PHYSICAL REVIEW A VOLUME 49, NUMBER 6 JUNE 1994

Some calculations on the ground and lowest-triplet state of helium in the fixed-nucleus approximation

Hazel Cox
Department of Mathematics, University of York, Heslington, York, YO1 5DD, England

Stephen J. Smith and Brian T. Sutcliffe
Department of Chemistry, University of York, Heslington, York, YO1 5DD, England

(Received 20 December 1993)

The series solution method developed by Pekeris [Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959)] for the Schrödinger equation for two-electron atoms, as generalized by Frost *et al.* [J. Chem. Phys. **41**, 482 (1964)] to handle any three particles with a Coulomb interaction has been used. The wave function is expanded in a triple orthogonal set in three *perimetric* coordinates. From the Schrödinger equation an explicit recursion relation for the coefficients in the expansion is obtained, and the vanishing of the determinant of these coefficients provides the condition for the energy eigenvalues and for the eigenvectors. The Schrödinger equation is solved and the matrix elements are produced algebraically by using the computer algebra system MAPLE. The substitutions for a particular atom and diagonalization were performed by a program written in the C language. Since the determinant is sparse, it is possible to go to the order of 1078 as Pekeris did without using excessive memory or computer CPU time. By using a nonlinear variational parameter in the expression used to remove the energy, nonrelativistic energies, within the fixed-nucleus approximation, have been obtained. For the ground-state singlet $1\,^1S$ state this is of the accuracy claimed by Frankowski and Pekeris [Phys. Rev. **146**, 46 (1966); **150**, 366(E) (1966)] using logarithmic terms for Z from 1 to 10, and for the triplet $2\,^3S$ state, energies have been obtained to 12 decimal places of accuracy, which, with the exception of $Z = 2$, are lower than any previously published, for all Z from 3 to 10.

PACS number(s): 31.20.Di, 31.10.+z, 31.15.+q, 31.90.+s

I. INTRODUCTION

The helium and heliumlike atoms have attracted the attention of many authors using different methods to obtain estimates for the energies and expectation values of various operators. The pioneering work of Hylleraas [1] in 1929 demonstrated the importance of including basis functions which take account of electron correlation explicitly. However, the expansion in powers of the interparticle distances he used for the wave function was shown by Bartlett *et al.* [2] not to satisfy formally the Schrödinger equation. In later work Bartlett [3] suggested that logarithmic terms were necessary in any series expansion. Fock [4] showed and Morgan [5] proved that such terms were necessary.

However, some of the most accurate results for the nonrelativistic energies of the helium isoelectronic sequence, $Z = 1$ to 10, were provided by Pekeris [6] using a wave function which did not explicitly contain logarithmic terms. He used an expansion that consisted of products of three Laguerre polynomials multiplied by an exponential with perimetric coordinates as the variables. These coordinates were first introduced by Coolidge and James [7]. Using a method to be described later in the text, Pekeris obtained recursion relations that led to sparse matrices in which the number of nonzero matrix elements grows only linearly with the number of functional terms and this allows a large number of terms to be used in any truncated solution.

In 1966 Frankowski and Pekeris [8] (FP) developed the Hylleraas approach by including logarithmic terms in the series expansion. FP obtained their lowest eigenvalue variationally to precision of one part in 10^9 to 10^{10} from a nonsparse 246×246 matrix. By modifying the algorithm for selecting the basis functions Freund *et al.* [9] obtained energies accurate to better than a few parts in 10^{13} using a 230-term wave function for $Z = 1$ to 10. Drake [10] superseded these results using 616 Hylleraas-type functions with multiple exponential scale parameters, and the most accurate energies to date for H^- and He are presented in the paper by Baker *et al.* [11], who perform a 476-order variational perturbation calculation by using a combined modified FP basis and a Frankowski basis [12] as one composite basis, similar to that of Kono and Hattori [13] in their variational calculations on excited states of helium.

Very accurate energies and expectation values of operators have also been calculated using less traditional methods such as the finite element method by Braun *et al.* [14], and exact solutions using hyperspherical coordinates by Zhang and Deng [15]. Haftel and Mandelzweig [16] have also used a hyperspherical method for infinite and finite nuclear masses and all other expectation values to a precision of a few parts in 10^8 and 10^9 for the ground state.

The purpose of this paper is not to better these energy calculations but to show that one can increase the rate of convergence of Pekeris's algorithm [6] with the aid of a nonlinear variation parameter in the calculation, and without going to a higher order of matrix still obtain sparse matrices which yield energies to the accuracy claimed by Frankowski and Pekeris. The wave function cusps and the virial energies are also presented to show that the wave functions obtained by this method are of excellent quality using criteria other than the total energy. In the following paper this will be extended to the case where the nuclear mass is finite and all three particles are in relative motion.

The algorithm of Pekeris for S states of two-electron atoms has been generalized to spaces of arbitrary dimensionality by Loeser and Herschbach [17]. Numerical calculations were reported for the ground state ($1\,^1S$) and first two excited states ($2\,^3S$ and $2\,^1S$) for a wide range of dimensions, $1 < D < \infty$, and nuclear charge, $1 \leq Z \leq 6$. They used the same definition of the perimetric coordinates and wave function as Pekeris except that they used a product of three generalized Laguerre polynomials where the degree of the Laguerre α was set equal to $(D-3)/2$. For real atoms, with $D = 3$ and thus $\alpha = 0$, the calculations give precisely the results obtained by Pekeris.

Frost [18] showed how the series solution (which is the basis of the Pekeris algorithm) is equivalent to the linear variation method, and Frost, Inokuti, and Lowe [19] generalized the series solution method to handle *any* three particles with Coulomb interaction.

II. SCHRÖDINGER EQUATION AND CHOICE OF COORDINATES

The equation to be solved is

$$\hat{H}\Psi = E\Psi, \tag{1}$$

where the Hamiltonian operator $\hat{H}$ is the sum of the kinetic energy and the potential energy operators.

The laboratory-fixed form of the Schrödinger Hamiltonian describing a system of three particles is

$$\hat{H}(\underline{x}) = -\frac{\hbar^2}{2}\sum_{i=1}^{3} m_i^{-1}\nabla^2(\underline{x}_i) + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{3}{}' \frac{Z_i Z_j}{x_{ij}}, \tag{2}$$

where $\underline{x}_i$ denotes a column matrix of the three Cartesian components of the variable and $\underline{x}$ denotes the matrix of the variables collectively. Otherwise the notation is standard and the separation between particles is defined by

$$x_{ij}^2 = \sum_{\alpha}(x_{\alpha j} - x_{\alpha i})^2, \tag{3}$$

with the α sum running over x, y, and z. However, Eq. (2) has a continuous spectrum and so cannot be solved for bound states as it stands. Fortunately, it is possible by a linear transformation to separate the center-of-mass motion from the full Hamiltonian of Eq. (2) and for that motion to carry the continuous part of the spectrum.

The required linear transformation may be written as

$$(\underline{t}\;\underline{X}_T) = \underline{x}\;\underline{V}. \tag{4}$$

In the three-particle case $\underline{V}$ may be written in general as

$$\underline{V} = \begin{pmatrix} a_1 - b_1 & a_2 - b_2 & M_T^{-1}m_1 \\ b_1 - c_1 & b_2 - c_2 & M_T^{-1}m_2 \\ c_1 - a_1 & c_2 - a_2 & M_T^{-1}m_3 \end{pmatrix} \tag{5}$$

corresponding to a choice for $\underline{t}_i$ of

$$\underline{t}_i = a_i(\underline{x}_1 - \underline{x}_3) + b_i(\underline{x}_2 - \underline{x}_1) + c_i(\underline{x}_3 - \underline{x}_2), \tag{6}$$

and $M_T = (m_1 + m_2 + m_3)$.

Hence the Hamiltonian Eq. (2) in the new coordinates becomes

$$\hat{H}(\underline{t},\underline{X}_T) = -\frac{\hbar^2}{2M_T}\nabla^2(\underline{X}_T) - \frac{\hbar^2}{2}\sum_{i,j=1}^{2}\mu_{ij}^{-1}\vec{\nabla}(\underline{t}_i)\cdot\vec{\nabla}(\underline{t}_j) + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{3}{}'\frac{Z_iZ_j}{f_{ij}(\underline{t})}. \tag{7}$$

Here

$$\mu_{ij}^{-1} = \sum_{k=1}^{N} m_k^{-1}V_{ki}V_{kj}, \qquad i,j = 12,\ldots,N-1 \tag{8}$$

and f_{ij} is just x_{ij} as given by Eq. (3) but expressed as a function of the $\underline{t}_i$. Thus

$$f_{ij}(\underline{t}) = \left[\sum_{\alpha}\left(\sum_{k=1}^{N-1}[(\underline{V}^{-1})_{kj} - (\underline{V}^{-1})_{ki}]t_{\alpha k}\right)^2\right]^{1/2}. \tag{9}$$

In Eq. (7), the $\vec{\nabla}(\underline{t}_i)$ are the usual grad operators expressed in the Cartesian components of $\underline{t}_i$ and the first term represents the center-of-mass kinetic energy. Since the center-of-mass variable does not enter the potential term, the center-of-mass problem may be separated off completely so that the full solution is of the form

$$T(\underline{X}_T)\Psi(\underline{t}), \tag{10}$$

where

$$T(\underline{X}_T) = \exp(i\underline{k}\,\underline{X}_T), \qquad \underline{k} \equiv (k_x, k_y, k_z), \tag{11}$$

and where the associated translational energy is

$$E_T = \frac{|\underline{k}|^2}{2M_T}. \tag{12}$$

From now on the center-of-mass motion will be ignored and we shall just consider solutions of the translation-free problem specified by the last two terms in Eq. (7).

