Finite-element calculations for the S states of helium

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The finite-element method provides a convenient and accurate procedure for the calculation of the expectation values of quantum observables. We calculated energies, wave functions, and expectation values of r_1^n for $n = -1$, 1, and 2, and of $\pi\delta(\mathbf{r}_1)$ for the singlet $n\,{}^1S$ and triplet $n\,{}^3S$ states ($n = 1,2,3,4$) of helium. In contrast to the standard methods with globally defined basis functions, the accuracy of the expectation values of physical observables is comparable to the accuracy of the eigenvalues. The results are reported here and compared with those of Baker *et al.* [*Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms*, edited by Walter Johnson, Peter Mohr, and Joseph Sucher, AIP Conf. Proc. No. 189 (AIP, New York, 1989); Phys. Rev. A **41**, 1247 (1990)], Drake [Nucl. Instrum. Methods Phys. Res. B **31**, 7 (1988)], Pekeris [Phys. Rev. **115**, 1216 (1959)], Accad *et al.* [Phys. Rev. A **4**, 516 (1971)], and Haftel and Mandelzweig [Phys. Rev. A **38**, 5995 (1988)].

I. INTRODUCTION

The three-body Coulomb problem of quantum mechanics has over the years attracted the efforts of many authors using different methods to obtain estimates for the energies and expectation values of various operators. Besides the fundamental physical importance of three-body atomic systems, helium and heliumlike atoms have attracted much attention because of their applications in astrophysics [1].

Some of the most accurate results for the energy values of the S and P states of helium and heliumlike atoms were provided by Pekeris and co-workers [2–4], where they used an expansion in Laguerre polynomials and exponentials of the perimetric coordinates first introduced by James and Coolidge [5]. They also reported some expectation values of powers of r. More recently, high-precision variational calculations have been performed by Baker and co-workers [6,7] and Drake [8,9] yielding nonrelativistic energies accurate to 12 digits or better.

Other approaches to the problem include the Hartree-Fock method [10], the CFHH (correlation-function hyperspherical-harmonic) method [11,12] and the method of finite differences [13]. One of the more recent approaches to the problem is the method of finite elements (FEM), which was pioneered by Levin and Shertzer [14] to determine the nonrelativistic ground-state energy of helium and expectation values with respect to the ground state of the operators r_1^{-2}, r_1^{-1}, r_1, and r_1^2. One of the advantages of the FEM is that no globally defined expansion basis is required. This flexible approach is useful in such physical situations, where analytical basis functions do not capture the essential physics. (A general introduction about the FEM for calculating energy eigenvalues of quantum-mechanical systems can be found in Ram-Mohan *et al.* [15].) In addition to work published by Levin and Shertzer [14] we calculated both triplet and excited states making rigorous use of the an-tisymmetry conditions thus significantly reducing the number of necessary elements for the explicit calculation.

II. THE METHOD OF FINITE ELEMENTS FOR HELIUM S STATES

The spin-independent nonrelativistic Hamiltonian for the helium atom reads in spherical coordinates and Z-scaled atomic units [energies in Z^2 ($=4$) Ry and lengths in $a_Z = a_{\text{Bohr}}/Z = \frac{1}{2}a_{\text{Bohr}}$]

$$H = \sum_{i=1}^{2}\left[-\nabla_i^2 - \frac{2}{r_i}\right] + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\ . \tag{1}$$

As is well known, the wave function of the S states depends only on the two radial coordinates and the interelectronic angle θ. To apply the FEM, the infinite volume of coordinate space spanned by r_1, r_2, and $u = \cos\theta$ is truncated by introducing a cutoff $r_{\max}$. The wave function is set equal to zero for $r_i \geq r_{\max}$, $i = 1, 2$ and the truncated domain subdivided into parallelepipedal elements as shown in Fig. 1. The nodes R_i along r_1 and r_2 are given by

$$R_i = \frac{i^2}{n_r^2}r_{\max}\ , \quad i = 0, \ldots, n_r\ , \tag{2}$$

where n_r is the number of intervals in the radial directions, hence concentrating the elements near the origin, where the Coulomb interaction is strongest. The nodes U_i in the direction of u are equidistantly placed in the interelectronic angle, i.e.,

$$U_i = \cos\left[\pi - \frac{i}{n_u}\pi\right]\ , \quad i = 0, \ldots, n_u\ , \tag{3}$$

with n_u the number of intervals in this direction.

