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Numerical Calculation of the Wave Functions and Energies of the $1\,{}^1S$ and $2\,{}^3S$ States of Helium*

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An exact iteration method for obtaining solutions to the eigenvalue problems of quantum mechanics is used as the basis for developing a numerical iteration scheme for the approximate solution of such problems. The connection between an approximate analytic iteration method and the standard variational method is made and the former method is applied to the $1\,{}^1S$ state of He. The wave functions so determined are linear combinations of products of hydrogen-like wave functions. The best value of the energy obtained with twenty parameters is $E(1\,{}^1S) = -2.900938$ au. By using the theory of Gaussian quadrature and least-squares approximation, a systematic transition from an exact iteration method to the numerical iteration method can be made. The resulting numerical scheme is applied to the $1\,{}^1S$ and $2\,{}^3S$ states of He. The energies obtained are $E(1\,{}^1S) = -2.903443$ au. and $E(2\,{}^3S) = -2.174823$ au. The $2\,{}^3S$ wave function yields a He^3 hyperfine splitting $\nu = 6664$ Mc/sec, which is lower than the experimental value by about 1%. The wave functions obtained are expressible in both the coordinate and momentum representations.

1. INTRODUCTION

We shall describe a numerical iteration calculation of approximations to the wave functions of the $1\,{}^1S$ and $2\,{}^3S$ states of helium. The method gives results which are expressed as expansions in products of hydrogenic functions. The resulting analytic wave functions can be used to calculate upper bounds on the energies of the states under consideration.

The numerical scheme derives from a general iteration method[1] for solving eigenvalue problems arising in quantum mechanics. This general method is presented in a form that is convenient for our purpose. The relationship between the iteration method and the usual variational method is made explicit and it is seen that the iteration method is equivalent to the variational method when truncated discrete representations are used. This latter fact allows us to study the dependence of the solutions on a certain parameter appearing in the iteration operator by doing a preliminary twenty-parameter variational calculation of the $1\,{}^1S$ state. The principal difficulties in setting up a numerical method stem from the Coulomb singularities. The numerical procedure used is derived from an exact scheme by making use of the theory of Gaussian quadrature and least-squares orthogonal polynomial approximations. The results obtained are compared to results calculated in other ways and possible improvements in the method are discussed.

2. THE EXACT ITERATION METHOD

The methods which will be developed and applied below are based on the following iterative procedure[1] for obtaining discrete solutions to the eigenvalue problem

$$A\psi = \lambda B\psi, \tag{2.1}$$

where A and B are Hermitian operators operating on a class of functions of certain variables x. Let $\psi_1, \psi_2, \cdots$ be eigenfunctions of (2.1) belonging to the eigenvalues $\lambda_1, \lambda_2, \cdots$, respectively. Let φ_0 be an arbitrary function in this class. Then

$$\varphi_0 = \textstyle\sum_r c_r \psi_r. \tag{2.2}$$

If λ_1 is the eigenvalue of least magnitude and is discrete, and if $c_1 \neq 0$, then

$$\varphi_n = (A^{-1}B)^n \varphi_0 \rightarrow c_1\psi_1/\lambda_1{}^n \quad \text{as} \quad n \rightarrow \infty, \tag{2.3}$$

and we have a method for obtaining the eigensolution corresponding to the eigenvalue of least absolute value.

If the eigenfunctions of (2.1) can be divided into symmetry classes, iterating on a φ_0 belonging to a particular class leads to the eigensolution corresponding to the eigenvalue of least magnitude within that symmetry class.

Let the vector C_n represent the nth approximation, φ_n, in a particular representation and the matrices $\mathbf{A}$ and $\mathbf{B}$ represent the operators A and B in that representation. Then the iteration algorithm becomes

$$C_n = \mathbf{A}^{-1}\mathbf{B}C_{n-1}. \tag{2.4}$$

In the calculations to be discussed it has been found advantageous to work with the operator A in one representation and the operator B in another representation. Let the complete set of functions $\{f_k(x)\}$ define the f representation and the complete set $\{g_l(x)\}$ define the g representation. Let $\mathbf{S}$ have matrix elements such that

$$g_l(r) = \textstyle\sum_k S_{kl} f_k(r). \tag{2.5}$$

Then the iteration algorithm can be written as

$$C_n = \mathbf{S}(\mathbf{A}')^{-1}\mathbf{S}^\dagger \mathbf{B} C_{n-1}, \tag{2.6}$$

where $\mathbf{A}'$ represents A in the g representation, $\mathbf{B}$, C_n,

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[1] L. H. Thomas, Phys. Rev. **51**, 202 (1937).

and C_{n-1} are in the f representation, and $\mathbf{S}^{\dagger}$ is the Hermitian adjoint of $\mathbf{S}$.

