PHYSICAL REVIEW A VOLUME 32, NUMBER 6 DECEMBER 1985

Finite-element solution of the Schrödinger equation for the helium ground state

F. S. Levin and J. Shertzer*
Department of Physics, Brown University, Providence, Rhode Island 02916

(Received 24 April 1985)

The finite-element method has been used to obtain numerical solutions to the Schrödinger equation for the ground state of the helium atom. In contrast to the globally defined trial functions of the standard variational approach, the finite-element algorithm employs locally defined interpolation functions to approximate the unknown wave function. The calculation reported herein used a three-dimensional grid containing nine nodal points along the radial coordinates of the two electrons and four nodal points along the direction corresponding to the cosine of the interelectronic angle. This produced an energy of -2.9032 a.u., which lies 0.017% above the Frankowski-Pekeris value. The values of $\langle r^n \rangle$, for $n=-2,-1$, 1, and 2, are closer to those of Frankowski and Pekeris than from all of the variational calculations with the exception of the calculation performed by Weiss, whose energy and $\langle r^n \rangle$ values are comparable to those of the finite-element computation.

I. INTRODUCTION

The finite-element method is a numerical algorithm that uses local interpolation methods to solve second-order differential equations describing boundary-value problems.[1-5] Initially used to solve problems of stress analysis, the finite-element method has been more recently applied to problems in quantum mechanics and chemical dynamics.[6-8] This paper describes a finite-element calculation of the helium ground-state energy and wave function; by comparing with the values obtained by Pekeris and collaborators, our set of results are seen to be among the most accurate available, particularly the finite-element approximation to the helium wave function.

The lack of an exact analytic solution to the Schrödinger equation for the two-electron atom combined with the relative simplicity of the system has made helium the target of many approximate calculations, both variational and numerical.[9-21] In Sec. II, we tabulate the results of a number of these calculations so that we can compare their accuracy with that obtained by use of finite elements. A common feature of these calculations is a higher error in the non-Hamiltonian expectation values than in the energy, an indication that the approximate wave functions are less accurate than one might originally assume from the well-converged energies. This behavior provides the motivation for applying the finite-element technique to the helium problem: A local interpolation scheme should be superior to (global) variational approaches in yielding an accurate wave function because of the ease by which local improvements to the approximate wave function can be introduced in the finite-element method. In principle, therefore, it is expected that this algorithm may provide new insights into the structure of molecules and atoms.

II. REVIEW OF SOME PREVIOUS CALCULATIONS

In spherical coordinates, the spin-independent, nonrelativistic Schrödinger equation for the two electrons (denoted 1 and 2) in the helium atom is[9]

$$\left[-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}-E\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=0\ , \tag{2.1}$$

where

$$r_{12}=(r_1^2+r_2^2-2r_1r_2\cos\theta_{12})^{1/2}\ . \tag{2.2}$$

Here θ_{12} is the interelectronic angle, related to the spherical angles of the two electrons by

$$\cos\theta_{12}=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)\ . \tag{2.3}$$

In general, the wave function is dependent on all six coordinates and Eq. (2.1) is nonseparable. However, in 1933, Breit showed that the Schrödinger equation is separable if the coordinate system is rotated such that the z axis is aligned with one of the radius vectors.[11] The interelectronic angle is now identical to the azimuthal angle. In this new coordinate system, the wave function can be written as a sum of products of two functions,

$$\psi(r_1,r_2)=\sum_i f_i(r_1,r_2,\theta_{12})u_i(\phi,\theta',\phi')\ , \tag{2.4}$$

where f_i depends on the two radial coordinates and the interelectronic angle, and u_i depends on the three Euler angles which uniquely define the rotation. The angular momentum operator $\mathbf{L}^2$, of which the wave function is an eigenstate, is independent of θ_{12} and the radial coordinates. Expressing $\mathbf{L}^2$ in terms of the Euler angles, one can show[11] that the u_i must satisfy the equation for a symmetric top:

$$\left[\frac{\partial^2}{\partial\theta'^2}+\cot\theta'\frac{\partial}{\partial\theta'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi^2}-\frac{2\cos\theta'}{\sin^2\theta'}\frac{\partial^2}{\partial\phi\,\partial\phi'}+\frac{1}{\sin^2\theta'}\frac{\partial^2}{\partial\phi'^2}+l(l+1)\right]u_i=0\ . \tag{2.5}$$