Due to the (anti)symmetry of the wave function on interchange of the two radial coordinates, only the elements $\mathcal{E}_k$ ($k = 1, \ldots, \mathcal{N}$) below and intersected by the
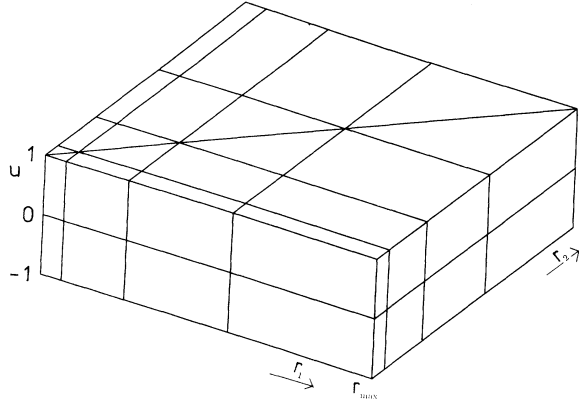
FIG. 1. Discretization used in the finite-element calculation for $n_r = 4$ and $n_u = 2$. Only the elements below and intersected by the diagonal plane $(r_1 = r_2)$ are actually used in the calculation.

plane $r_1 = r_2$ (see Fig. 1) are actually used in the calculations.

The key of the calculation is to approximate the unknown wave function *locally* on each parallelepipedal element $\mathscr{E}_k$ as a linear combination of shape functions, defined as a product of interpolating polynomials for equidistant nodes of degree ω in each direction. By construction there are in each direction $\omega + 1$ such polynomials and nodes. Therefore on each element $\mathscr{E}_k$ there are $n = (\omega + 1)^3$ shape functions $f_i^{(k)}$ and corresponding nodes $\mathbf{r}_i^{(k)}$, $i = 1, \ldots, n$ with

$$f_i^{(k)}(\mathbf{r}_j^{(k)}) = \delta_{ij} . \tag{4}$$

The wave function is then given by

$$\Psi(\mathbf{r}) = \sum_{i=1}^{n} (\mathbf{v}^{(k)})_i f_i^{(k)}(\mathbf{r}) , \tag{5}$$

with $\Psi(\mathbf{r}_i^{(k)}) = (\mathbf{v}^{(k)})_i$.

Substituting Eq. (5) in Eq. (1) we get

$$\langle \Psi | H | \Psi \rangle = \sum_{k=1}^{\mathscr{N}} c_k \langle \mathbf{v}^{(k)} | \{ E_{\text{rad}}^{(k)} + V_1^{(k)} + \tfrac{1}{2} V_2^{(k)} \} | \mathbf{v}^{(k)} \rangle , \tag{6}$$

where the local matrices reduce for S states to

$$(E_{\text{rad}}^{(k)})_{ij} = \int_{\mathscr{E}_k} \left[\frac{\partial f_i^{(k)}(\mathbf{r})}{\partial r_1} \frac{\partial f_j^{(k)}(\mathbf{r})}{\partial r_1} + \frac{\partial f_i^{(k)}(\mathbf{r})}{\partial r_2} \frac{\partial f_j^{(k)}(\mathbf{r})}{\partial r_2} + \left[\frac{1}{r_1^2} + \frac{1}{r_2^2} \right] (1 - u^2) \frac{\partial f_i^{(k)}(\mathbf{r})}{\partial u} \frac{\partial f_j^{(k)}(\mathbf{r})}{\partial u} \right] r_1^2 r_2^2 dr_1 dr_2 du , \tag{7}$$