When applying the iteration method to atomic problems[1] the Schrödinger equation,

$$(T+V)\psi(\mathbf{r}_i)=E\psi(\mathbf{r}_i), \tag{2.7}$$

where $\psi(\mathbf{r}_i)\equiv\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_n)$, is replaced by the scaled equation,

$$(\mathfrak{T}+b\mathfrak{I})\chi(\boldsymbol{\varrho}_i)=-\lambda\mathfrak{V}\chi(\boldsymbol{\varrho}_i), \tag{2.8}$$

where

$$\mathfrak{T}=\sum_{i=1}^{n}-\frac{\nabla_i^2}{2}, \tag{2.9}$$

and

$$\mathfrak{V}=\sum_{i=1}^{n}-\frac{Z}{\rho_i}+\sum_{i>j=1}^{n}\frac{1}{\rho_{ij}} \tag{2.10}$$

in the coordinate representation. $\mathfrak{I}$ is the identity operator and b is an arbitrary positive number. For bound states, $\chi(\boldsymbol{\varrho}_i)$ must vanish at infinity. If $\chi_k(\boldsymbol{\varrho}_i)$ is an eigenfunction of (2.8) belonging to the eigenvalue[2] $\lambda_k>0$, then

$$\psi_k(\mathbf{r}_i)=\chi_k(\mathbf{r}_i/\lambda_k) \tag{2.11}$$

is an eigenfunction of (2.7) belonging to the eigenvalue

$$E_k=-b/\lambda_k^2. \tag{2.12}$$

For any λ, the connections are made by using the scale change

$$\mathbf{r}_i=\lambda\boldsymbol{\varrho}_i,\quad (i=1,\cdots n) \tag{2.13}$$

and the corresponding relations

$$\mathfrak{T}=\lambda^2 T, \tag{2.14}$$

and

$$\mathfrak{V}=\lambda V. \tag{2.15}$$

If λ_1 is the eigenvalue of (2.8) of least magnitude and is positive, then iteration with the operators

$$A=\mathfrak{T}+b\mathfrak{I}\quad\text{and}\quad B=-\mathfrak{V} \tag{2.16}$$

yields the eigensolution of (2.8) belonging to λ_1 and thus, through Eqs. (2.11) and (2.12), the eigensolution of (2.7) corresponding to the lowest energy, E_1.

Generally, we do not obtain exact solutions to Eq. (2.8). For example, after a finite number of the above iterations we have a function $\chi(\boldsymbol{\varrho}_i)$ which is an approximation to the eigenfunction $\chi_1(\boldsymbol{\varrho}_i)$. We seek an approximation, $\psi(\mathbf{r}_i)$ to the eigenfunction $\psi_1(\mathbf{r}_i)$ of Eq. (2.7). The variational principle leads to the solution

$$\psi(\mathbf{r}_i)=\chi(\mathbf{r}_i/\lambda_M), \tag{2.17}$$

where

$$\lambda_M=-2\langle\mathfrak{T}\rangle/\langle\mathfrak{V}\rangle. \tag{2.18}$$

The corresponding value of the energy is given by

$$E_M=-\tfrac{1}{4}\langle\mathfrak{V}\rangle^2/\langle\mathfrak{T}\rangle. \tag{2.19}$$

Here, $\langle\mathfrak{V}\rangle$ and $\langle\mathfrak{T}\rangle$ are averages of the operators $\mathfrak{V}$ and $\mathfrak{T}$ evaluated according to the formula

$$\langle O\rangle=\frac{\int\chi^*(\boldsymbol{\varrho}_i)O\chi(\boldsymbol{\varrho}_i)d\tau}{\int\chi^*(\boldsymbol{\varrho}_i)\chi(\boldsymbol{\varrho}_i)d\tau}\equiv\frac{(\chi,O\chi)}{(\chi,\chi)}. \tag{2.20}$$

This choice of λ is equivalent to making the virial theorem hold exactly in the state $\psi(\mathbf{r}_i)$.