The solutions of Eq. (2.5) are known; for the particular case $l=0$, u_i must be constant. Thus, for any s state, the wave function can depend only on r_1, r_2, and θ_{12}. Expressing the kinetic energy operators in Eq. (2.1) in the new coordinates and requiring that the total s-state wave function ψ be independent of the Euler angles, one obtains a three-variable Schrödinger equation for $\psi=f$:

$$\left[-\frac{1}{2r_1^2}\frac{\partial}{\partial r_1}\left[r_1^2\frac{\partial\psi}{\partial r_1}\right]-\frac{1}{2r_2^2}\frac{\partial}{\partial r_2}\left[r_2^2\frac{\partial\psi}{\partial r_2}\right]-\frac{1}{2\sin^2\theta_{12}}\left[\frac{1}{r_1^2}+\frac{1}{r_2^2}\right]\frac{\partial}{\partial\theta_{12}}\left[\sin\theta_{12}\frac{\partial\psi}{\partial\theta_{12}}\right]+\left[\frac{1}{r_{12}}-\frac{2}{r_1}-\frac{2}{r_2}-E\right]\psi\right]=0\;. \tag{2.6}$$

This equation is not solvable analytically and one seeks to construct an approximate solution. Since the spatial portion of the s-state multiplies a singlet spin state, any approximate wave function ψ, like the exact solution ψ, must be symmetric with respect to electron exchange:

$$P_{12}\psi(r_1,r_2,\theta_{12})=\psi(r_1,r_2,\theta_{12})\;. \tag{2.7}$$

Substituting ψ into Eq. (2.6) yields an approximate energy E via

$$E=\frac{\langle\psi\,|\,H\,|\,\psi\rangle}{\langle\psi\,|\,\psi\rangle}\;, \tag{2.8}$$

where H is the total Hamiltonian from (2.6). The min-max principle guarantees that E is an upper bound to the exact energy E. By introducing variational parameters a_i into ψ, one can minimize E with respect to each a_i, thereby systematically lowering the approximate energy and approaching the exact limit.

The classic work on the helium ground state is the set of extensive calculations of Frankowski and Pekeris.[12] Using a 246-term trial function, they obtained an upper bound to the energy of the helium ground state of $-2.903\,724\,353\,770\,326$ a.u. Correcting the Pekeris ionization potential for mass polarization, relativistic effects, and the Lamb shift, this value agrees with the measured ionization potential of helium within the experimental error.[12] (A recent variational calculations by Freund *et al.* has lowered the upper bound to $-2.903\,724\,353\,770\,340$.[21])

It is clear that a calculation of the magnitude of Pekeris is unfeasible for multielectron systems since the presence of even one additional electron doubles the number of Hylleraas coordinates.[10] Hence there is strong motivation to construct simpler electronic wave functions that still yield energies accurate to one part in 10^4 or better. Table I lists the values for the helium ground state obtained with various variational wave functions. In general, the error in the expectation values calculated with the trial wave functions is consistently higher than the error of the approximate energies as noted above. This discrepancy is not a surprising result: it is a direct consequence of the variational principle. If we consider a trial wave function $\tilde{\psi}=\psi+\delta\psi$, where the error $\delta\psi$ in the trial wave function is orthogonal to ψ, then the approximate energy E is given by

$$E=E+\frac{\langle\delta\psi\,|\,(H-E)\,|\,\delta\psi\rangle}{\langle\tilde{\psi}\,|\,\tilde{\psi}\rangle}\;; \tag{2.9}$$

the error in E is of order $(\delta\psi)^2$. This result holds only for the expectation value of the Hamiltonian, which is an eigen operator for the wave function; the error in $\langle r^n\rangle$ is linear in $\delta\psi$. Hence, as is well known, the energy is an insensitive criterion for judging the accuracy of the wave function. The error in the other expectation values is a better indication of the accuracy of the wave function.[9]

Because the error in the contributions from the kinetic energy and potential energy tend to cancel each other, one

TABLE I. Values of energy and $\langle r^n\rangle$.