The general form of the reciprocal reduced masses for the three-particle system is, from Eq. (8) and Eq. (5),

$$\begin{aligned} \frac{1}{\mu_i} &= \frac{(a_i - b_i)^2}{m_1} + \frac{(b_i - c_i)^2}{m_2} + \frac{(c_i - a_i)^2}{m_3}, \qquad i = 1,2 \\ \frac{1}{\mu_{12}} &= \frac{(a_1 - b_1)(a_2 - b_2)}{m_1} + \frac{(b_1 - c_1)(b_2 - c_2)}{m_2} + \frac{(c_1 - a_1)(c_2 - a_2)}{m_3}. \end{aligned} \tag{13}$$

If interparticle coordinates are chosen by means of

$$a_1 = 1, \quad b_1 = c_1 = 0 \quad \text{and} \quad c_2 = -1, \quad a_2 = b_2 = 0 \tag{14}$$

to give

$$\underline{t}_1 = (\underline{x}_1 - \underline{x}_3) \quad \text{and} \quad \underline{t}_2 = (\underline{x}_2 - \underline{x}_3), \tag{15}$$

then the reduced masses take the form

$$\mu_i^{-1} = m_i^{-1} + m_3^{-1}, \quad i = 1,2 \quad \text{and} \quad \mu_{i2}^{-1} = m_3^{-1}. \tag{16}$$

The two-electron atomic problem can be considered a special case of this where the $\underline{t}_i$ are defined in Eq. (15) and $\underline{x}_3$ is taken as the nuclear coordinate.

At this stage, one can either attempt to separate off the angular momentum to get a body-fixed coordinate system or one can try to construct angular momentum eigenfunctions for the translation-free problem directly. When considering atoms, in general it is not usual to separate off angular momentum because there is no unique choice of a body-fixed coordinate system. However, in the case of the two-electron atom or ion there is a unique choice, namely, that system in which the three particles define a plane. Two axes lie in the plane and the third axis is perpendicular to the plane so that the whole system is right handed. It is this body-fixed approach that will be used here and it is described in detail in Sutcliffe and Tennyson [20]. For present purposes, however, it is sufficient to note that the the body-fixed Hamiltonian is of the form

$$\hat{H}(\underline{\phi}, \underline{q}) = \hat{K}_{VR}(\underline{\phi}, \underline{q}) + \hat{K}_V(\underline{q}) + V(\underline{q}). \tag{17}$$

The three internal coordinates q_k are invariant under orthogonal transformations of the translation-free coordinates $\underline{t}$. The three orientation variables are specified by means of an orthogonal matrix $\underline{C}$ that puts the three particles in the plane and which can be parametrized by the three Euler angles ϕ_m, $m = 1,2,3$. The term $\hat{K}_V$ contains operators and functions that depend only on the q_k. $\hat{K}_{VR}$ contains the angular momentum operators, $\hat{L}_\alpha$, which are operators involving the ϕ_m only. These are multiplied by operators that depend on the q_k and so the term couples the angular motion with the internal motion. This term vanishes for states with angular momentum $J = 0$ and there will be no need to consider this term further in the present work, which is concerned only with S states of two-electron systems.

$V(\underline{q})$ arises from the electrostatic interactions and, since these are invariant under the operations of O(3), it depends only on the q_k.

The form of $\hat{K}_{VR}$ depends on the precise details of the choice of $\underline{C}$ but the form of $\hat{K}_V$ is independent of that choice and depends only on the choice of the q_k. Following Hylleraas we shall make the initial choice of the three internal coordinates as the interparticle distances, r_1, r_2, and r_3 which are, respectively, the 3-1, 3-2 and 1-2 interparticle distances. These are obtained by making the choice Eq. (14) for the $\underline{t}_i$ as in Eq. (15), then choosing

$$r_i = |\underline{t}_i|, \quad i = 1,2 \quad \text{and} \quad r_3 = r_{12} = |\underline{t}_j - \underline{t}_i|. \tag{18}$$

In these coordinates $\hat{K}_V$ becomes

$$\hat{K}_V(r_1, r_2, r_3) = -\frac{\hbar^2}{2}\left[\sum_{i=1}^{3} \frac{1}{\mu_i r_i^2}\left(\frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i}\right) + \sum_{j>i=1}^{2} \frac{b_{ij}}{\mu_{ij}} \frac{\partial^2}{\partial r_i \partial r_j}\right], \tag{19}$$

where the internal coordinate part of the Jacobian is $r_1 r_2 r_3$. In this equation, along with Eq. (16), the reduced mass terms are defined as

$$\frac{1}{\mu_3} = \frac{1}{\mu_1} + \frac{1}{\mu_2} - \frac{2}{\mu_{12}}, \qquad \frac{1}{\mu_{i3}} = \frac{1}{\mu_i} - \frac{1}{\mu_{12}}, \quad i = 1,2 \tag{20}$$

and the b_{ij} as

$$b_{ij} = \frac{r_i^2 + r_j^2 - r_k^2}{r_i r_j}, \tag{21}$$

where here and hereafter i, j, and k denote the distinct different choices of the indices $1,2$, and 3.

The problem with these coordinates is that since r_1, r_2, and r_3 ($= r_{12}$) are sides of a triangle and so connected by the triangular condition, the domains of the variables are not independent. This makes integration difficult, but Coolidge and James [7] showed that a linear combination of them could be chosen to have independent ranges. These *perimetric* coordinates are given by the relations

$$z_i = (-r_i + r_j + r_k), \tag{22}$$

where i, j, k denote each of the choices 123, 231, and 312, and r_1, r_2, and r_3 are as above. Each perimetric coordinate ranges from 0 to ∞.

The kinetic energy operator in these coordinates has the form [21]

$$\hat{K}_V(z_1, z_2, z_3) = -\frac{\hbar^2}{2}\left[\sum_{i=1}^{3}\left(v_{ii}\frac{\partial^2}{\partial z_i^2} + v_i \frac{\partial}{\partial z_i}\right) + \sum_{j>i=1}^{2} v_{ij} \frac{\partial^2}{\partial z_i \partial z_j}\right], \tag{23}$$

where the internal coordinate part of the Jacobian becomes $x/8$ where x is given by

$$x = (z_1 + z_2)(z_2 + z_3)(z_3 + z_1). \tag{24}$$

The quantities v_i above are defined as

$$v_i = 4\left(-\frac{1}{\mu_i(z_j + z_k)} + \frac{1}{\mu_j(z_i + z_k)} + \frac{1}{\mu_k(z_i + z_j)}\right), \tag{25}$$

while the quantities v_{ii} are

$$v_{ii} = \left(\frac{1}{\mu_1} + \frac{1}{\mu_2} + \frac{1}{\mu_3} - \frac{b_{ij}}{\mu_{ij}} - \frac{b_{ik}}{\mu_{ik}} + \frac{b_{jk}}{\mu_{jk}}\right), \tag{26}$$

and the v_{ij} are

$$v_{ij} = 2\left(-\frac{1}{\mu_i} - \frac{1}{\mu_j} + \frac{1}{\mu_k} + \frac{b_{ij}}{\mu_{ij}}\right). \tag{27}$$

The b_{ij} are just as defined in Eq. (21) above but expressed in terms of the z_i are

$$b_{ij} = 2[x - 2z_i z_j(z_i + z_j)]/x, \tag{28}$$

where x is given in Eq. (24).

The two-electron atomic problem with fixed nucleus

In the special case of a two-electron atom or ion with the r_i defined as in Eq. (18), m_3 can be considered the nuclear mass. The fixed-nucleus approximation is then the same as the infinite nuclear mass approximation where $m_3 \to \infty$ and $m_1 = m_2 = m$, the electronic mass, so that

$$\frac{1}{\mu_1} = \frac{1}{m}, \quad \frac{1}{\mu_2} = \frac{1}{m}, \quad \frac{1}{\mu_3} = \frac{2}{m},$$
$$\frac{1}{\mu_{12}} = 0, \quad \frac{1}{\mu_{13}} = \frac{1}{m}, \quad \frac{1}{\mu_{23}} = \frac{1}{m}, \tag{29}$$

and the Hamiltonian simplifies somewhat.

