \Psi_{s}^{(0)} \rangle - \frac{1}{2} E_{2}^{(0)} + \frac{1}{2} \langle \Psi_{s}^{(0)}(R), \rho^{-1} \Psi_{s}^{(0)}(R) \rangle = \frac{1}{2} E_{2}^{(0)}.
\]

The simple value of unity for the ratio \( E_{2}^{(2)}/E_{2}^{(0)} \) appears to be unique for the Hooke model. The values for the actual Coulombic two-electron atom and for the closely related two-electron delta model are as follows:

<table>
<thead>
<tr>
<th>System</th>
<th>( \text{Ratio } E_{2}^{(2)}/E_{2}^{(0)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulomb</td>
<td>0.2066</td>
</tr>
<tr>
<td>Hooke</td>
<td>1</td>
</tr>
<tr>
<td>Delta</td>
<td>0.3024</td>
</tr>
</tbody>
</table>

Although a treatment for all Legendre components \( l \) is difficult to give, the result for \( l = 0 \) is straightforward and presented here for illustrative purposes. By definition

\[
\Psi_{s}^{(1)} = \frac{1}{2} \int_{0}^{\pi} \Psi_{s}^{(0)} \sin \theta_{12} d\theta_{12},
\]

where

\[
\Psi_{s}^{(0)} = 2^{-1/2} \Psi_{s}^{(0)}(r_{1}, r_{2}) \rho_{s}^{(0)}(2^{-1/2} r_{12}).
\]

In this last equation, \( \Psi_{s}^{(0)} \) is defined by Eq. (102) and \( \rho \) is defined by Eqs. (26) and (28). Carrying out the integration in Eq. (115) leads to the result

\[
\Psi_{s}^{(1)} = \Psi_{s}^{(0)} \left[ -\frac{3}{2} \left( \frac{2}{s} \right)^{1/2} - \frac{3}{2} \left( \frac{2}{s} \right)^{1/2} \log 2 + \frac{2t}{s+t} + \frac{2t}{s+t} \right]
\]

\[
\times \left( 2s^{2} - 1 \right) \int_{0}^{\infty} \exp(sx) \operatorname{erf}cx dx - \left( 2s^{2} - 1 \right)
\]

\[
\times \int_{0}^{\infty} \exp(sx) \operatorname{erf}cx dx \int_{0}^{\infty} \exp(tx) \operatorname{erf}cx dx,
\]

where

\[
s = 2^{-1/2} (r_{1} + r_{2}),
\]

and

\[
l = 2^{-1/2} |r_{1} - r_{2}|.
\]

The corresponding \( l = 0 \) contribution to the second-order energy is

\[
E_{0}^{(2)} = -\left( \frac{2}{\pi} \right) \left( \log 2 + \frac{3}{2} - \pi \right) = -0.0032821.
\]

For large \( l \) the asymptotic form of \( \Psi_{s}^{(1)} \) and \( E_{l}^{(2)} \) has previously been given\(^{27}\), that for \( E_{l}^{(2)} \) is

\[
E_{l}^{(2)} \sim -\left( \frac{3}{4\pi} \right) (l + \frac{1}{2})^{-4} \left[ 1 - \frac{1}{3} (l + \frac{1}{2})^{-2} + O(l^{-4}) \right],
\]
The corresponding result for the actual Coulombic two-electron atom is also known,\textsuperscript{12}

\[
E_{1}^{\text{Coul}} \sim - \frac{45}{256} \left( l + \frac{1}{2} \right)^{2} \left[ 1 - \frac{1}{4} (l + \frac{1}{2})^{2} + O(l^{-4}) \right],
\]

and is seen to be similar to the model.