Wave function	Reference	$\langle r^2\rangle$	$\langle r^2\rangle$	$\langle r^1\rangle$	$\langle r^2\rangle$	Energy
Frankowski-Pekeris	12	12.035	3.3766	1.8589	2.3870	−2.90372
Weiss (35-term configuration interaction)	17	12.037	3.3764	1.8587	2.3843	−2.9032
Green *et al.* (Hylleraas correction)	13	12.025	3.3754	1.8592	2.3871	−2.9026
Stuart-Martsen (6 term configuration interaction)	15	12.043	3.3784	1.8574	2.3787	−2.9015
Roothaan *et al.* (Hartree-Fock)	14	11.991	3.3744	1.8544	2.3696	−2.8617
Shustek-Kreiger (Ritz)	19	11.391	3.3750	1.777	2.1070	
Shustek-Kreiger (Delves)	19	11.953	3.3750	1.8462	2.3392	
Shustek-Kreiger (Aranoff-Percus)	19		3.3750	1.8478	2.3506	
Hawk-Hardcastle (Finite difference)	20	11.132	3.3830	1.8566	2.3812	−2.9036
Finite elements		12.034	3.3766	1.8586	2.3827	−2.9032

can actually lower the energy by introducing a variational parameter without an overall improvement in the approximate wave function. To elucidate this last remark, recall that all of the cited variational calculations employ globally defined basis sets. Because the approximate energy is strongly dependent on the behavior of ψ near the origin, any trial wave function which simulates the exact wave function for small r will give a good value for E, even through the large-r behavior may be relatively poor. It is not possible to improve the wave function near the origin without affecting the large-r behavior; this latter effect does not necessarily have to be improvement. In fact, an examination of the relative magnitude of the error in $\langle r^n \rangle$ from Table I suggests the energy may be lowered at the expense of the accuracy of the wave function in the large-r region.

These observations provide a strong argument in support of a calculation which uses a local basis set. One procedure which employs local interpolation is the finite element method. In this procedure, the domain of the independent variables is divided into a set of nonoverlapping subdomains or elements. In each element, the unknown function is approximated by a simple interpolating function, generally a product of low-order polynomials in each of the independent variables. Thus, when applied to the helium ground state Schrödinger equation, each piece of the unknown wave function is approximated by a simple polynomial. As the number of elements is systematically increased, the accuracy of the approximation increases, and both the resultant eigenvalue and eigenvector will converge to the exact energy and wave function.[2] Verification that this approximate wave function is in fact converging will be a reduction in the relative error in the expectation values. We anticipate that the error in the expectation values of non-Hamiltonian operators will be comparable to the error in the energy.

III. THE FINITE-ELEMENT METHOD

The finite-element method solves the variational equivalent of a second-order differential equation which for the helium atom takes the form [from (2.6)]

$$\int\int\int\left[\frac{1}{2}\frac{\partial\delta\psi}{\partial r_1}\frac{\partial\psi}{\partial r_1}+\frac{1}{2}\frac{\partial\delta\psi}{\partial r_2}\frac{\partial\psi}{\partial r_2}+\frac{1}{2}\left[\frac{1}{r_1^2}+\frac{1}{r_2^2}\right]\frac{\partial\delta\psi}{\partial\cos\theta}\,\frac{\partial\psi}{\partial\cos\theta}\right.$$

$$\left.+\delta\psi\left[-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}-E\right]\psi\right]r_1^2r_2^2\,dr_1dr_2\,d\cos\theta=0\ , \tag{3.1}$$

where θ hereafter refers to the interelectronic angle. In order to evaluate (3.1) numerically, the infinite volume of coordinate space spanned by r_1, r_2, and $\cos\theta$ was made finite by truncation, i.e., r_1 and r_2 were each limited to the domain $[0,r_c]$. The wave function ψ was set equal to zero for $r>r_c$. The truncated domain was then discretized into small rectangular parallelapipedal elements by the placement of nodes (Fig. 1). It is an advantage of this algorithm that the size of the elements may vary, since it is desirable to use a finer discretization in the region of small r where the potential is strong.