Hylleraas discovered that asymptotically the wave function behaves as $\exp(-ks/2)$ where $s = r_1 + r_2$. The asymptotic behavior of the solution of the Schrödinger equation, Ψ, for large s requires that in the exact solution k equal 2ϵ, where

$$\epsilon = +\sqrt{-E}, \tag{30}$$

and E is the electronic energy. Hence, Pekeris set $k = +2\sqrt{-E} \equiv 2\epsilon$. However, we use the relation suggested by Frost *et al.* [19] to remove the energy, i.e.,

$$E = -K\epsilon^2, \tag{31}$$

where K is a nonlinear variation parameter which with a suitable value increases the rate of convergence. To reduce calculation, Pekeris defined his perimetric coordinates by including the energy parameter ϵ, and including a factor 2 in his third coordinate so that his somewhat asymmetric coordinates and their inverse were defined as

$$u = \epsilon(r_2 + r_3 - r_1), \qquad v = \epsilon(r_1 + r_3 - r_2),$$
$$w = 2\epsilon(r_1 + r_2 - r_3), \tag{32}$$
$$r_1 = \frac{2v + w}{4\epsilon}, \qquad r_2 = \frac{2u + w}{4\epsilon}, \quad \text{and} \quad r_3 = \frac{u + v}{2\epsilon}.$$

Thus

$$(u + v + w) = 2\epsilon(r_1 + r_2) = ks,$$

and the wave function takes the form

$$\Psi = e^{-\frac{1}{2}(u+v+w)}F(u, v, w). \tag{33}$$

If the wave function above is, in principle, an exact form, then, using the kinetic energy operator Eq. (23), the reduced masses of Eq. (29) for the case of infinite nuclear mass, and scaling the perimetrics of Eq. (22) as in Eq. (32) above, i.e.,

$$z_1 = \frac{u}{\epsilon}, \qquad z_2 = \frac{v}{\epsilon}, \quad \text{and} \quad z_3 = \frac{w}{2\epsilon},$$

the Schrödinger equation $(\hat{H} - E)\Psi = 0$ becomes (after dividing out the asymptotic factor and multiplying by the Jacobian, then dividing by ϵ)

$$Q + (P + KS)\epsilon = 0. \tag{34}$$

Here,

$$\begin{aligned}
P = {} & 4uv(u + v + w)(F_{uu} - F_u + F_{vv} - F_v) + 2uw(2u + w)(F_{uu} - F_w + 2F_{ww} - 2F_{uw}) \\
& +2vw(2v + w)(F_{vv} - F_w + 2F_{ww} - 2F_{vw}) - 4(u^2 - v^2)(F_u - F_v) + 2(2u + w)(2v + w)(F_u + F_v - 2F_w) \\
& +4(u + v)(u + v + w)(2F_w - F) + (1/2)(u + v)(2u + w)(2v + w)F, \\
Q = {} & 4Z(u + v)(u + v + w)F - (2u + w)(2v + w)F, \\
S = {} & -(1/2)(u + v)(2u + w)(2v + w)F,
\end{aligned}$$

where Z is the nuclear charge and the subscripts designate partial derivatives. The quantities P and Q arise from the Laplacians and the Coulomb terms in H, respectively, while S arises from the energy E.

III. METHOD OF SOLUTION

To solve Eq. (34) Pekeris chose F to have the form

$$F = \sum_{l,m,n=0}^{\infty} A(l, m, n)\, L_l(u) L_m(v) L_n(w), \tag{35}$$

where $L_p(x)$ denotes the normalized Laguerre polynomial of order p. The Laguerres are appropriate for the region zero to infinity and with an exponential weight factor, $e^{-\frac{x}{2}}$, are an orthogonal system.

By using the basis set involving Laguerre functions of perimetric coordinates Eq. (35) and use of the recursion relations

$$\begin{aligned}
xL_n''(x) &= (x - 1)L_n'(x) - nL_n(x), \\
xL_n'(x) &= nL_n(x) - nL_{n-1}(x), \\
xL_n(x) &= -(n + 1)L_{n+1}(x) + (2n + 1)L_n(x) \\
&\quad -nL_{n-1}(x),
\end{aligned} \tag{36}$$

TABLE I. Coefficients $C_{\alpha,\beta,\gamma}(l,m,n)$ in the recursion relation Eq. (37) for the nuclear mass M and atomic charge number Z.

α	β	γ	$C_{\alpha,\beta,\gamma}(l,m,n)$
2	1	0	$2\epsilon\,(l+2)\,(l+1)\,(K-1)\,(m+1)$
2	0	1	$\epsilon\,(l+2)\,(l+1)\,(KM-M-2)\,(n+1)\ /\ M$
1	2	0	$2\epsilon\,(m+2)\,(m+1)\,(K-1)\,(l+1)$
1	0	2	$\epsilon\,(n+2)\,(n+1)\,(KM-M-2)\,(l+1)\ /\ 2M$
0	2	1	$\epsilon\,(m+2)\,(m+1)\,(KM-M-2)\,(n+1)\ /\ M$
0	1	2	$\epsilon\,(n+2)\,(n+1)\,(KM-M-2)\,(m+1)\ /\ 2M$
1	1	1	$2\epsilon\,(KM-M-2)\,(l+1)\,(n+1)\,(m+1)\ /\ M$
2	0	0	$-(l+2)\,(l+1)\,(2\epsilon nM-4ZM+\epsilon M+4\epsilon n+2\epsilon+3K\epsilon M+4K\epsilon mM+2K\epsilon nM)\ /\ M$
0	2	0	$-(m+2)\,(m+1)\,(2K\epsilon nM-4ZM+2\epsilon nM+3K\epsilon M+4\epsilon n+2\epsilon+\epsilon M+4K\epsilon lM)\ /\ M$
0	0	2	$-(n+2)\,(n+1)\,(-2\epsilon l-\epsilon M-2\epsilon m-2\epsilon+M+K\epsilon M-\epsilon mM-\epsilon lM+K\epsilon mM+K\epsilon lM)\ /\ M$
1	1	0	$-(2l+2)\,(m+1)\,(4K\epsilon mM-2\epsilon mM-2\epsilon lM+4K\epsilon lM+4\epsilon n+2\epsilon+2M+2K\epsilon nM-5\epsilon M-4ZM-2\epsilon nM+9K\epsilon M)\ /\ M$
1	0	1	$-(2l+2)\,(n+1)\,(K\epsilon nM-2\epsilon lM+2K\epsilon lM-4\epsilon l+4K\epsilon M-4\epsilon m+2K\epsilon mM-6\epsilon+M-2\epsilon M-2ZM)\ /\ M$
0	1	1	$-(2n+2)\,(m+1)\,(2K\epsilon mM-4\epsilon m-2\epsilon mM+K\epsilon nM-6\epsilon+M-4\epsilon l-2ZM+2K\epsilon lM-2\epsilon M+4K\epsilon M)\ /\ M$
1	0	0	$(l+1)\,\Big(14\epsilon+6M+12\epsilon m+12\epsilon l+16\epsilon ln+8\epsilon ml+8mM+9\epsilon M+2\epsilon n^2-28ZM+4nM+4\epsilon mM+26\epsilon n+15\epsilon nM+19K\epsilon M$ $+3K\epsilon n^2M+16\epsilon mn-16ZmM-4\epsilon m^2M+12K\epsilon m^2M+16K\epsilon lmM+8K\epsilon lnM+8K\epsilon mnM+32K\epsilon mM+15K\epsilon nM+12K\epsilon lM-4\epsilon m^2$ $-8ZnM+16\epsilon lnM+8\epsilon mlM+12\epsilon lM-16ZlM-\epsilon n^2M\Big)\ /\ M$
0	1	0	$(m+1)\,\Big(14\epsilon+6M+12\epsilon m+12\epsilon l+16\epsilon ln+8\epsilon ml+9\epsilon M+2\epsilon n^2-28ZM+4nM+12\epsilon mM+26\epsilon n-4\epsilon l^2+15\epsilon nM$ $+19K\epsilon M+3K\epsilon n^2M+16\epsilon mn-16ZmM+16K\epsilon lmM+16\epsilon mnM+8K\epsilon lnM+8K\epsilon mnM+12K\epsilon mM+15K\epsilon nM+32K\epsilon lM-8ZnM$ $+12K\epsilon l^2M+8\epsilon mlM+8lM+4\epsilon lM-16ZlM-\epsilon n^2M-4\epsilon l^2M\Big)\ /\ M$
0	0	1	$(2n+2)\,\Big(4M-6\epsilon-10\epsilon m-10\epsilon l-8\epsilon ml+2mM-\epsilon M-4ZM+2nM-\epsilon mM-6\epsilon l^2+2\epsilon nM+5K\epsilon M-4ZmM-5\epsilon m^2M+3K\epsilon m^2M$ $+4K\epsilon lmM+2\epsilon mnM+2K\epsilon lnM+2K\epsilon mnM+7K\epsilon mM+2K\epsilon nM+7K\epsilon lM-6\epsilon m^2+3K\epsilon l^2M+2\epsilon lnM+4\epsilon mlM$ $+2lM-\epsilon lM-4ZlM-5\epsilon l^2M\Big)\ /\ M$
2	−1	0	$2\epsilon m\,(l+2)\,(l+1)\,(KM-2-M)\ /\ M$
−1	2	0	$2\epsilon l\,(m+2)\,(m+1)\,(KM-2-M)\ /\ M$
0	2	−1	$\epsilon n\,(m+2)\,(m+1)\,(KM-5M-2)\ /\ M$
2	0	−1	$\epsilon n\,(l+2)\,(l+1)\,(KM-5M-2)\ /\ M$
−1	0	2	$\epsilon l\,(n+2)\,(n+1)\,(KM-5M-2)\ /\ 2M$
0	−1	2	$\epsilon m\,(n+2)\,(n+1)\,(KM-5M-2)\ /\ 2M$
1	1	−1	$2\epsilon n\,(KM-2-M)\,(l+1)\,(m+1)\ /\ M$
1	−1	1	$2\epsilon m\,(KM-2-M)\,(l+1)\,(n+1)\ /\ M$
−1	1	1	$2\epsilon l\,(KM-2-M)\,(n+1)\,(m+1)\ /\ M$
0	0	0	$-16lmM+4\epsilon mn^2+44\epsilon ln+32\epsilon m+32\epsilon l+4\epsilon n^2+20\epsilon l^2+28\epsilon n+20\epsilon m^2+16\epsilon+16K\epsilon M+32\epsilon lmn+16\epsilon M+12mM+14nM+12lM$ $-32ZM+6n^2M+44\epsilon mn+10M+16\epsilon l^2m-48ZlM+8mnM+16\epsilon lm^2+48\epsilon lm+24\epsilon l^2n+4\epsilon ln^2+24\epsilon m^2n+8lnM-48ZmM$ $-24Zm^2M-24Zl^2M-16ZnM+32\epsilon mM+32\epsilon lM+10\epsilon n^2M+22\epsilon l^2M+30\epsilon nM+22\epsilon m^2M-32ZlmM+10\epsilon mn^2M+32K\epsilon lM$ $+46\epsilon lnM+16\epsilon lmnM+16K\epsilon lmnM+26K\epsilon mnM+6K\epsilon ln^2M+6K\epsilon mn^2M+26K\epsilon lnM+12K\epsilon l^2nM+24K\epsilon l^2mM$ $+56K\epsilon lmM+24K\epsilon lm^2M+12K\epsilon m^2nM+46\epsilon mnM+16\epsilon l^2mM+16\epsilon lm^2M+40\epsilon lmM+28\epsilon l^2nM+10\epsilon ln^2M+18K\epsilon m^2M$ $+32K\epsilon mM+28\epsilon m^2nM-16ZlnM+18K\epsilon l^2M+6K\epsilon n^2M+18K\epsilon nM-16ZmnM\ /\ M$
−1	1	0	$-2l\,(m+1)\,(4K\epsilon mM-2\epsilon mM-4\epsilon m+4K\epsilon lM+5K\epsilon M-2\epsilon+2M-2\epsilon nM-4ZM-2\epsilon lM+2K\epsilon nM+4\epsilon n-3\epsilon M-4\epsilon l)\ /\ M$
1	−1	0	$-2m\,(l+1)\,(4K\epsilon lM-2\epsilon lM-4\epsilon l-2\epsilon+2M-4\epsilon m+2K\epsilon nM+4\epsilon n-3\epsilon M-4ZM+5K\epsilon M-2\epsilon mM-2\epsilon nM+4K\epsilon mM)\ /\ M$
−1	0	1	$-2l\,(n+1)\,(K\epsilon nM-2\epsilon nM+M+2K\epsilon lM+2K\epsilon M-4\epsilon m-2ZM-2\epsilon-6\epsilon lM+2K\epsilon mM-4\epsilon l-2\epsilon M)\ /\ M$
0	−1	1	$-2m\,(n+1)\,(K\epsilon nM-2\epsilon nM-2ZM+M+2K\epsilon mM-4\epsilon l+2K\epsilon M-2\epsilon-6\epsilon mM+2K\epsilon lM-2\epsilon M-4\epsilon m)\ /\ M$