$$(V_1^{(k)})_{ij} = \int_{\mathscr{E}_k} f_i^{(k)}(\mathbf{r}) \left[-\frac{2}{r_1} - \frac{2}{r_2} \right] f_j^{(k)}(\mathbf{r}) r_1^2 r_2^2 dr_1 dr_2 du , \tag{8}$$

$$(V_2^{(k)})_{ij} = \int_{\mathscr{E}_k} f_i^{(k)}(\mathbf{r}) \frac{2}{r_{12}} f_j^{(k)}(\mathbf{r}) r_1^2 r_2^2 dr_1 dr_2 du , \tag{9}$$

and the factor

$$c_k = \begin{cases} 1 & \text{if } \mathscr{E}_k \text{ is intersected by the plane } r_1 = r_2 \\ 2 & \text{otherwise ,} \end{cases} \tag{10}$$

due to the Pauli exclusion principle.

By the values of the wave function Ψ on the finite-element grid given above, the global vector $\mathbf{w}$ is defined. Its connection with the local vectors $\mathbf{v}^{(k)}$ is given by the connectivity matrices I_k

$$(I_k)_{ij} = \begin{cases} 1 & \text{if the local node } j \text{ has the global index } i \text{ and lies below or on the plane } r_1 = r_2 \\ (-1)^S & \text{if the local node } j \text{ has the global index } i \text{ and lies above the plane } r_1 = r_2 \\ 0 & \text{otherwise .} \end{cases} \tag{11}$$

These matrices allow an easy implementation of boundary conditions: if the wave function vanishes on a local node, the corresponding column of I_k vanishes. The values which depend on S take care of the (anti)symmetry requirements.

The local vectors can be written in terms of the global vector $\mathbf{w}$,

$$\mathbf{v}^{(k)} = (I_k)^T \mathbf{w} . \tag{12}$$

Inserting this in Eq. (6), we finally arrive at

$$\langle \Psi | H | \Psi \rangle = \langle \mathbf{w} | \mathscr{H} | \mathbf{w} \rangle , \tag{13}$$

with

$$\mathscr{H} = \sum_{k=1}^{\mathscr{N}} c_k I_k [E_{\text{rad}}^{(k)} + V_1^{(k)} + \tfrac{1}{2} V_2^{(k)}] (I_k)^T . \tag{14}$$

By defining local normalization matrices

$$(U^{(k)})_{ij} = \int_{\mathscr{E}_k} f_i^{(k)}(\mathbf{r}) f_j^{(k)}(\mathbf{r}) r_1^2 r_2^2 dr_1 dr_2 du \tag{15}$$

a similar treatment as above yields for the normalization

TABLE I. Comparison of the energy (in units of 4 Ry) for the helium ground state from this finite-element calculation with already published values.

Calculation	E	ΔE
Baker et al. [7]	$-1.451\,862\,188\,517\,059\,2$	
Pekeris [4]	$-1.451\,862\,188$	5×10^{-10}
Baker, Hill, and Morgan [6]	$-1.451\,862\,188\,517\,04$	2×10^{-14}
Drake [8]	$-1.451\,862\,188\,517\,053$	6×10^{-15}
Haftel and Mandelzweig [11]	$-1.451\,862\,184$	5×10^{-9}
Leven and Shertzer [14]	$-1.451\,6$	3×10^{-4}
Hawk and Hardcastle [13]	$-1.451\,80$	6×10^{-5}
This work	$-1.451\,805\,9$	5.6×10^{-5}

condition

$$\langle \Psi | \Psi \rangle = \langle \mathbf{w} | \mathcal{U} | \mathbf{w} \rangle = 1 \ , \tag{16}$$