In each volume element e, a local coordinate system was introduced whose axes x, y, and z are parallel to the global axes r_1, r_2, and $\cos\theta$ (Fig. 2). The range of x, y, and z is (0,1) in each element and the local representation of the eight corner nodes are (0,0,0), (0,0,1), (0,1,0), (0,1,1), (1,0,0), (1,0,1), (1,1,0), and (1,1,1). The two sets of coordinates are simply related by

$$\begin{aligned} r_1&=x_0^e+h_x^e x\ ,\\ r_2&=y_0^e+h_y^e y\ ,\\ \cos\theta&=z_0^e+h_z^e z\ , \end{aligned} \tag{3.2}$$

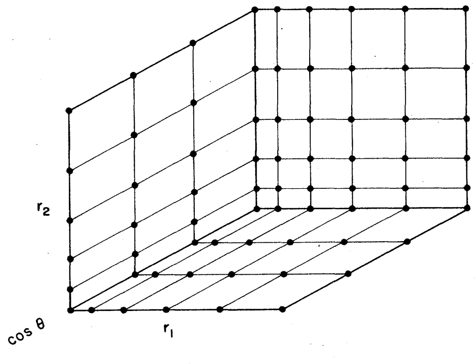

FIG. 1. Discretization of the continuum by the placement of nodes.

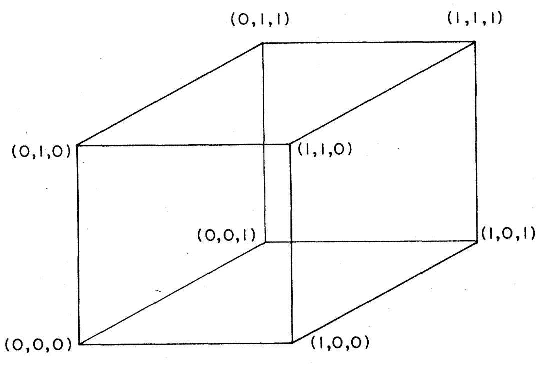

FIG. 2. Local coordinates (x,y,z) of an element.

where x_0^e, y_0^e, and z_0^e are the values of r_1, r_2, and $\cos\theta$ at the node corresponding to (0,0,0) in element e and h_x^e, h_y^e, and h_z^e are the lengths of the three sides of the element.

The integration over the original volume of configuration space is replaced by the sum over the volumes of the individual elements

$$\int dr_1 \int dr_2 \int d\cos\theta \rightarrow \sum h_x^e h_y^e h_z^e \int dx \int dy \int dz \; . \qquad (3.3)$$

Similarly, partial derivatives with respect to the global coordinates are expressible as partial derivatives with respect to local coordinates:

$$\frac{\partial}{\partial r_1}=\frac{1}{h_x^e}\frac{\partial}{\partial x} \; ,$$
$$\frac{\partial}{\partial r_2}=\frac{1}{h_y^e}\frac{\partial}{\partial y} \; , \qquad (3.4)$$
$$\frac{\partial}{\partial \cos\theta}=\frac{1}{h_z^e}\frac{\partial}{\partial z} \; .$$