TABLE I. *(Continued)*.

α	β	γ	$C_{\alpha,\beta,\gamma}(l,m,n)$
1	0	−1	$-2n\,(l+1)\,(2\,K\epsilon lM - 6\,\epsilon lM - 4\,\epsilon l + M - 2\,ZM + K\epsilon nM - 6\,\epsilon - 6\,\epsilon M + 2\,K\epsilon mM + 3\,K\epsilon M - 4\,\epsilon m - 2\,\epsilon nM)\ /\ M$
0	1	−1	$-2n\,(m+1)\,(2\,K\epsilon mM - 6\,\epsilon mM - 4\,\epsilon m + M - 6\,\epsilon - 2\,ZM - 6\,\epsilon M - 4\,\epsilon l + K\epsilon nM + 3\,K\epsilon M + 2\,K\epsilon lM - 2\,\epsilon nM)\ /\ M$
−1	0	0	$l\,\Big(2\,\epsilon + 6\,M + 4\,\epsilon m + 8\,\epsilon ml + 4\,nM + 10\,\epsilon n - 3\,\epsilon M - 12\,ZM + 12\,\epsilon l - 4\,\epsilon m^2M - 16\,ZmM - 4\,\epsilon mM + 16\,\epsilon mn + 3\,K\epsilon n^2M - \epsilon n^2M - 8\,ZnM - 4\,\epsilon m^2 + 12\,K\epsilon lM + 8\,K\epsilon lnM - 16\,ZlM + 7\,K\epsilon M + 7\,K\epsilon nM + 16\,\epsilon lnM - \epsilon nM + 12\,\epsilon lM + 8\,K\epsilon mnM + 16\,\epsilon ln + 8\,\epsilon mlM + 16\,K\epsilon mM + 12\,K\epsilon m^2M + 16\,K\epsilon lmM + 8\,mM + 2\,\epsilon n^2\Big)\ /\ M$
0	−1	0	$m\,\Big(2\,\epsilon + 6\,M + 12\,\epsilon m + 8\,\epsilon ml + 4\,nM + 10\,\epsilon n - 3\,\epsilon M - 12\,ZM + 8\,lM + 4\,\epsilon l - 4\,\epsilon l^2 - 16\,ZmM + 12\,\epsilon mM + 16\,\epsilon mn + 3\,K\epsilon n^2M - \epsilon n^2M - 8\,ZnM + 16\,K\epsilon lM + 8\,K\epsilon lnM - 16\,ZlM + 7\,K\epsilon M + 7\,K\epsilon nM - \epsilon nM - 4\,\epsilon lM + 8\,K\epsilon mnM + 16\,\epsilon ln + 8\,\epsilon mlM + 12\,K\epsilon mM + 16\,K\epsilon lmM - 4\,\epsilon l^2M + 2\,\epsilon n^2 + 12\,K\epsilon l^2M + 16\,\epsilon mnM\Big)\ /\ M$
0	0	−1	$2n\,\Big(2\,M - 6\,\epsilon - 10\,\epsilon m - 8\,\epsilon ml + 2\,nM - 3\,\epsilon M - 4\,ZM + 2\,lM - 10\,\epsilon l - 6\,\epsilon l^2 - 5\,\epsilon m^2M - 4\,ZmM - 3\,\epsilon mM - 6\,\epsilon m^2 + 5\,K\epsilon lM + 2\,K\epsilon lnM - 4\,ZlM + 3\,K\epsilon M + 2\,K\epsilon nM + 2\,\epsilon lnM + 2\,\epsilon nM - 3\,\epsilon lM + 2\,K\epsilon mnM + 4\,\epsilon mlM + 5\,K\epsilon mM + 3\,K\epsilon m^2M + 4\,K\epsilon lmM + 2\,mM - 5\,\epsilon l^2M + 3\,K\epsilon l^2M + 2\,\epsilon mnM\Big)\ /\ M$
1	0	−2	$\epsilon n\,(KM - 5\,M - 2)\,(l+1)\,(n-1)\ /\ 2\,M$
0	1	−2	$\epsilon n\,(KM - 5\,M - 2)\,(n-1)\,(m+1)\ /\ 2\,M$
−2	0	1	$\epsilon l\,(KM - 5\,M - 2)\,(l-1)\,(n+1)\ /\ M$
0	−2	1	$\epsilon m\,(KM - 5\,M - 2)\,(n+1)\,(m-1)\ /\ M$
1	−2	0	$2\,\epsilon m\,(KM - M - 2)\,(l+1)\,(m-1)\ /\ M$
−2	1	0	$2\,\epsilon l\,(KM - M - 2)\,(l-1)\,(m+1)\ /\ M$
1	−1	−1	$2\,\epsilon mn\,(KM - M - 2)\,(l+1)\ /\ M$
−1	1	−1	$2\,\epsilon ln\,(KM - M - 2)\,(m+1)\ /\ M$
−1	−1	1	$2\,\epsilon ml\,(KM - M - 2)\,(n+1)\ /\ M$
−2	0	0	$-l\,(l-1)\,(2\,\epsilon nM - 4\,ZM + 4\,\epsilon n + 2\,K\epsilon nM + 4\,K\epsilon mM + \epsilon M + 2\,\epsilon + 3\,K\epsilon M)\ /\ M$
0	−2	0	$-m\,(m-1)\,(4\,K\epsilon lM - 4\,ZM + \epsilon M + 2\,K\epsilon nM + 2\,\epsilon nM + 4\,\epsilon n + 2\,\epsilon + 3\,K\epsilon M)\ /\ M$
0	0	−2	$-n\,(n-1)\,(K\epsilon mM - \epsilon mM - \epsilon lM + M - 2\,\epsilon + K\epsilon M - 2\,\epsilon l - 2\,\epsilon m + K\epsilon lM - \epsilon M)\ /\ M$
−1	−1	0	$-2\,lm\,(2\,M + K\epsilon M + 2\,K\epsilon nM + 4\,K\epsilon mM + 4\,K\epsilon lM - 4\,ZM + 4\,\epsilon n - \epsilon M - 2\,\epsilon nM - 2\,\epsilon lM + 2\,\epsilon - 2\,\epsilon mM)\ /\ M$
−1	0	−1	$-2\,ln\,(M + K\epsilon M + 2\,K\epsilon lM + 2\,K\epsilon mM + K\epsilon nM - 2\,ZM - 4\,\epsilon m - 2\,\epsilon lM - 2\,\epsilon - 4\,\epsilon l)\ /\ M$
0	−1	−1	$-2\,mn\,(M + 2\,K\epsilon lM + K\epsilon nM + K\epsilon M + 2\,K\epsilon mM - 2\,ZM - 2\,\epsilon mM - 4\,\epsilon l - 2\,\epsilon - 4\,\epsilon m)\ /\ M$
−2	−1	0	$2\,\epsilon lm\,(K-1)\,(l-1)$
−2	0	−1	$\epsilon ln\,(KM - M - 2)\,(l-1)\ /\ M$
−1	−2	0	$2\,\epsilon ml\,(K-1)\,(m-1)$
−1	0	−2	$\epsilon ln\,(KM - M - 2)\,(n-1)\ /\ 2\,M$
0	−1	−2	$\epsilon mn\,(KM - M - 2)\,(n-1)\ /\ 2\,M$
0	−2	−1	$\epsilon mn\,(KM - M - 2)\,(m-1)\ /\ M$
−1	−1	−1	$2\,\epsilon lmn\,(KM - M - 2)\ /\ M$