with

$$\mathcal{U} = \sum_{k=1}^{N} c_k I_k U^{(k)} (I_k)^T \ . \tag{17}$$

The variational principle for $\mathcal{H}$ under the condition (16) leads to the generalized eigenvalue problem

$$\mathcal{H} \mathbf{w} = \lambda \mathcal{U} \mathbf{w} \ . \tag{18}$$

III. RESULTS

The local matrices were determined by numerical integration. As the integrands of $V_1^{(k)}$, $E_{\text{rad}}^{(k)}$, and $U^{(k)}$ are polynomials of the three coordinates, it is straightforward to calculate them analytically. However, for larger values of ω each of these matrix elements is a sum of alternating contributions, which leads to a significant loss of accuracy for the computation of these analytical expressions [16]. Therefore we used three-dimensional Gauss-Legendre quadrature with seven abscissas in each direction. The discretization parameters chosen for the FE calculation are $n_r = 18$, $n_u = 2$, $\omega = 4$, and $r_{\max} = 120$. The dimension N of the generalized eigenvalue problem is given by $N = \omega n_r (\omega n_r + 1)(\omega n_u + 1)/2$ in the singlet and by $N = \omega n_r (\omega n_r - 1)(\omega n_u + 1)/2$ in the triplet case, hence $N = 23\,652$ for the singlet and $N = 23\,004$ for the triplet calculation for the parameters given above and was solved by the spectral transformation Lanczos method [17].

A. Energies of the helium S states

The energies obtained from the finite-element calculation are shown in Tables I and II. In Table I the energy of the ground state determined with the method of finite elements is compared with already published values. (The value from Baker et al. [7] is considered exact and used to calculate the error.) In Table III the ground-state energy and its error are given for three values of n_r. Doubling the number of intervals results in a reduction of the error by a factor of ≈ 200. This strong dependence is a consequence of using polynomials of high order for the interpolation.

In Table II the energies of the excited states are compared with the results from Pekeris [4], Accad, Pekeris, and Schiff [2], Drake [8], and Baker, Hill, and Morgan [6]. The relative accuracy of the energy for the ground state is 3.9×10^{-5}, and the relative accuracy of the energies of the excited states is better than 10^{-5}. The ground-state energy from the finite-elements calculation is less accurate than for the excited states, because the interaction between the electrons is stronger for the ground state.

B. Expectation values for the helium S states

The expectation values of $1/r_1, r_1, r_1^2, \pi\delta(\mathbf{r}_1)$ for the states considered above have been calculated with respect to the wave functions determined by the FEM. Note that due to the symmetry properties of the eigenstates these expectation values are independent of the particle under consideration.

To obtain the expectation value of an operator O we define, for convenience, the local matrices o^k by

TABLE II. Comparison of the energies (in units of 4 Ry) of excited helium S states from the finite-element calculation with energies from Pekeris [4], Accad, Pekeris, and Schiff [2], Drake [8], and Baker, Hill, and Morgan [6].

State	Energy				
	FEM	Ref. [4]	Ref. [2]	Ref. [8]	Ref. [6]
$2\,^1S$	$-1.072\,980\,0$		$-1.072\,987\,022$	$-1.072\,987\,023\,027\,14$	$-1.072\,987\,023\,027\,10$
$3\,^1S$	$-1.030\,631\,3$		$-1.030\,636\,0$		$-1.030\,635\,994\,870\,305$
$4\,^1S$	$-1.016\,788\,9$		$-1.016\,793$		$-1.016\,793\,358\,513\,92$
$2\,^3S$	$-1.087\,610\,7$	$-1.087\,614\,689\,12$		$-1.087\,614\,689\,118\,395\,5$	$-1.087\,614\,689\,118\,39$
$3\,^3S$	$-1.034\,340\,7$		$-1.034\,344\,531$		$-1.034\,344\,533\,736\,18$
$4\,^3S$	$-1.018\,252\,2$		$-1.018\,256\,04$		$-1.018\,256\,041\,549\,02$