Using Eqs. (3.2), (3.3), and (3.4), the kinetic-energy operator and the Coulomb potential can be written entirely in terms of the local coordinates. In order to express the wave function in element e, viz. ψ^e, in terms of the local coordinates, we expand it in a basis set which is a product of cubic hermite polynomials in x, y, and z:

$$\psi^e(x,y,z)=\psi_{ijk}^e\phi_i(x)\phi_j(y)\phi_k(z) \; . \qquad (3.5)$$

(Summation over repeated indices is implicit here and in the following equations; summation over the elements will be denoted explicitly by $\sum$.) The explicit form of these polynomials is

$$\phi_1(x)=1-3x^2+2x^3 \; ,$$
$$\phi_2(x)=h_x^e(x-2x^2+x^3) \; ,$$
$$\phi_3(x)=3x^2-2x^3 \; , \qquad (3.6)$$
$$\phi_4(x)=h_x^e(x^3-x^2) \; .$$

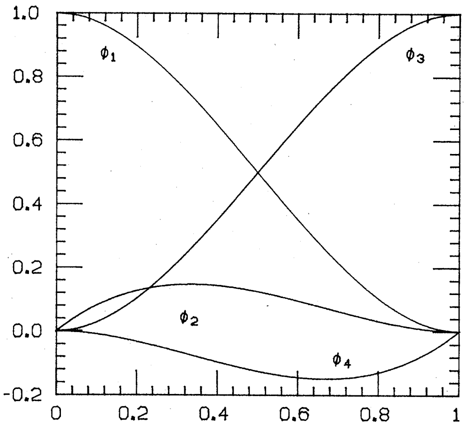

FIG. 3. Cubic Hermite polynomials.

These functions (shown in Fig. 3 for $h_x^e=1$) are defined such that the 64 unknown expansion coefficients ψ_{ijk}^e correspond to the value of the wave function and (seven) combinations of the first partial derivatives at the eight notes of the element. To illustrate this, we look at two examples: ψ_{111}^e, the value of $\psi(x,y,z)$ at the node (0,0,0), multiplies $\phi_1(x)\phi_1(y)\phi_1(z)$, a product which has the value 1 at (0,0,0) and vanishes at all other nodes; similarly ψ_{234}^e is the value of $\partial^2\psi/\partial x\partial z$ at the node (0,1,1) and the corresponding function $\phi_2'(x)\phi_3(y)\phi_4'(z)$ has the value 1 at (0,1,1). (The prime on ϕ_i indicates a derivative with respect to the appropriate argument.)

Using the local representation of the operators and substituting Eq. (3.6) into (3.1), we obtain

$$\sum \delta\psi_{ijk}^e(H_{ijk,lmn}^e-EU_{ijk,lmn}^e)\psi_{lmn}^e=0 \; , \qquad (3.7)$$

where

$$\begin{aligned}H_{ijk,lmn}^e=&\frac{1}{2}\frac{h_y^e h_z^e}{h_x^e}\int\int\int \phi_l'(x)\phi_j(y)\phi_k(z)\phi_l'(x)\phi_m(y)\phi_n(z)(x_0^e+x)^2(y_0^e+y)^2\,dx\,dy\,dz\\&+\frac{1}{2}\frac{h_x^e h_z^e}{h_y^e}\int\int\int \phi_i(x)\phi_j'(y)\phi_k(z)\phi_l(x)\phi_m'(y)\phi_n(z)(x_0^e+x)^2(y_0^e+y)^2\,dx\,dy\,dz\\&+\frac{1}{2}\frac{h_x^e h_y^e}{h_z^e}\int\int\int \phi_i(x)\phi_j(y)\phi_k'(z)\phi_l(x)\phi_m(y)\phi_n'(z)[(x_0^e+x)^2+(y_0^e+y)^2]dx\,dy\,dz\\&+h_x^e h_y^e h_z^e\int\int\int \phi_i(x)\phi_j(y)\phi_k(z)\phi_l(x)\phi_m(y)\phi_j(z)\left[-2(x_0^e+x)^2(y_0^e+y)-2(x_0^e+x)(y_0^e+y)^2\right.\\&\left.+\frac{(x_0^e+x)^2(y_0^e+y)^2}{[(x_0^e+x)^2+(y_0^e+y)^2-2(x_0^e+x)(y_0^e+y)(z_0^e+z)]^{1/2}}\right]dx\,dy\,dz\end{aligned} \qquad (3.8a)$$

and

$$U_{ijk,lmn}^e=h_x^e h_y^e h_z^e\int\int\int \phi_i(x)\phi_j(y)\phi_k(z)\phi_l(x)\phi_m(y)\phi_n(z)(x_0^e+x)^2(y_0^e+y)^2\,dx\,dy\,dz \; . \qquad (3.8b)$$