3. VARIATIONAL CALCULATIONS

Let $\{f_k(\boldsymbol{\varrho}_i)\}$ be a set of expansion functions which are chosen to satisfy certain boundary conditions imposed by the physical problem. In the standard variational method, approximations to the first N bound state wave functions are obtained in the form

$$\psi_j(\mathbf{r}_i)=\sum_{k=1}^{N}C_{jk}f_k(r_i/\lambda),\quad (j=1,\cdots,N) \tag{3.1}$$

by solving the algebraic eigenvalue problem

$$\left[\frac{1}{\lambda^2}\mathfrak{T}+\frac{1}{\lambda}\mathfrak{V}\right]C_j=E_j\mathfrak{I}C_j, \tag{3.2}$$

where the vector C_j has elements C_{jk} and $\mathfrak{T}$, $\mathfrak{V}$, and $\mathfrak{I}$ are $N\times N$ matrices having elements

$$\mathfrak{T}_{kk'}=(f_k,\mathfrak{T}f_{k'}),\ \text{etc.} \tag{3.3}$$

The quantity λ is a parameter which is varied until the lowest value of E_1 is found.[3]

Consider the eigenvalue problem

$$(\mathfrak{T}+b\mathfrak{I})d_j=-\lambda_j\mathfrak{V}d_j, \tag{3.4}$$

where d_j is the eigenvector belonging to the eigenvalue λ_j and b is a positive number. If (λ_i,d_i) is a particular solution of (3.4), then $E_i=-b/\lambda_i^2$, $C_i=d_i$ is a solution of (3.2) with $\lambda=\lambda_i$. In particular, if (λ_1,d_1) is that solution of (3.4) such that $|\lambda_1|\leq|\lambda_j|$, $j=1,\cdots,N$, then $E_1=-b/\lambda_1^2$, $C_1=d_1$ is that solution of (3.2) with $\lambda=\lambda_1$ such that $E_1\leq E_j$, $j=1,\cdots,N$. Thus, in cases where only the ground state is of interest, we may replace (3.2) by (3.4) and solve for the solution corresponding to the eigenvalue of least magnitude. The above iteration scheme can be used to obtain this solution. The parameter b can be varied to give the lowest value of E_1, a procedure which is equivalent to varying λ in the standard variational method.

This reformulation of the variational method approaches the iteration scheme for obtaining an exact solution as $N\to\infty$. The solution would be obtained in the f representation.

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[2] If $\lambda_k<0$, (2.11) and (2.12) form an eigensolution to the problem $(T-V)\psi=E\psi$.

[3] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 408.

In general, the representatives of the operators and vectors in function space are matrices of infinite dimensions. In practice, when carrying out the iteration (2.6) with discrete representations, it is necessary to use only a finite subspace spanned by N basis functions. Such a calculation is equivalent to a variational calculation

A calculation using continuous representations can be done exactly if the implied operations can be carried out analytically. If numerical methods must be used, the introduction of a finite grid with finite intervals corresponds to the truncation of the matrices in the discrete case and evaluation of the matrix elements by numerical integration. Because of the latter, such a calculation can be considered as an approximation to a variational calculation.

4. A PRELIMINARY VARIATIONAL CALCULATION

In order to study the dependence of the solution on the parameter b in the case of the $1\,^1S$ state of He, iteration calculations using truncated discrete representations were carried out for several values of b.