**ASYMPTOTIC WAVEFUNCTION FOR LARGE $\rho$**

An interesting check is available on the asymptotic form of $\psi_{1}$, Eq. (39). The asymptotic form of the total wavefunction for large $\rho$ can be deduced directly from Eq. (8). If the substitution

\[
\psi(\rho) = \psi_{0}(\rho) f(\rho)
\]

is made in Eq. (8), where $\psi_{0}$ is given by (16), then the equation for $f$ is

\[
\left[ \frac{d^{2}}{d\rho^{2}} + 2 \left( \rho^{-1} - \rho \right) \frac{d}{d\rho} - 2 \Delta E + 2 \Delta E \right] f = 0,
\]

where $\Delta E = E - (3/2)$ is the perturbation energy. If this equation is considered for large $\rho$ and all zero $O(\rho^{-1})$ and $O(\rho^{-2})$ terms are neglected (here $f$ is assumed to behave like $\rho^{p}$), the result is

\[
f \sim \rho^{2}(\text{large } \rho).
\]

The asymptotic form of $f$ is therefore

\[
f \sim 1 + \Delta E_{1} \log \rho + \cdots.
\]

Since $E_{1} = 2\pi^{-1/2}$, this agrees with Eq. (39).

**ASYMPTOTIC ENERGY EXPANSION FOR LARGE $\Lambda$**

The perturbation solution of Eq. (8) is valid for small enough values of $\Lambda$, but for large values of $\Lambda$ the perturbation treatment fails although, unlike the Coulomb atom, the system remains bound. It is still possible to obtain an asymptotic form of the energy valid for large $\Lambda$. The eigenvalue Eq. (8) is

\[
\left[ - \frac{1}{2} \nabla^{2} + \frac{1}{2} \rho^{2} + (\Lambda / \rho) \right] \psi = E \psi.
\]

The potential energy term in Eq. (117) has a minimum at $\rho_{0} = \Lambda^{1/3}$. Thus the potential energy may be expanded in a MacLaurin series about $\rho_{0}$,

\[
U(\rho) - \frac{1}{2} \rho^{2} + (\Lambda / \rho)
\]

\[
= \frac{3}{2} \Lambda^{2/3} \left( \rho - \Lambda^{1/3} \right)^{2} - \Lambda^{-1/3} \left( \rho - \Lambda^{1/3} \right)^{3} + \cdots.
\]

If the shift of origin

\[
\sigma = \rho - \Lambda^{1/3}
\]

is made and if large $\Lambda (\Lambda \to \infty)$ is considered, Eq. (126) may be written as

\[
\left[ - \frac{1}{2} \frac{d^{2}}{d\sigma^{2}} + \frac{3}{2} \sigma^{2} - E' \right] \psi \sim 0,
\]

where

\[
E' = \lim_{\Lambda \to \infty} \left( E - \frac{3}{2} \Lambda^{2/3} \right).
\]

Equation (120) is the equation for a one-dimensional harmonic oscillator with range $\sigma = (\infty, -\Lambda^{1/3})$. Its lowest energy solution for $\Lambda \to \infty$ is

\[
E' = 3^{1/2}/2.
\]

It is then easy to see from Eq. (130) that

\[
E_{\psi} \sim \frac{3}{2} \Lambda^{2/3} + (3/2) + O(\Lambda^{-2/3}), \quad \Lambda \to \infty,
\]

or in terms of $\lambda (= 2^{1/3} \Lambda)$

\[
E_{\psi} \sim \frac{3}{2} \lambda^{2/3} + (3/2) + O(\lambda^{-2/3}), \quad \lambda \to \infty.
\]

This equation is compared with the power series expansion in the discussion. The same dependence on $\lambda$ can be deduced from the scaling approximation (82).

For $\Lambda$ large but negative, Eq. (126) may be treated by perturbation theory with the term $\frac{1}{2} \rho^{2}$ as the perturbation. This leads to the result

\[
E_{\psi} \sim -\frac{1}{2} \Lambda^{2/3} \frac{3}{2} \Lambda^{2} + O(\Lambda^{-4}), \quad \Lambda \to -\infty,
\]

or in terms of $\lambda$

\[
E_{\psi} \sim -\frac{1}{2} \lambda^{2/3} + 3 \lambda^{-2} + O(\lambda^{-4}), \quad \lambda \to -\infty.
\]

The asymptotic formulas (133) and (135) indicate clearly that the power series expansion (49) has a finite radius of convergence.