Equation (3.7) can now be expressed in simple matrix notation as

$$\sum \delta \underline{\boldsymbol{\Psi}}^{e}(\underline{\mathbf{H}}^{e}-E\underline{\mathbf{U}}^{e})\underline{\boldsymbol{\Psi}}^{e}=\underline{0}\ , \tag{3.9}$$

where $\underline{\mathbf{H}}^e$ and $\underline{\mathbf{U}}^e$ denote 64×64 local matrices for element e, and $\underline{\boldsymbol{\Psi}}^e$ is a (column) vector of order 64 containing the unknown coefficients corresponding to the same element.

The local matrices $\underline{\mathbf{U}}^e$ and $\underline{\mathbf{H}}^e$ are symmetric and contain no unknown quantities. Except for the element-dependent constants, the matrix elements are identical for every element. With the exception of the electron-electron repulsion term in the potential operator, all of the integrals are simple polynomials and can be performed analytically; the integral involving r_{12}^{-1} was computed numerically using 16-point Gauss quadrature.

In order to obtain the global equations, we need to sum over all the elements in such a way that the solution is a smooth, continuous function. This requires that a node which is shared by more than one element be assigned the same values of expansion coefficients in each element. To accomplish this, we introduce connectivity matrices $\underline{\boldsymbol{\Delta}}^e$ for each element which map the local matrices $\underline{\mathbf{H}}^e$ and $\underline{\mathbf{U}}^e$ and local vector $\underline{\boldsymbol{\Psi}}^e$ onto global matrices $\underline{\mathbf{H}}$ and $\underline{\mathbf{U}}$ and global vector $\underline{\boldsymbol{\Psi}}$.[1] If there are N nodes in the volume, then the global matrices are $8N\times 8N$ and the global vector is of order $8N$. The mapping relations are as follows:

$$H_{ABC,DEF}=\Delta^{e}_{ABC,ijk}H^{e}_{ijk,lmn}\Delta^{e}_{lmn,DEF}\ , \tag{3.10a}$$

$$U_{ABC,DEF}=\Delta^{e}_{ABC,ijk}U^{e}_{ijk,lmn}\Delta^{e}_{lmn,DEF}\ , \tag{3.10b}$$

$$\psi_{ABC}=\Delta^{e}_{ABC,ijk}\psi^{e}_{ijk}\ . \tag{3.10c}$$

Using relations (3.10a)—(3.10c) and the unitarity of the connectivity matrices

$$\Delta^{e}_{ijk,ABC}\Delta^{e}_{ABC,ijk}=1\ , \tag{3.11}$$

we can perform the summation in Eq. (3.9). Introducing a global matrix notation, we have

$$\delta\underline{\boldsymbol{\Psi}}(\underline{\mathbf{H}}-E\underline{\mathbf{U}})\underline{\boldsymbol{\Psi}}=\underline{\mathbf{0}}\ , \tag{3.12}$$

which has the form of a generalized eigenvalue problem with symmetric banded matrices. The eigenvector $\underline{\boldsymbol{\Psi}}$ contains the expansion coefficients, which are the value of the unknown wave function and its partial derivatives at every node.

In order to satisfy the boundary condition that the wave function vanishes as $r\rightarrow\infty$, those m coefficients ψ_{ABC} corresponding to the value of ψ and its partial derivatives at $r=r_c$ must be set equal to zero. This is equivalent to eliminating the rows and columns of the global matrices that correspond to those components. The resultant $(8N-m)\times(8N-m)$ eigenvalue problem may now be solved for the remaining components of the global vector.