The iteration operators for the helium problem are, in the coordinate representation,

$$A=\mathfrak{T}+b\mathfrak{J}=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+b, \tag{4.1}$$

$$B=-\mathfrak{B}=\frac{2}{\rho_1}+\frac{2}{\rho_2}-\frac{1}{\rho_{12}}. \tag{4.2}$$

The primary set of basis functions was the complete set of functions

$$f_{ln_1n_2}(\rho_1,\rho_2,\theta_{12})=\bar{R}_{n_1l}(\rho_1)\bar{R}_{n_2l}(\rho_2)\tilde{P}_l(\cos\theta_{12}), \tag{4.3}$$

where $\tilde{P}_l(x)$ is the lth normalized Legendre polynomial and θ_{12} is the angle between $\boldsymbol{\varrho}_1$ and $\boldsymbol{\varrho}_2$.

$$\bar{R}_{nl}(\rho)=\frac{2^l}{(n+l)!}\left[\frac{(n-l-1)!}{\pi n(n+l)!}\right]^{\frac{1}{2}}e^{-\rho}\rho^l \times L_{n+l}^{2l+1}(2\rho)\quad(n=l+1,\cdots), \tag{4.4}$$

where $L_m^k(x)$ is the usual associated Laguerre polynomial.[4] Only $f_{ln_1n_2}$ such that $0\leq l\leq 3$, $l+1\leq n_1\leq 4$, and $l+1\leq n_2\leq 4$ were used. Thus, by a variational calculation, we determined the coefficients $C(l,n_1,n_2)$ in the expression

$$\chi(\rho_1,\rho_2,\theta_{12})=\sum_{l=0}^{3}\sum_{n_1=l+1}^{4}\sum_{n_2=l+1}^{4} \times C(l,n_1,n_2)f_{ln_1n_2}(\rho_1,\rho_2,\theta_{12}), \tag{4.5}$$

TABLE I. Results of the 20-parameter variational calculation for the $1\,^1S$ state of He. The normalized wave function is $\psi(r_1,r_2,\theta_{12})=\mathfrak{N}^{-\frac{1}{2}}\sum C(l,n_1,n_2)\bar{R}_{n_1l}(r_1/\lambda_M)\bar{R}_{n_2l}(r_2/\lambda_M)\tilde{P}_l(\cos\theta_{12})$.

b	1.000	0.875	0.750	0.500
$\mathfrak{N}\times10^{-3}$	5.434401	6.282075	7.508409	12.62438
$\langle\mathfrak{T}\rangle\times10$	9.971750	8.731157	7.488355	5.014177
$-\langle\mathfrak{B}\rangle$	3.401082	3.182753	2.947753	2.412121
$\lambda_M\times10$	5.863869	5.486544	5.080720	4.157484
$-E_M$	2.900032	2.900508	2.900921	2.900938
ln_1n_2	$c(l,n_1,n_2)$			
011	1.0000000	1.0000000	1.0000000	1.0000000
021	−0.0585522	−0.1245153	−0.2003958	−0.3963826
022	−0.0969924	−0.0869617	−0.0643140	0.0493882
031	0.0576329	0.0675673	0.0868166	0.1739854
032	−0.0151173	−0.0112846	−0.0095875	−0.0325059
033	−0.0149084	−0.0143533	−0.0141389	−0.0085636
041	0.0149173	0.0075985	−0.0028465	−0.0452116
042	−0.0005056	0.0002312	0.0015315	0.0125124
043	−0.0067053	−0.0063235	−0.0058258	−0.0056533
044	−0.0048915	−0.0047899	−0.0046856	−0.0044525
122	−0.0812585	−0.0853009	−0.0898427	−0.1008847
132	−0.0344793	−0.0305090	−0.0251599	−0.0076564
133	−0.0292201	−0.0276061	−0.0262791	−0.0268149
142	−0.0097641	−0.0072174	−0.0045348	−0.0000271
143	−0.0142989	−0.0131207	−0.0118713	−0.0083956
144	−0.0094764	−0.0090110	−0.0085967	−0.0082796
233	−0.0136360	−0.0154477	−0.0176588	−0.0239524
243	−0.0092256	−0.0096897	−0.0100061	−0.0094123
244	−0.0076769	−0.0080353	−0.0083944	−0.0093387
344	−0.0021258	−0.0027079	−0.0035162	−0.0067125

where $C(l,n_2,n_1)=C(l,n_1,n_2)$. These coefficients were calculated using the iteration algorithm (2.6). Here, $\mathbf{B}$ has matrix elements

$$(ln_1n_2|B|l'n_1'n_2') =\int f_{ln_1n_2}\left(\frac{2}{\rho_1}+\frac{2}{\rho_2}-\frac{1}{\rho_{12}}\right)f_{l'n_1'n_2'}d\boldsymbol{\varrho}_1d\boldsymbol{\varrho}_2. \tag{4.6}$$