all the derivatives and powers of the variables (u, v, w) can be eliminated to obtain a 57-term recursion relation between the coefficients $A(l, m, n)$ in the expansion. (In the case where $K = 1$ the 33-term recursion relation of Pekeris is obtained.) This recursion relation has the form

$$\sum_{\alpha,\beta,\gamma=-2}^{+2} C_{\alpha,\beta,\gamma}(l,m,n)A(l+\alpha,m+\beta,n+\gamma) = 0. \quad (37)$$

[The α, β, and γ are defined by choosing a particular $A(l+\alpha, m+\beta, n+\gamma)$, see the coefficients of the recurrence relation which are given in Table I for the general case where Z, K, and M are arbitrary. The coefficient of that A will be $C_{\alpha,\beta,\gamma}$ and this is a function of l, m, and n, i.e., $C_{\alpha,\beta,\gamma}(l,m,n)$. Therefore once an $A(l+\alpha, m+\beta, n+\gamma)$ is chosen all one needs to know is the value of l, m, and n which is to be substituted into its coefficient. Hence, $C_{\alpha,\beta,\gamma}(l,m,n)$ of Eq. (37) could equally well be written as $C((l,m,n)(l',m',n'))$ where l', m' and n' are $l+\alpha$, $m+\beta$ and $n+\gamma$, respectively. This notation will be used later.]

Because the coordinates u and v are electronic coordinates, the Pauli principle requires that in Eq. (37)

$$A(l,m,n) = \begin{cases} A(m,l,n) & \text{(singlet spin state, para, or symmetric)} \\ -A(m,l,n) & \text{(triplet spin state, ortho, or antisymmetric)} \end{cases}$$

so that there are two solution sets in Eq. (35),

$$\begin{aligned} F_s(u,v,w) &= F_s(v,u,w), \\ F_a(u,v,w) &= -F_a(v,u,w). \end{aligned} \quad (38)$$

The symmetric form for the singlet is

$$\begin{aligned} F_s(u,v,w) = {} & \sum_{l,n=0}^{\infty} A^s(l,l,n)L_l(u)L_l(v)L_n(w) \\ & + \sum_{l<m=1}^{\infty}\sum_{n=0}^{\infty} A^s(l,m,n) \\ & \times[L_l(u)L_m(v)L_n(w) + L_m(u)L_l(v)L_n(w)] \end{aligned}$$

while the antisymmetric form for the triplet is

$$\begin{aligned} F_a(u,v,w) = {} & \sum_{l<m=1}^{\infty}\sum_{n=0}^{\infty} A^a(l,m,n)[L_l(u)L_m(v)L_n(w) \\ & -L_m(u)L_l(v)L_n(w)]. \end{aligned}$$

This symmetry also manifests itself in the matrix elements generated, thus this is taken account of in our programs.

The "rules" used for the symmetric case are

$$\text{or} \quad \begin{aligned} & l,l,n \leftrightarrow l',l',n' \rightarrow C((l,l,n),(l',l',n'))/2, \\ & l,l,n \leftrightarrow l',m',n' \rightarrow C((l,l,n),(l',m',n')), \\ & l,m,n \leftrightarrow l',l',n' \rightarrow C((l,m,n),(l',l',n')), \\ & l,m,n \leftrightarrow l',m',n' \rightarrow C((l,m,n),(l',m',n')) \\ & \qquad\qquad +C((m,l,n),(l',m',n')), \end{aligned}$$

where $l' = l+\alpha$, $m' = m+\beta$, and $n' = n+\gamma$ as noted earlier.

These rules also apply for the antisymmetric case except that the last condition becomes

$$\begin{aligned} l,m,n \leftrightarrow l',m',n' \rightarrow {} & C((l,m,n),(l',m',n')) \\ & -C((m,l,n),(l',m',n')). \end{aligned}$$

The numbering scheme involves collapsing each triple of indices (l,m,n) to a single index. Equation (37) then becomes

$$\sum_k C_{ik}B_k = 0, \quad (39)$$

where for any given i $(\equiv l,m,n)$ a particular set of k $(\equiv l+\alpha, m+\beta, n+\gamma)$ are generated such that the C_{ik} are given by the terms that coefficient $A(l+\alpha, m+\beta, n+\gamma) \equiv B_k$ in the 57-term recursion relation. Each triple of indices (l,m,n) is collapsed to a single index by means of

$$\begin{aligned} k(l,m,n) = {} & \frac{w(w+2)(2w+5)}{24} + \frac{1-(-1)^w}{16} + \frac{(l+m)}{2} \\ & + \frac{(l+m)^2}{4} + \frac{1-(-1)^{l+m}}{8} + l + 1 \end{aligned} \quad (40)$$

for the symmetrical case and

TABLE II. Ordering of the indices l, m, n for the symmetrical and the antisymmetrical cases.

Symmetrical					Antisymmetrical				
l	m	n	w	k	l	m	n	w	p
0	0	0	0	1	0	1	0	1	1
0	0	1	1	2	0	1	1	2	2
0	1	0	1	3	0	2	0	2	3
0	0	2	2	4	0	1	2	3	4
0	1	1	2	5	0	2	1	3	5
0	2	0	2	6	0	3	0	3	6
1	1	0	2	7	1	2	0	3	7
0	0	3	3	8	0	1	3	4	8
0	1	2	3	9	0	2	2	4	9
0	2	1	3	10	0	3	1	4	10

TABLE III. Energy of the $1\,^1S$ state of H^- ($Z = 1$) with fixed nucleus showing the increased rate of convergence when a scale parameter K is used.

		$-E$ (hartree)		
Highest degree	Matrix size	Pekeris value ($K = 1$)	Scaled value	K
4	22	0.527 630 681 42	0.527 669 054 63	1.3
8	95	0.527 750 016 51	0.527 750 058 06	1.1
9	125	0.527 750 610 25	0.527 750 610 25	1.0
10	161	0.527 750 859 79	0.527 750 860 44	0.9
11	203	0.527 750 935 60	0.527 750 942 98	0.9
12	252	0.527 750 973 84	0.527 750 984 57	0.8
15	444	0.527 751 006 30	0.527 751 011 88	0.7
18	715	0.527 751 013 39	0.527 751 015 84	0.6
21	1078	0.527 751 015 36	0.527 751 016 36	0.6

$$p(l,m,n) = \frac{w(w+2)(2w-1)}{24} - \frac{1-(-1)^w}{16} + l(m+n) + m \tag{41}$$

for the antisymmetric case, where $w = l + m + n$. [The term $\frac{(l+m)}{2}$ was omitted from $k(l,m,n)$ in the Pekeris paper because of a typographic error.]