Since the global matrices for a three-dimensional finite-element calculation are generally of order 10^3 or greater, standard algorithms for solving generalized eigenproblems are impractical, both in terms of computer storage and CPU (central processing unit) time. Fortunately, there exists an algorithm specifically designed to handle the large matrix equations of finite-element calculations. This subspace iteration method exploits the banded, symmetric nature of the global matrices and provides rapid convergence with a minimal amount of computer work area.[3] Unlike simultaneous vector iteration, subspace iteration does not require that each of the n trial vectors separately converges to the n lowest eigenvectors. Rather, one iterates using a trial subspace which is spanned by an approximation to a linear combination of the lowest eigenvectors. When the trial subspace is converged to the desired accuracy, the lowest eigenvectors are found via Gram-Schmidt orthogonalization. Details of the algorithm are found in Ref. 3.

IV. RESULTS OF FINITE-ELEMENT CALCULATION

The results of the finite element calculation are included in Table I. These final figures were obtained from a grid of $9\times 9\times 4$ or 324 global nodes. In order to verify the symmetry of the wave function with respect to electron exchange, nodes were placed symmetrically along r_1 and r_2 at 0.0, $0.1a_0$, $0.2a_0$, $0.4a_0$, $0.8a_0$, $1.4a_0$, $2.2a_0$, $4.0a_0$, and $6.0a_0$. The greater concentration of nodes near the origin anticipates the effect of the Coulomb interaction. The four nodes along $\cos\theta$ were placed at -1.0, -0.5, 0.5, and 1.0. Minor variation in the site of the nodes did not affect the final results.

In order to impose the boundary condition that ψ and its partial derivatives vanish for $r=r_c$, 576 expansion coefficients were set equal to zero. In addition to the 68 nodes satisfying $r_i=r_c$, $i=1,2$, we also set the wave function equal to zero at the four additional nodes satisfying $(r_1+r_2)>r_c$. This reduced the order of the global matrices from 2592 to 2016. Because the matrix manipulations involved in calculating the lowest eigenvalues necessitated the use of double precision, storage of the matrices in skyline mode[3] exceeded 14 megabytes. Calculation of the lowest two eigenvectors required 16 CPU hours on the Brown University IBM 3081. Calculation of the expectation values $\langle r^n\rangle$, $n=-2$, -1, 1, and 2 required an additional 49 CPU hours.

The ground-state energy of helium obtained with finite elements was -2.9032 a.u. This energy lies 0.017% above the Frankowski-Pekeris result and is comparable in accuracy to Weiss's result.[17] Only the energy obtained by Hawk and Hardcastle[20] lies closer to the Pekeris energy. However, the expectation values $\langle r^n\rangle$ calculated with the finite-element wave function are superior to those obtained in any of the variational or the finite difference approaches, again, with the exception of Weiss. In particular, although the error in the energy obtained by Hawk and Hardcastle[20] is less than 0.004%, the error in the expectation values is as high as 7% for $\langle r^{-1}\rangle$. On the contrary, with the exception of $\langle r^2\rangle$, the error in the expectation values obtained with the finite-element wave function were less than the error in the energy. The values of $\langle r^n\rangle$, for $n=-2$ and -1, are superior to those obtained by Weiss, while the latter has better results for $n=1$ and 2. The larger error in the finite element value of $\langle r^2\rangle$ is a result of the crudeness of discretization for $r>4a_0$. A single third-order polynomial in r_1 and r_2 is used to approximate the behavior of the wave function in this region, and $\langle r^2 \rangle$ is most sensitive to the accuracy of the wave function at large r. We are confident that a slightly more refined discretization in the large-r region would lower the error in $\langle r^2 \rangle$ and improve the energy. Unfortunately, the addition of a single node in r_1 and r_2 resulted in global matrices whose storage exceeded the core capacity of the IBM 370. The additional time required for data retrieval during subspace iteration made out-of-core storage impractical for this calculation.