$\mathbf{A}'$ and $\mathbf{S}$ are determined by the simultaneous diagonalization of the two matrices $\mathfrak{T}$ and $\mathfrak{J}$ having elements

$$(ln_1n_2|\mathfrak{T}|l'n_1'n_2') =\int f_{ln_1n_2}(-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2)f_{l'n_1'n_2'}d\boldsymbol{\varrho}_1d\boldsymbol{\varrho}_2, \tag{4.7}$$

and

$$(ln_1n_2|\mathfrak{J}|l'n_1'n_2')=\int f_{ln_1n_2}f_{l'n_1'n_2'}d\boldsymbol{\varrho}_1d\boldsymbol{\varrho}_2, \tag{4.8}$$

respectively. With the operator A represented by a diagonal matrix, it was possible to change the parameter b easily.

A program was written for the IBM 650 which carried out an iteration in about two minutes. A solution was reached, for a given value of b, in 100 iterations, and this was done for $b=1$, 0.875, 0.75, and 0.5. The quantities $\langle\mathfrak{T}\rangle$, $\langle\mathfrak{B}\rangle$, λ_M, and E_M were calculated from each $\chi(\rho_1,\rho_2,\theta_{12})$. The results of these calculations are given in Table I. We note that the energy is quite insensitive to variations of b in the neighborhood of the minimum and that the best value of b is close to $b=0.5$ in the approximation used here.

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[4] The bar over this function refers to the particular normalization used here.

5. NUMERICAL ITERATION CALCULATIONS

The numerical iteration method is based on an exact scheme in which continuous representations are used. The operator $-\mathfrak{V}$ is taken in the coordinate representation and $(\mathfrak{T}+\mathfrak{J}b)$ in the momentum representation. If $\chi_n(\pi_1,\pi_2,\Theta_{12})$ is the nth approximation to the solution of the equation

$$(\mathfrak{T}+b\mathfrak{J})\chi=-\lambda\mathfrak{V}\chi$$

in the momentum representation, then $\chi_{n+1}(\pi_1,\pi_2,\Theta_{12})$ is given by

$$\chi_{n+1}(\pi_1,\pi_2,\Theta_{12})=\frac{1}{(2\pi)^3}(\tfrac{1}{2}\pi_1{}^2+\tfrac{1}{2}\pi_2{}^2+b)^{-1} \times\int \exp[-i(\boldsymbol{\pi}_1\cdot\boldsymbol{\rho}_1+\boldsymbol{\pi}_2\cdot\boldsymbol{\rho}_2)] \times g_n(\rho_1,\rho_2,\theta_{12})d\boldsymbol{\rho}_1d\boldsymbol{\rho}_2, \quad (5.1)$$

where

$$g_n(\rho_1,\rho_2,\theta_{12})=\frac{1}{(2\pi)^3}\left(\frac{2}{\rho_1}+\frac{2}{\rho_2}-\frac{1}{\rho_{12}}\right) \times\int \exp[i(\boldsymbol{\pi}_1\cdot\boldsymbol{\rho}_1+\boldsymbol{\pi}_2\cdot\boldsymbol{\rho}_2)] \times\chi_n(\pi_1,\pi_2,\Theta_{12})d\boldsymbol{\pi}_1d\boldsymbol{\pi}_2. \quad (5.2)$$

Θ_{12} is the angle between $\boldsymbol{\pi}_1$ and $\boldsymbol{\pi}_2$. This application of the mixed representation scheme leads to a considerable reduction in the number of arithmetic operations involved in a numerical iteration. This is because of the separability of the Fourier integrals.[5]