TABLE III. Ground-state energy (in units of 4 Ry) of helium as a function of the number n_r of radial intervals.

n_r	E	ΔE
9	$-1.450\,619\,2$	1.2×10^{-3}
12	$-1.451\,658\,0$	2.0×10^{-4}
18	$-1.451\,805\,9$	5.6×10^{-5}

$$(o^k)_{ij} = \int_{\mathscr{E}_k} f_i^{(k)}(\mathbf{r}) O f_j^{(k)}(\mathbf{r}) r_1^2 r_2^2 dr_1 dr_2 du \ , \tag{19}$$

which yields

$$\langle \Psi | O | \Psi \rangle = \langle \mathbf{w} | \mathscr{O} | \mathbf{w} \rangle \ , \tag{20}$$

with

$$\mathscr{O} = \sum_{k=1}^{\mathscr{N}} c_k I_k o^k (I_k)^T \ . \tag{21}$$

The results for the expectation values are shown in Table IV and are compared with the expectation values of Pekeris [4], Accad, Pekeris, and Schiff [2], Hawk and Hardcastle [13], Levin and Shertzer [14], Haftel and Mandelzweig [11], Drake [8], and Krivec, Haftel, and Mandelzweig [12]. For the ground state $1\,^1S$ a comparison is possible for all expectation values. Pekeris [4] and Haftel

and Mandelzweig [11], who used different methods, are in excellent agreement. Therefore their results should have an accuracy of at least seven digits. With respect to those values, our results show a relative deviation of 2.9×10^{-5} for $\langle 1/r_1 \rangle$, 8.3×10^{-5} for $\langle r_1 \rangle$, and 8.8×10^{-5} for $\langle r_1^2 \rangle$, which is of the same order of magnitude as the relative error of the energy. This is one of the positive properties of a FE calculation using a locally defined basis set as compared to the expansion in global functions, where the relative error of the non-Hamiltonian expectation values is much larger than the relative error of the energies.

The expectation values from the other finite-element calculation by Levin and Shertzer are superior to our results for $1/r_1$ and inferior for all other cases but they did not calculate $\langle \delta(\mathbf{r}_1) \rangle$. The finite-difference results by Hawk and Hardcastle are, especially for $1/r_1$, less accurate than the finite-element calculations, although their ground-state energy is almost as accurate as ours.

IV. CONCLUSION

It has been shown that the method of finite elements, applied to the S states of helium, yields accurate results for the energies and the expectation values of r_i^n, $i = 1, 2$, $n = -1, 1, 2$ and of $\pi\delta(\mathbf{r}_1)$. In contrast to other methods

TABLE IV. Expectation values of the operators r_i^n, $n = -1, 1, 2$, $i = 1, 2$ and $\pi\delta(\mathbf{r}_1)$; r_i in units of $\frac{1}{2} a_{\mathrm{Bohr}}$.