**TOTAL ENERGY**

The total energy $E(\lambda)$ for the Hooke model is plotted as a function of the perturbation parameter $\lambda$ in Fig. 1. The most accurate value, provided $\lambda$ is not too large, is given by the truncated power series expansion $E_{\text{exp}}(\lambda)$ evaluated numerically through tenth order in a companion paper\textsuperscript{18} (solid curve). Also plotted are the asymptotic form, Eq. (133), which is accurate for

![](image-url)
large $\lambda$, and the upper bound given by the wavefunction through first order, $\Psi^{(0)}+\lambda\Psi^{(1)}$,

$$E_{\text{upper}} = E^{(0)}+\lambda E^{(1)} + \frac{\lambda^2 E^{(2)}+\lambda^3 E^{(3)}}{1+\lambda^3\langle\Psi^{(1)},\Psi^{(0)}\rangle}.$$  \hfill (136)

The upper bound (136) is a good approximation for $\lambda$ less than 1.5, but starts to deviate at $\lambda = 2$. It can be seen that the power series $E_{\text{asy}}$ and the asymptotic curve approach each other as $\lambda$ increases. They cross for $\lambda$ about 4.5, and for larger values the truncated expansion becomes negative. The perturbation series probably diverges for these values of $\lambda$. In the case of heliumlike atoms, the ground-state energy appears to have a branch point\(^\dagger\) at $\lambda = 1.18$, and is not bound beyond this value.

**DISCUSSION**

The Hooke's law model considered in this paper is mathematically similar in certain respects to the actual two-electron atom. The similarity between the first-order equations for $\Psi^{(1)} = F\Psi^{(0)}$ is particularly striking. That for the actual atom is

$$[(\nabla_x^2+\nabla_y^2)F - \left(\frac{\partial F}{\partial r_1} + \frac{\partial F}{\partial r_2}\right)] = r_{12}^{-1} \hat{\delta},$$  \hfill (D.1)

while for the model atom

$$[(\nabla_x^2+\nabla_y^2)F - \left[r_1(\partial F/\partial r_1) + r_2(\partial F/\partial r_2)\right] = r_{12}^{-1} - (2/\pi)^{1/2}.$$  \hfill (D.2)

As we have seen, Eq. (D.2) is separable, and the solution $F$ is a function of $r_{12}$ only, given by Eq. (38) and plotted in Fig. 2. Note that contrary to Kestner and Sinanoğlu,\(^\dagger\) $F$ has marked curvature. This difference most probably results from the different scaling they use in their numerical work. It is difficult to compare the Hooke $F$ directly with the actual $F$ satisfying (D.1), which depends on $r_1$, $r_2$, and $r_{12}$, and whose asymptotic form is not even established.

It is easier to compare the perturbation energies for the two systems, which reflect their similarities. In the first place, the correlation energies are remarkably alike. The correlation energy is defined as the difference between the exact energy and the Hartree–Fock energy, so that for the Hooke model from Eqs. (49) and (81),

$$E_{\text{corr}}(\text{Hooke}) = E - E_{\text{HF}} = -\lambda^2(0.049703) + \lambda^3(0.009369) + \cdots.$$  \hfill (D.3)

For the actual two-electron atom, using Linderberg's\(^\ddagger\) values for the Hartree–Fock perturbation energies, the correlation energy is

$$E_{\text{corr}}(\text{Coulomb}) = -\lambda^2(0.046663) + \lambda^3(0.0097539) + \cdots.$$  \hfill (D.4)

The individual coefficients are numerically close, but this is partly a coincidence, depending on the choice of $\omega$ in Eq. (1). However, the sign of the third-order correlation energy is positive in both cases, and the ratio of third order to second order is similar in both cases.

Second, the other usual variational approximations (in addition to the Hartree–Fock) behave in a similar way in both cases. The results of all the calculations of the exact and approximate perturbation energies are collected in Table I for comparison. In addition to the Hooke model, the results for the delta model\(^\dagger\) are presented, and also follow the general pattern of the other two.