In carrying out the iteration defined by Eqs. (5.1) and (5.2) numerically, special care must be given to the regions near the singularities at $\rho_1=0$, $\rho_2=0$, and $\rho_{12}=0$. By introducing expansions in terms of hydrogenic functions, these singularities can be handled analytically. Let

$$R_{nl}(\rho)=\frac{2^{l+1}}{(n+l)!}\left[\frac{(n-l-1)!}{(n+l)!}\right]^{\frac{1}{2}}(-i)^l \times e^{-\rho}\rho^l L_{n+l}{}^{2l+1}(2\rho). \quad (5.3)$$

These functions satisfy the scaled hydrogen equation,

$$(-\nabla^2+1)R_{nl}{}^{(\rho)}\tilde{P}_l(\cos\theta)=\frac{2n}{\rho}R_{nl}(\rho)\tilde{P}_l(\cos\theta), \quad (5.4)$$

and the orthogonality relation

$$\int_0^\infty R_{nl}{}^*(\rho)R_{n'l}(\rho)\rho d\rho=\delta_{nn'}. \quad (5.5)$$

We make the transformation

$$\pi_i=\tan\varphi_i, \quad (0\leq\varphi_i\leq\tfrac{1}{2}\pi), \quad (i=1,2),$$

and define momentum-space radial functions

$$F_{nl}(\varphi)=(-1)^n2^{2l+1}l!\left[\frac{n(n-l-1)!}{\pi(n+l)!}\right]^{\frac{1}{2}}\frac{\cos^3\varphi}{\sin\varphi} \times\sin^{l+1}2\varphi C_{n-l-1}{}^{l+1}(\cos2\varphi), \quad (5.6)$$

where the $C_n{}^\nu$ are Gegenbauer polynomials.[6] The $F_{nl}(\varphi)$ satisfy the orthogonality relation[6]

$$\int_0^{\pi/2} F_{nl}(\varphi)F_{n'l}(\varphi)\left(\frac{\sin\varphi}{\cos^3\varphi}\right)^2 d\varphi=\delta nn'. \quad (5.7)$$

The R_{nl} and F_{nl} are related by the Fourier transformation[7]

$$(2n)^{\frac{1}{2}}F_{nl}(\varphi)\tilde{P}_l(\cos\Theta)=\frac{1}{(2\pi)^{\frac{3}{2}}} \times\int \exp(-i\boldsymbol{\pi}\cdot\boldsymbol{\rho})R_{nl}(\rho)\tilde{P}_l(\cos\theta)d\boldsymbol{\rho}. \quad (5.8)$$

Consider the process of multiplying the Fourier transform of $\chi_n(\pi_1,\pi_2,\Theta_{12})$ by $2/\rho_1$ and then taking the inverse Fourier transform of the result. Let F_i be the Fourier transformation operator for the ith electron and suppose χ_n has been expanded as

$$\chi_n(\pi_1,\pi_2,\Theta_{12}) =\sum_{l=0}^{\infty}\sum_{n_1=l+1}^{\infty}\sum_{n_2=l+1}^{\infty} a_n(l,n_1,n_2)F_{n_1l}(\varphi_1) \times F_{n_2l}(\varphi_2)\tilde{P}_l(\cos\Theta_{12}). \quad (5.9)$$

Then, using (5.4) and (5.8),

$$F_1{}^{-1}\left(\frac{2}{\rho_1}\right)F_1\chi_n =\sec^2\varphi_1\sum\frac{a_n(l,n_1,n_2)}{n_1}F_{n_1l}(\varphi_1)F_{n_2l}(\varphi_2) \times\tilde{P}_l(\cos\Theta_{12})\equiv\nu_n(\varphi_1,\varphi_2,\Theta_{12}). \quad (5.10)$$

The $2/\rho_2$ term is given by

$$F_2{}^{-1}\frac{2}{\rho_2}F_2\chi_n=\pm\nu_n(\varphi_2,\varphi_1,\Theta_{12}), \quad (5.11)$$

where the positive sign refers to ${}^1S$ states and the negative sign to ${}^3S$ states.

Consider the $1/\rho_{12}$ term. If the origin of coordinates is taken at the position of electron 1, then $\boldsymbol{\rho}_{12}$ is the position vector of electron 2 and the calculation could be handled as above. Let $d_1\equiv\exp(i\boldsymbol{\pi}_2\cdot\boldsymbol{\rho}_1)$ and

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[5] L. H. Thomas, "Lecture Notes on the Numerical Solution of Differential Equations" (unpublished).