State	Source	$\left\langle \dfrac{1}{r_i} \right\rangle$	$\langle r_i \rangle$	$\langle r_i^2 \rangle$	$\langle \pi\delta(\mathbf{r}_1) \rangle$
$1\,^1S$	Finite elements	0.844\,133\,8	1.859\,016\,3	4.774\,354\,4	0.710\,890\,8
	Pekeris [4]	0.844\,158\,4	1.858\,944\,6	4.773\,932\,0	0.710\,953\,0
	Haftel and Mandelzweig [11]	0.844\,158\,4	1.858\,944\,7	4.773\,932\,5	0.710\,952\,26
	Leven and Shertzer [14]	0.844\,15	1.858\,6	4.765\,4	
	Hawk and Hardcastle [13]	0.845\,8	1.856\,6	4.762\,4	
	Drake [8]				0.710\,953\,931
$2\,^1S$	Finite elements	0.567\,695\,8	5.946\,364\,3	64.362\,524	0.514\,201\,6
	Accad, Pekeris, and Schiff [2]		5.946\,12	64.356\,4	0.514\,220
	Krivec, Haftel, and Mandelzweig [12]	0.567\,712\,3	5.944\,970\,2	64.322\,608	0.514\,217\,654
	Drake [8]				0.514\,224\,045
$3\,^1S$	Finite elements	0.529\,251\,0	13.023\,729	343.580\,92	0.503\,584\,6
	Accad, Pekeris, and Schift [2]		13.024	343.6	0.503\,88
	Krivec, Haftel, and Mandelzweig [12]	0.529\,317\,2	12.993\,636	341.848\,45	0.503\,856\,2
$4\,^1S$	Finite elements	0.516\,238\,1	23.098\,478	1124.994\,8	0.501\,551\,1
	Accad, Pekeris, and Schiff [2]		23.1	1126	0.501\,56
	Krivec, Haftel, and Mandelzweig [12]	0.516\,321\,6	23.047\,382	1120.920\,2	0.501\,597\,3
$2\,^3S$	Finite elements	0.577\,326\,2	5.100\,940\,7	45.857\,519	0.518\,473\,0
	Pekeris [4]	0.577\,332\,1	5.100\,925\,4	45.857\,287	0.518\,502\,2
	Drake [8]				0.518\,502\,228\,4
$3\,^3S$	Finite elements	0.531\,831\,3	11.711\,961	274.834\,48	0.504\,290\,9
	Accad, Pekeris, and Schiff [2]		11.711\,960	274.836	0.504\,642
$4\,^3S$	Finite elements	0.517\,280\,3	21.321\,109	954.149\,27	0.501\,313\,7
	Accad, Pekeris, and Schiff [2]		21.322\,4	954.32	0.501\,812

that use globally defined basis functions, the relative errors of the expectation values are not much larger than those of the energies. By extending r_{max} to larger values and increasing the number of intervals in the u direction, we are confident to lower the error of the ground-state energy and to cover higher excited states. The major disadvantage of FEM is the need for large computer storage and the requirements of CPU time. However, if one is, e.g., interested in the isoelectronic sequence, it is sufficient to calculate the local matrices only once. We also intend to apply the method of finite elements to the two-electron problem in a superstrong magnetic field in order to understand the observed absorption spectra of magnetic white dwarfs.

ACKNOWLEDGMENTS

[1] G. D. Schmidt, W. B. Latter, and Craig B. Foltz, Astrophys. J. **350**, 758 (1990).

[2] A. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[3] C. L. Pekeris, Phys. Rev. **112**, 1649 (1985).

[4] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[5] H. M. James and A. S. Coolidge, Phys. Rev. **51**, 857 (1937).

[6] J. Baker, R. N. Hill, and J. D. Morgan III, in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms*, edited by Walter Johnson, Peter Mohr, and Joseph Sucher, AIP Conf. Proc. No. 189 (American Institute of Physics, New York, 1989), pp. 123–145.

[7] J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).

[8] G. W. F. Drake, Nucl. Instrum. Methods Phys. Res. B **31**, 7 (1988).

[9] G. W. F. Drake, in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms* (Ref. [6]), pp. 146–164.

[10] Ch. Froese-Fischer, *The Hartree-Fock-Method for Atoms* (Wiley-Interscience, New York, 1977).

[11] M. I. Haftel and V. B. Mandelzweig, Phys. Rev. A **38**, 5995 (1988).

[12] R. Krivec, M. I. Haftel, and V. B. Mandelzweig, Phys. Rev. A **44**, 7158 (1991).

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

[14] F. S. Levin and J. Shertzer, Phys. Rev. A **32**, 3285 (1985).

[15] L. R. Ram-Mohan, Sunil Saigal, Don Sossa, and J. Shertzer, Comput. Phys. **4**, 50 (1990).

[16] R. Jaquet, Comput. Phys. Commun. **58**, 257 (1990).

[17] T. Ericsson and A. Ruhe, Math. Comput. **35**, 1251 (1980).