Loeser and Herschbach used these formulas in a slightly more general form

$$k(l,m,n) = \frac{\sigma(\sigma+2)(2\sigma+5)}{24} + \frac{1-(-1)^\sigma}{16} + \frac{(l+m+1)^2}{4} + \frac{1-(-1)^{l+m}}{8} + \min(l,m) + \frac{3}{4} \tag{42}$$

for spin, $s = 0$–parahelium, and

$$p(l,m,n) = \frac{(\sigma+1)(\sigma+3)(2\sigma+1)}{24} + \frac{1-(-1)^\sigma}{16} + l + m + lm + (n-1)\min(l,m) - \frac{1}{8} \tag{43}$$

for $s = 1$–orthohelium, where $\sigma = l+m+n-s$. A sample of these numbering systems is given in Table II.

The infinite secular problem can then be written as

$$\sum_k (F_{ik} - \epsilon G_{ik}) B_k = 0, \tag{44}$$

with the form of a generalized eigenvalue problem. The elements of F arise from the potential term Q and those of G from the kinetic energy term P and the energy term S given below Eq. (34). The infinite secular equation is solved in truncated form of increasing size of up to any order k (or p).

IV. RESULTS AND DISCUSSION

To show the effect that the scale parameter K has on the energy it has been varied at each order of the matrix and is shown in Table III for the hydride ion and Table IV for helium.

In Table IV the energies in the third column can be found in [6] but have been reevaluated here and are presented to 12 significant figures. The fourth column contains the energies obtained for the fixed-nucleus problem using a scale parameter, hence the heading of the column.

The best value presented by Pekeris, in his second (1959) paper, for helium was rounded to nine decimal places, i.e., 2.903 724 375, the value in the last row of the third column of Table IV (in bold type). As can be seen from Table IV (also in bold type), this value was achieved at a matrix size of 252 by using a scale parameter of 0.4, and if one goes on to a matrix size of 1078 as Pekeris did, a marked improvement in the last digit can be seen, i.e., 2.903 724 377, which is better than his *extrapolated* value. It is obvious, therefore, that a scale parameter is invaluable in a calculation of this form.

TABLE IV. Energies of the $1\,^1S$ state of He ($Z = 2$) with fixed nucleus showing the increased rate of convergence when a scale parameter K is used.

		$-E$ (hartree)		
Highest degree	Matrix size	Pekeris value ($K = 1$)	Scaled value	K
4	22	2.903 688 986 12	2.903 713 944 25	0.7
8	95	2.903 723 389 08	2.903 724 304 91	0.5
9	125	2.903 723 878 62	2.903 724 340 00	0.5
10	161	2.903 724 111 15	2.903 724 364 62	0.4
11	203	2.903 724 228 32	2.903 724 371 60	0.4
12	252	2.903 724 290 41	**2.903 724 374 68**	0.4
15	444	2.903 724 356 22	2.903 724 376 75	0.3
18	715	2.903 724 370 81	2.903 724 376 98	0.3
21	1078	**2.903 724 374 76**	2.903 724 377 02	0.2

TABLE V. The scale parameter K, the energy parameter ϵ, the energy $-K\epsilon^2$ (in hartrees), and various expectation values for the virial theorem. ϵ is in units of (hartrees)$^{\frac{1}{2}}$ and the expectation values are also in these units. U is the electron-nucleus cusp value and T is the electron-electron cusp value as described in the text. The four subrows in each row correspond to matrix sizes of order 252, 444, 715, and 1078 and the fifth row of U and T are the cusp values obtained from a 1078 Pekeris calculation (K=1). This is for the $1\,^1S$ state with nucleus fixed.

Z	1	2	3	4	5	6	7	8	9	10
K	0.8	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	0.7	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	0.6	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	0.6	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2
$-\epsilon$	0.8122122448729	2.694310846337	4.266120430238	5.842851665882	7.421416909456	9.000867541412	10.58081343117	12.16106441888	13.74151668860	15.32210874132
	0.8682914355088	3.111122185942	4.926091558375	6.746743964859	8.569514101360	10.39330659634	12.21767096580	14.04238763204	15.86733671874	17.69244721294
	0.9378619442114	3.111122186061	4.926091558431	6.746743964898	8.569514101392	10.39330659637	12.21767096582	14.04238763206	15.86733671875	17.69244721296
	0.9378619446730	3.810330941675	6.033205372214	8.263040069616	8.569514101399	12.72914895071	14.96352985575	17.19834223446	19.43343926894	21.66873398644
$K\epsilon^2$	0.5277509845772	2.903724374675	7.279913410118	13.655566235800	22.030971577583	32.406246599217	44.781445146076	59.156595120049	75.531712361240	93.906806512308
	0.5277510118846	2.903724376758	7.279913412449	13.655566238207	22.030971580025	32.406246601677	44.781445148548	59.156595122528	75.531712363724	93.906806514796
	0.5277510158400	2.903724376981	7.279913412613	13.655566238366	22.030971580185	32.406246601841	44.781445148715	59.156595122700	75.531712363902	93.906806514980
	0.5277510163595	2.903724377017	7.279913412662	13.655566238417	22.030971580222	32.406246601891	44.781445148765	59.156595122749	75.531712363950	93.906806515027
$-\langle\hat{V}\rangle$	1.624424666863	5.388621677612	8.532240848912	11.68570332308	14.84283381204	18.00173507717	21.16162685756	24.32212883365	27.48303337361	30.64421747946
	1.736582897778	6.222244373406	9.852183116369	13.49348792936	17.13902820246	20.78661319252	24.43534193151	28.08477526406	31.73467343751	35.38489442597
	1.875723893767	6.222244371667	9.852183116556	13.49348792957	17.13902820261	20.78661319259	24.43534193152	28.08477526401	31.73467343741	35.38489442583
	1.875723888467	7.620661883936	12.06641074451	16.52608013928	17.13902820273	25.45829790147	29.92705971154	34.39668446898	38.86687853795	43.33746797294
$-\langle\hat{K}\rangle$	-0.8122124219902	-2.694310831275	-4.266120418674	-5.842851657201	-7.421416902583	-9.000867535759	-10.58081342639	-12.16106441477	-13.74151668501	-15.32210873814
	-0.8682914622697	-3.111122187464	-4.926091557994	-6.746743964500	-8.569514101102	-10.39330659618	-12.21767096571	-14.04238763202	-15.86733671878	-17.69244721303
	-0.9378619495559	-3.111122185606	-4.926091558126	-6.746743964673	-8.569514101214	-10.39330659622	-12.21767096570	-14.04238763195	-15.86733671866	-17.69244721287
	-0.9378619437943	-3.810330942261	-6.033205372300	-8.263040069667	-8.569514101333	-12.72914895076	-14.96352985580	-17.19834223452	-19.43343926900	-21.66873398650
$-\langle\epsilon\rangle$	0.8122122448729	2.694310846337	4.266120430238	5.842851665882	7.421416909456	9.000867541412	10.58081343117	12.16106441888	13.74151668860	15.32210874132
	0.8682914355088	3.111122185942	4.926091558375	6.746743964859	8.569514101360	10.39330659634	12.21767096580	14.04238763204	15.86733671874	17.69244721294
	0.9378619442114	3.111122186061	4.926091558431	6.746743964898	8.569514101392	10.39330659637	12.21767096582	14.04238763206	15.86733671875	17.69244721296
	0.9378619446730	3.810330941675	6.033205372214	8.263040069616	8.569514101399	12.72914895071	14.96352985575	17.19834223446	19.43343926895	21.66873398644
$-(\langle\hat{V}\rangle+\langle\hat{K}\rangle)$	0.8122122448729	2.694310846337	4.266120430238	5.842851665882	7.421416909456	9.000867541412	10.58081343117	12.16106441888	13.74151668860	15.32210874132
	0.8682914355088	3.111122185942	4.926091558375	6.746743964859	8.569514101361	10.39330659634	12.21767096580	14.04238763204	15.86733671878	17.69244721294
	0.9378619442114	3.111122186061	4.926091558431	6.746743964898	8.569514101391	10.39330659637	12.21767096582	14.04238763206	15.86733671875	17.69244721296
	0.9378619446730	3.810330941675	6.033205372214	8.263040069616	8.569514101398	12.72914895071	14.96352985575	17.19834223446	19.43343926894	21.66873398644
U	0.972386892299	1.98500739840	2.98555937762	3.98597970026	4.98629316628	5.98654717766	6.98676594744	7.98696232664	8.98714365108	9.98731438726
	0.978932990052	1.98633846917	2.98743281740	3.98761201244	4.98756012574	5.98741166268	6.98721305087	7.98698491358	8.98673788156	9.98647801123
	0.983671945185	1.99051010001	2.99093322562	3.99116858826	4.99131660460	5.99142040460	6.99149900007	7.99156191951	8.99161443849	9.99165970896
	0.985729799657	1.99016379823	2.99114651868	3.99117576354	4.99226594662	5.99071635898	6.99040105998	7.99006106712	8.98970551314	9.98933951132
	0.98112641	1.98375409	2.98457791	3.98497305	4.98520454	5.98535652	6.98546392	7.98554383	8.98560562	9.98565481
T	0.455125861507	0.473414663542	0.475129265233	0.475847269757	0.476253369541	0.476516129032	0.476700517599	0.476837262296	0.476942846750	0.477026925500
	0.466678502844	0.482878233392	0.483158344125	0.483467595804	0.483672359445	0.483812653694	0.483913519791	0.483988975943	0.484047209849	0.484093269087
	0.473195407095	0.484275798912	0.485167057200	0.485568179410	0.485799798787	0.485950951825	0.486057440607	0.486136543990	0.486197639168	0.486246257570
	0.477049834978	0.489857567478	0.490078089147	0.490252203960	0.487822391351	0.490429163665	0.490474835652	0.490505487777	0.490525981022	0.490539299114
	0.47005853	0.47425890	0.47557084	0.47619978	0476568158	0.47680996	0.47698083	0.47710796	0.477206244	0.477284489