In its response to an external electric field the Hooke model is disappointingly different from the two-electron atom.\(^\dagger\) There is no interaction between the field and the electron interaction, so the polarizability $\alpha = 2$ is simply twice that of a harmonic oscillator, and all the hyperpolarizabilities vanish.

The object of this paper was to draw attention to the Hooke law model for heliumlike atoms by presenting some exact analytical results for low-order perturbation theory, and comparing them with the perturbation variation calculations on the actual two-electron atoms. Our conclusion is that the model has sufficient features in common with the real system to serve as a test case for new methods of solution and approximation, and to justify further study.

**ACKNOWLEDGMENTS**

We would like to thank Dr. J. D. Power for help with calculating some of the numbers which appear in Table I. One of us (R.J.W.) would like to thank the National Aeronautics and Space Administration for a traineeship held at the University of Wisconsin.
APPENDIX

The integral $J(\alpha, \beta)$ is defined by Eq. (45) which may be written in the form

$$J(\alpha, \beta) = \int_0^\infty \exp(-r^2) g_\alpha(r) g_\beta(r) \, dr, \quad (\alpha, \beta > 1),$$

where

$$g_\alpha(r) = \int_0^r \exp(x^2) \text{erfc}(sx) \, ds.$$

By exhibiting the integrals in $g_\alpha(r)$, $J$ becomes

$$J = 2\pi^{-1/2} \int_0^\infty dr \exp(-r^2) g_\alpha(r) \int_0^\infty ds \exp(s^2) \int_0^\infty \exp(-r^2) \, dr,$$

and putting $t = xs$,

$$J = 2\pi^{-1/2} \int_0^\infty dr \exp(-r^2) g_\alpha(r) \int_0^\infty ds \exp[s^2(1-x^2)] \, ds.$$

Performing the integration over $s$, and interchanging the order of integration,

$$J = \pi^{-1/2} \int_0^\infty dr \int_0^\infty \left[ \exp(-r^2) - \exp(-x^2r^2) \right] g_\alpha(r) \, dr.$$

Introducing the definition of $g_\beta$,

$$J = \pi^{-1/2} \int_0^\infty dx \int_0^\infty \left[ \exp(-r^2) - \exp(-x^2r^2) \right] g_\alpha(r) \, dr,$$

and interchanging the order of the $r$ and $s$ integrations,

$$J = \pi^{-1/2} \int_0^\infty dx \int_0^\infty \left[ \exp(-r^2) - \exp(-x^2r^2) \right] \text{erfc}(\beta x) \, ds,$$

$$= \frac{1}{2} \int_0^\infty dx \int_0^\infty \left[ \exp(s^2) \text{erfc}(\beta s) \right] \left[ \text{erfc}(s) - x^{-1} \text{erfc}(xs) \right] \, ds.$$

The integration over $s$ can be written in terms of the integral $I$ defined by Eq. (36),

$$J(\alpha, \beta) = \frac{1}{2} \int_0^\infty dx \frac{dx}{x^2-1} \left[ I(1, \beta) - x^{-1} I(x, \beta) \right],$$

$$= \frac{1}{2} \pi^{-1/2} \left[ \log(\beta+1) \int_0^\infty dx \frac{dx}{x^2-1} - \int_0^\infty \log\left( \frac{x+1}{\beta+1} \left( x^2+\beta^2-1 \right)^{1/2} \right) \frac{dx}{x(x^2-1)} \right].$$

To facilitate the reduction of the second integral, put

$$\log\left( \frac{x+1}{\beta+1} \left( x^2+\beta^2-1 \right)^{1/2} \right) = \frac{1}{2} \log\left( \frac{x\beta+\left( x^2+\beta^2-1 \right)^{1/2}}{x\beta-\left( x^2+\beta^2-1 \right)^{1/2}} \right) + \frac{1}{2} \log(x^2-1) + \frac{1}{2} \log(\beta^2) - \frac{1}{2} \log\left( \frac{x+1}{\beta+1} \right).$$