V. DISCUSSION

This calculation for helium has shown that the finite-element method provides an accurate, alternate approach for solving certain atomic and molecular problems. There are many advantages to a local interpolation technique. Unlike expansion in a global basis set, the restriction that all functions of the basis set must satisfy the boundary conditions of the problem is removed. Furthermore, no *a priori* structure (other than at the boundaries) is imposed on the wave function. The major disadvantage to the method is the need for extensive computer core memory. Calculations involving more than three variables require the capabilities of a supercomputer. However, computational limits are not the same as analytical restrictions. With the rapid advance in computer technology, it is not unreasonable to expect that highly accurate, n-dimensional finite-element calculations will be possible in the near future. In the meantime, it may be possible to combine a global variational approach with the finite element method.

ACKNOWLEDGMENTS

This material represents a portion of the thesis of J. Shertzer, submitted to Brown University in partial fulfillment of the requirements of the Ph.D degree. The work was supported in part by the U. S. Department of Energy. We thank Brown University for making its computing facilities available to us.

---

[*] Present address: Department of Physics, Holy Cross College, Worcester, MA 01610.

[1] T. J. Chung, *Finite Element Analysis in Fluid Dynamics* (McGraw-Hill, New York, 1978).

[2] G. Strang and G. Fix, *An Analysis of the Finite Element Method* (Prentice-Hall, New Jersey, 1973).

[3] K. Bathe and E. Wilson, *Numerical Methods in Finite Element Analysis* (Prentice-Hall, New Jersey, 1976).

[4] M. J. Turner, R. W. Clough, H. C. Martin, and L. P. Topp, J. Aeron. Sci. 23, 805 (1976).

[5] O. C. Zienkiewicz and Y. K. Cheung, *Finite Methods in Structural and Continuum Mechanics* (McGraw-Hill, New York, 1967).

[6] A. Askar and M. Demiralp, J. Chem. Phys. **60**, 2762 (1974); A. Askar, *ibid.* **62**, 732 (1975); A. Askar, A. S. Cakmak, and H. A. Rabitz, *ibid.* **33**, 267 (1978); M. Duff, H. Rabitz, A. Askar, A. Cakmak, and M. Ablowitz, *ibid.* **72**, 1543 (1980); G. D. Barg and A. Askar, Chem. Phys. Lett. **76**, 609 (1980).

[7] C. Bottcher, J. Phys. B **14**, 349 (1981); **15**, 463 (1982); in *The Physics of Electronic and Atomic Collisions,* edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (Elsevier, New York, 1984).

[8] W. K. Ford and F. S. Levin, Phys. Rev. A **29**, 43 (1984); W. K. Ford, Ph. D. thesis, Brown University, 1980 (unpublished); J. Shertzer, Ph. D. thesis, Brown University, 1984 (unpublshed); R. Kozack, Ph. D. thesis, Brown University, 1984 (unpublished).

[9] H. A. Bethe and E. E. Saltpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

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

[11] G. Breit, Phys. Rev. **35**, 569 (1930).

[12] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959); K. Frankowski and C. L. Pekeris, *ibid.* **146**, 46 (1966); **150**, 366 (1966).

[13] L. C. Green, S. Matsushima, C. Stephens, E. K. Kolchin, M. M. Kohler, Y. Wang, B. B. Baldwin, and R. J. Wisner, Phys. Rev. **112**, 1187 (1958).

[14] C. C. J. Roothann, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960); J. J. C. Roothaan and L. M. Sachs, *ibid.* **32**, 194 (1960).

[15] J. D. Stuart and F. A. Matsen, J. Chem. Phys. **41**, 1646 (1964).

[16] H. O. Pritchard, J. Chem. Phys. **40**, 1496 (1964); **42**, 3548 (1965).

[17] A. W. Weiss, Phys. Rev. **122**, 1826 (1966).

[18] K. E. Banyard and C. C. Baker, J. Chem. Phys. **58**, 2680 (1969); Phys. Rev. **188**, 57 (1969).

[19] L. J. Shustek and J. B. Krieger, Phys. Rev. A 3, 1253 (1971).

[20] I. L. Hawk and D. L. Hardcastle, Comput. Phys. Commun. **16**, 159 (1979).

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