TABLE VI. The scale parameter K, the energy parameter ϵ, the energy $-K\epsilon^2$ (in hartrees), and various expectation values for the virial theorem. ϵ is in units of (hartrees)$^{\frac{1}{2}}$ and the expectation values are also in these units. The four subrows in each row correspond to matrix sizes of order 252, 444, 715, and 1078. This is for the $2\,^3S$ state with nucleus fixed.

Z	2	3	4	5	6	7	8	9	10
K	1.7	1.3	1.2	1.1	1.1	1.1	1.0	1.0	1.0
	1.4	1.2	1.3	0.9	0.9	0.9	0.9	0.9	0.9
	1.4	1.3	1.2	1.2	0.8	0.8	0.8	0.8	0.7
	1.4	1.4	0.7	1.2	0.8	0.8	0.8	0.8	0.8
$-\epsilon$	1.131170496495	1.982757864131	2.783458069478	3.659843184490	4.412869186416	5.166120554082	6.208433564101	6.998688329201	7.789008061612
	1.246489177702	2.063719815556	2.674260011195	4.046108878197	4.878610446781	5.711361166568	6.544263588151	7.377265251321	8.210335396050
	1.246489177717	1.982757864220	2.783458069526	3.504033074997	5.174547794531	6.057813316029	6.941239741581	7.824771428732	9.309645273591
	1.246489177718	1.910633285545	3.644402084955	3.504033074998	5.174547794531	6.057813316029	6.941239741581	7.824771428732	8.708375751545
$K\epsilon^2$	2.175229376640	5.110727372106	9.297166589451	14.733897348560	21.420755902064	29.357681737245	38.544647319856	48.981638329298	60.668646583856
	2.175229378178	5.110727372542	9.297166589721	14.733897348802	21.420755902297	29.357681737481	38.544647320074	48.981638329508	60.668646584063
	2.175229378230	5.110727372563	9.297166589771	14.733897348807	21.420755902307	29.357681737490	38.544647320084	48.981638329517	60.668646584073
	2.175229378235	5.110727372568	9.297166589777	14.733897348813	21.420755902308	29.357681737491	38.544647320085	48.981638329518	60.668646584073
$-\langle\hat{V}\rangle$	2.262340995506	3.965515727931	5.566916138401	7.319686368903	8.825738372553	10.33224110784	12.41686712850	13.99737665861	15.57801612337
	2.492978355469	4.127439630992	5.348520022202	8.092217756409	9.757220893559	11.42272233313	13.08852717629	14.75453050263	16.42067079209
	2.492978355391	3.965515728404	5.566916139030	7.008066149974	10.34909558906	12.11562663206	13.88247948316	15.64954285746	18.61929054718
	2.492978355426	3.821266571079	7.288804169912	7.008066149990	10.34909558906	12.11562663206	13.88247948316	15.64954285746	17.41675150309
$-\langle\hat{K}\rangle$	-1.131170499010	-1.982757863799	-2.783458068923	-3.659843184413	-4.412869186137	-5.166120553759	-6.208433564403	-6.998688329405	-7.789008061762
	-1.246489177767	-2.063719815436	-2.674260011007	-4.046108878212	-4.878610446778	-5.711361166559	-6.544263588140	-7.377265251310	-8.210335396039
	-1.246489177675	-1.982757864185	-2.783458069504	-3.504033074977	-5.174547794529	-6.057813316027	-6.941239741579	-7.824771428730	-9.309645273593
	-1.246489177708	-1.910633285533	-3.644402084957	-3.504033074993	-5.174547794530	-6.057813316029	-6.941239741581	-7.824771428731	-8.708375751544
$-\langle\epsilon\rangle$	1.131170496495	1.982757864131	2.783458069478	3.659843184489	4.412869186416	5.166120554083	6.208433564101	6.998688329201	7.789008061612
	1.246489177702	2.063719815556	2.674260011195	4.046108878197	4.878610446781	5.711361166568	6.544263588151	7.377265251321	8.210335396050
	1.246489177717	1.982757864220	2.783458069526	3.504033074997	5.174547794531	6.057813316029	6.941239741581	7.824771428732	9.309645273591
	1.246489177718	1.910633285545	3.644402084955	3.504033074997	5.174547794531	6.057813316030	6.941239741581	7.824771428732	8.708375751545
$-(\langle\hat{V}\rangle + \langle\hat{K}\rangle)$	1.131170496495	1.982757864131	2.783458069478	3.659843184489	4.412869186416	5.166120554083	6.208433564101	6.998688329201	7.789008061612
	1.246489177702	2.063719815556	2.674260011195	4.046108878197	4.878610446781	5.711361166568	6.544263588151	7.377265251321	8.210335396050
	1.246489177717	1.982757864220	2.783458069526	3.504033074997	5.174547794531	6.057813316029	6.941239741581	7.824771428732	9.309645273591
	1.246489177718	1.910633285545	3.644402084955	3.504033074997	5.174547794531	6.057813316029	6.941239741581	7.824771428732	8.708375751544

Pekeris, in his second paper, took only helium to increased convergence. In his first paper he calculates the ground-state energy for Z from 1 to 10 using a matrix of size 203 and then extrapolates. His energy for helium has only converged to six decimal places at this matrix size. He then proceeds, in his second paper, to take helium to nine decimal places of convergence, corresponding to a matrix size of 1078. Therefore Table V fills in the gaps that Pekeris left. The $1\,^1S$ state energy of the helium isoelectronic sequence $Z = 1$ to 10 is taken to increased convergence and shown in the third row of Table V. The four subrows correspond to energies from matrices of order 252, 444, 715, and 1078. These are presented so as to exhibit the rate of convergence of E with increase in the order of the polynomial used.

Of the triplet states, Pekeris discussed only the triplet, $2\,^3S$, state of helium. The convergence of the $2\,^3S$ state was more rapid than in the ground state, a determinant of order 715 was sufficient to achieve convergence to nine decimal places. In Table VI results for the triplet state for Z from 2 to 10 are given, including the reproduction of the helium results of Pekeris but with the aid of a scale parameter. The value of the scale parameter and the energy parameter is shown in the first and second rows with the energy in the third row. Again, the four subrows of each property row correspond to data obtained from matrices of order 252, 444, 715, and 1078.

The H^- ion ($Z = 1$) does not appear in Table VI as it only has one bound state, which is the singlet state. This was proved rigorously by Nyden Hill within the fixed-nucleus (infinite-mass) approximation [22] and for the case where the nuclear mass is finite [23].

A. The virial condition

Consider any system of charged particles interacting by Coulomb forces. If in a certain system its Hamiltonian is

$$\hat{H} = \hat{K} + \hat{V}$$

and its expectation energy

$$E = \langle \hat{K} \rangle + \langle \hat{V} \rangle, \tag{45}$$

where $\hat{K}$ and $\hat{V}$ are kinetic and potential energy operators and

$$\langle \hat{K} \rangle = \frac{\int \psi^* \hat{K} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \quad \text{and} \quad \langle \hat{V} \rangle = \frac{\int \psi^* \hat{V} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

are kinetic and potential expectation values, respectively, and if ψ is a true wave function then, given that the potential is Coulombic, the virial theorem holds in the form that the negative of the potential energy is twice the kinetic energy.

Although the energy of an approximate wave function may be good even if the virial theorem is not well satisfied, the extent to which the virial theorem is obeyed is an added indication of the quality of the wave function.