The following integral is required,

$$K(\alpha) = \int_0^\infty \log\left( \frac{x+1}{x-1} \right) \frac{dx}{x(x^2-1)},$$

and may be reduced to the form

$$K(\alpha) = \frac{1}{2} \left[ Li_2 \left( \frac{\alpha-1}{2\alpha} \right) - Li_2 \left( \frac{\alpha+1}{2\alpha} \right) \right] + \frac{1}{4} \left[ \log^2 \left( \frac{\alpha-1}{2\alpha} \right) - \log^2 \left( \frac{\alpha+1}{2\alpha} \right) \right],$$

where $Li_2$ is the dilogarithm function\footnote{defined by Eq. (80). The other unfamiliar integral required may be reduced to the $K$ integral by the substitution $y = x\beta / (x^2+\beta^2-1)^{1/2}$ which leads to the result}

$$\int_0^\infty \log\left( \frac{x\beta-\left( x^2+\beta^2-1 \right)^{1/2}}{x\beta+\left( x^2+\beta^2-1 \right)^{1/2}} \right) \frac{dx}{x(x^2-1)} = K(\beta) - K \left( \frac{\alpha\beta}{(\alpha^2+\beta^2-1)^{1/2}} \right).$$
Hence, finally

\[ J(\alpha, \beta) = \frac{1}{2} \pi^{-1/2} \left[ \log \left( \frac{\alpha+1}{\alpha-1} \right) \log \left( \frac{\beta+1}{\beta-1} \right) + \log \left( \frac{\alpha+1}{\beta+1} \right) \log \left( \frac{\alpha+1}{\beta-1} \right) \right. \]

\[ \left. - \frac{1}{2} \log \left( \frac{\alpha+1}{\alpha-1} \right) \log \left( \frac{\beta+1}{\beta-1} \right) - K(\alpha) - K(\beta) + K \left( \frac{\alpha \beta}{(\alpha^2 + \beta^2 - 1)^{1/2}} \right) \right] \]

which is explicitly symmetric in \( \alpha \) and \( \beta \) as required by the definition (45).

Certain other integrals are necessary in this work and since they do not appear to be in the literature (in particular Größner and Hofreiter\(^\ast\)) they are listed below.

\[ \int_0^\infty \log x \text{erf} x \, dx = - \pi^{-1/2} (1 + \frac{3}{4} \gamma), \quad (\gamma = 0.577215 \cdots), \]

\[ \int_0^\infty xe^{x^2} \text{erf} x \, dx = 2 \pi \left( C - 1 - \frac{1}{2} \gamma + \frac{1}{3} \pi \gamma \right), \quad (C = 0.915965 \cdots), \]

\[ \int_0^\infty x \exp(-x^2) \text{erf} x \, dx = \frac{1}{2} \left( 1 - \frac{\alpha}{(1 + \alpha^2)^{1/2}} \right), \quad \alpha \geq 0, \]

\[ \int_0^\infty \exp(-x^2) \text{erf} x \, dx = \pi^{-1/2} \left[ \frac{3}{4} \pi + \tan^{-1} \left( \frac{\alpha \beta}{1 + (\alpha^2 + \beta^2)^{1/2}} \right) - \tan^{-1} \alpha - \tan^{-1} \beta \right], \quad \alpha, \beta \geq 0, \]

\[ \int_0^\infty \log \left( \frac{x+1}{x-1} \right) \frac{dx}{x(x^2-1)} = \frac{1}{4} \log^2 \left( \frac{\alpha-1}{2\alpha} \right) - \frac{1}{4} \log^2 \left( \frac{\alpha+1}{2\alpha} \right) + \frac{1}{4} \log \left( \frac{\alpha-1}{2\alpha} \right) + \frac{1}{4} \log \left( \frac{\alpha+1}{2\alpha} \right), \quad \alpha > 1, \]

\[ \int_0^\infty \exp(-x^2) \int_0^\infty \exp(x^2) \frac{\text{erfc}(x)}{s} \, ds = \frac{1}{2} \log \left( 1 + \frac{1}{\alpha} \right), \quad \alpha > 0. \]