The fourth through seventh rows of both Table V and Table VI show the components of the virial theorem. As can be seen for both the singlet and the triplet states $\langle \hat{K} \rangle$ is in good agreement with the energy parameter ϵ and $\langle \hat{V} \rangle$ is twice that. The virial $\langle \hat{K} \rangle + \langle \hat{V} \rangle$ gives ϵ in all cases for all order of matrices (where $E = -K\epsilon^2$). For completeness, $\langle \epsilon \rangle$ is calculated from

$$\langle \epsilon \rangle = \frac{\int \psi^* S \psi \, d\tau}{\int \psi^* \psi \, d\tau},$$

where S is defined below Eq. (34). This is possible because of the unusual formalism of the problem as the energy parameter ϵ is implicit in the wave function.

B. Cusps

The cusp conditions describe the behavior of the wave function at the singularities of the Coulomb potential corresponding to the coalescence of two or more particles.

For an N-electron atom with the infinite nuclear mass approximation, Kato [24], proved the following cusp conditions:

$$\left(\frac{\partial \hat{\Phi}}{\partial r_{12}} \right)_{r_{12}=0} = \gamma (\Phi)_{r_{12}=0}, \tag{46}$$

where r_{12} is the distance between the coalescing particles 1 and 2; $\hat{\Phi}$ is Φ averaged over a small sphere about the singularity. $\gamma = 1/2$ for an electron-electron singularity while at a nucleus-electron singularity $\gamma = -Z$ where Z is the nuclear charge.

Bingel [25] integrated Kato's result and removed the spherical average restriction by adding an angular dependent term. He used the resulting equation to derive the cusp conditions on the first order probability density. Steiner [26] has also derived the cusp conditions on the probability density of an N-electron atom.

Roothaan and Weiss [27] showed that the exact wave function for the ground state of heliumlike systems satisfies

$$\begin{gathered} \left(\frac{1}{\Phi} \frac{\partial \Phi}{\partial r_1} \right)_{r_1=0} = \left(\frac{1}{\Phi} \frac{\partial \Phi}{\partial r_2} \right)_{r_2=0} = -Z, \\ \left(\frac{1}{\Phi} \frac{\partial \Phi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2}, \end{gathered} \tag{47}$$

where r_1, r_2, and r_{12} are the electronic and interelectronic coordinates.

Pack and Byers Brown [28] extended the earlier studies by deriving the more general conditions for the coalescence of a pair of particles when all the particles are in motion. They showed that the cusp condition for a particle pair, provided that the wave function does not vanish at coalescence, could be expressed in Bingel's form as

$$\Phi = (\Phi)_{r_{12}=0} [1 + Z_1 Z_2 \mu_{12} r_{12} + \vec{r}_{12} \cdot \vec{u}_{12} + O(r_{12}^2)]. \tag{48}$$

Here Z_i is the signed magnitude of the charge of particle i in units of the proton charge and μ_{12} is the re-

TABLE VII. Table to show how cusps are related to the scale parameter K and the energy E (hartrees) for a selection of atoms.

Z	K	U	T	$E=-K\epsilon^2$
2	0.2	1.99016379823	0.489857567478	−2.903724377017
	0.3	1.99148850079	0.486600579669	−2.903724377014
6	0.2	5.99071635898	0.490429163665	−32.406246601891
	0.3	5.99234587013	0.487949802254	−32.406246601877
10	0.2	9.98933951132	0.490539299114	−93.906806515027
	0.3	9.99250079790	0.488199510524	−93.906806515017

duced mass of the particle pair. The coefficient of r_{12} is the equivalent of γ in Eq. (46). The vector $\vec{u}_{12}$ is an unknown vector. If the wave function does vanish at coalescence then the cusp behavior is not determined by the Coulomb singularity. In the present case this means that the electron-electron cusp values should vanish in the triplet states.

The energy eigenvalues, discussed previously, depend on the whole of space, rather than on its properties at a particular point and good results for a cusp value cannot, of course, guarantee good energy results. But good energy results and good cusp values indicate that the wave function is good. In the clamped nucleus approach it would be expected that the exact solution for the singlet, up to linear terms, could be written, after suitable scaling, as

$$\Phi = 1 - Z(r_1 + r_2) + \tfrac{1}{2}r_{12} + \cdots,$$

i.e., with cusp values $-Z$ and 1/2.

Representing the expansion of our solution in the form

$$\Psi = 1 - U(r_1 + r_2) + Tr_{12} + \ldots,$$

the values of U and T should approach the exact values of Z and 1/2, respectively, as the basis set size increases, and are given in Table V for the wave functions for $Z = 1$ to 10, from the fixed-nucleus calculation.

The isolated fifth subrow for U and T contains the cusps obtained from a Pekeris-type calculation, i.e., with K=1 at a matrix of size 1078.

As can be seen, the scaled electron-nucleus cusp is better than the Pekeris cusp by 5×10^{-3} for $Z = 1$ and better by 2×10^{-2} for all other Z's. The improvement in using scaled energies rather than Pekeris-type energies is even more marked for the electron-electron cusp, i.e., 7×10^{-3} for $Z = 1$ and about 1.5×10^{-2} for all other Z.

Table VII shows some examples of the variation of energy and of cusp values with scale parameter for a basis set of size 1078. It is interesting to note that if a larger scale parameter was used, although a slightly worse energy was obtained, the electron-nucleus cusp was improved in the third decimal place. This confirms the observation made above about the behavior of the energy and cusp values.

An analysis of the behavior of our triplet wave function shows that for sufficiently small r_i it is of the form

$$X(r_1 - r_2)$$

and it thus exhibits the theoretical behavior for the electron-electron cusp value. There do not appear to be any results for the value of X in the exact solution and in the calculations carried out here, X became smaller and smaller as the basis was improved. It seems likely, therefore, that the triplet nuclear cusp values really should vanish and so the computed quantities are not recorded in Table VI.

ACKNOWLEDGMENTS

The calculations were carried out on a Silicon Graphics Power Series 4D/3805 computer funded by a Science and Engineering Research Council (SERC) Grant No. GR/G 09894 using MAPLE purchased by SERC Grant No. GR/H 68512. H.C. wishes to thank SERC, UK, for support. B.T.S. wishes to thank the Quantum Theory Project of the University of Florida for hospitality during which the writing of this paper was completed. We wish to thank Dr. Richard J. S. Crossley and Dr. David Harper for helpful discussions.

---

[1] E.A. Hylleraas, Z. Phys. **54**, 347 (1929).

[2] J.H. Bartlett, J.J. Gibbons, and C.G. Dunn, Phys. Rev. **47**, 679 (1935).

[3] J.H. Bartlett, Phys. Rev. **51**, 661 (1937).

[4] V. Fock, Izv. Akad. Nauk SSSR Ser. Fiz. **18**, 61 (1954). Translated into English by Fock in K. Nor. Vidensk. Selsk. Forh. **31**, 138 (1958).

[5] J. D. Morgan III, Theor. Chim. Acta **69**, 181 (1986).

[6] C.L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).

[7] A.S. Coolidge and H.M. James, Phys. Rev. **51**, 855 (1937).

[8] K. Frankowski and C. Pekeris, Phys. Rev. **146**, 46 (1966); **150**, 366(E) (1966).

[9] D.E. Freund, B.D. Huxtable, and J.D. Morgan III, Phys. Rev. A **29**, 980 (1984).

[10] G.W.F. Drake, Nucl. Instrum. Methods Phys. Res. Sect. B **31**, 7 (1988).
[11] J.D. Baker, D.E. Freund, R. Nyden Hill, and J.D. Morgan III, Phys. Rev. A **41**, 1247 (1990).
[12] K. Frankowski, Phys. Rev. **160**, 1 (1967).
[13] A. Kono and S. Hattori, Phys. Rev. A **29**, 2981 (1984).
[14] M. Braun, W. Schweizer, and H. Herold, Phys. Rev. A **48**, 1916 (1993).
[15] R. Zhang and C. Deng, Phys. Rev. A **47**, 71 (1993).
[16] M.I. Haftel and V.B. Mandelzweig, Phys. Rev. A **38**, 5995 (1988).
[17] J.G. Loeser and D.R. Herschbach, J. Chem. Phys. **84**, 3882 (1986).
[18] A.A. Frost, J. Chem. Phys. **41**, 478 (1964).
[19] A.A. Frost, M. Inokuti, and J.P. Lowe, J. Chem. Phys. **41**, 482 (1964).
[20] B.T. Sutcliffe and J. Tennyson, Int. J. Quantum Chem. **39**, 181 (1991).
[21] B.T. Sutcliffe, Mol. Phys. **75**, 1233 (1992).
[22] R. Nyden Hill, Phys. Rev. Lett. **38**, 643 (1977).
[23] R. Nyden Hill, J. Math. Phys. **18**, 2316 (1977).
[24] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[25] W.A. Bingel, Z. Naturforsch., Teil A **18**, 1249 (1960).
[26] E. Steiner, J. Chem. Phys. **39**, 2365 (1963).
[27] C.C.J. Roothaan and A.W. Weiss, Rev. Mod. Phys. **32**, 194 (1960).
[28] R.T. Pack and W. Byers Brown, J. Chem. Phys. **45**, 556 (1966).