[6] W. Magnus and F. Oberhettinger, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 76.

[7] B. Podolsky and L. Pauling, Phys. Rev. 34, 109 (1929).

$\mu_n(\varphi_1,\varphi_2,\Theta_{12})$ be the inverse Fourier transform of $1/\rho_{12}$ times the Fourier transform of χ_n. Then

$$\mu_n = F_1^{-1} d_1^{-1} F_2^{-1} \frac{1}{\rho_{12}} F_2 d_1 F_1 \chi_n. \qquad (5.12)$$

The Fourier coefficients of $d_1F_1\chi_n$ are evaluated in the usual way, the $F_2^{-1}(1/\rho_{12})F_2$ operation is performed as indicated in Eq. (5.10), the d_1^{-1} operation can then be done immediately, and the F_1^{-1} operation is accomplished by first transforming to Fourier coefficients and then summing over the $F_{nl}(\varphi_1)$ functions.

The iteration is completed by calculating

$$\begin{aligned}\chi_{n+1}(\pi_1,\pi_2,\Theta_{12}) = {}& (\tfrac{1}{2}\pi_1^2+\tfrac{1}{2}\pi_2^2+b)^{-1} \\ & \times\{\nu_n(\varphi_1,\varphi_2,\Theta_{12})\pm\nu_n(\varphi_2,\varphi_1,\Theta_{12}) \\ & -\mu_n(\varphi_1,\varphi_2,\Theta_{12})\}. \qquad (5.13)\end{aligned}$$

This exact scheme is converted to a numerical procedure by truncating the infinite series, replacing the continuous variables by discrete variables, and evaluating the Fourier coefficients by numerical integration. By the theory of Gaussian quadrature,[8] it is seen that replacing a continuous ρ variable by the N zeros of $L_N(\rho)$, a continuous $x=\cos\theta$ variable by the N zeros of $P_N(x)$, and a continuous φ variable by the N points $k\pi/2(N+1)$, $k=1, 2, \cdots N$, preserves the orthogonality relations for the functions R_{nl}, $\tilde{P}_l$, and F_{nl} when the integrals are replaced by Gaussian quadratures. Consequently, the infinite series used in the exact method become least-squares polynomial approximations[8] in the numerical method if the coefficients are evaluated by replacing the integrals in the exact calculation of Fourier coefficients by the appropriate Gaussian quadratures. Since the numerical scheme utilizes the same orthogonal functions that appear in the exact calculation, the properties of these functions, namely Eqs. (5.4) and (5.8), can be used to take care of the singularities.

The method outlined above was used to calculate the coefficients $A(l,n_1,n_2)$ in the approximation

$$\chi(\rho_1,\rho_2,\theta_{12}) = \sum_{l=0}^{N-1}\sum_{n_1=l+1}^{N}\sum_{n_2=l+1}^{N} A(l,n_1,n_2) \times R_{n_1l}(\rho_1)R_{n_2l}(\rho_2)\tilde{P}_l(\cos\theta_{12}) \qquad (5.14)$$

to the solution of the scaled helium equation,

$$(-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+\tfrac{1}{2})\chi = \lambda\left(\frac{2}{\rho_1}+\frac{2}{\rho_2}-\frac{1}{\rho_{12}}\right)\chi. \qquad (5.15)$$

TABLE II. Results of the energy calculations for the $1\,{}^1S$ and $2\,{}^3S$ states of He (in atomic units). The wave functions are of the form:

$$\psi(r_1,r_2,\theta_{12}) = \sum_{l=0}^{14}\sum_{n_1=l+1}^{15}\sum_{n_2=l+1}^{15} A(l,n_1n_2) \times R_{n_1l}\left(\frac{r_1}{\lambda_M}\right)R_{n_2l}\left(\frac{r_2}{\lambda_M}\right)\tilde{P}_l(\cos\theta_{12}),$$

where the $A(l,n_1,n_2)$ were determined by numerical iteration.

	$1\,{}^1S$	$2\,{}^3S$
$\langle 2/\rho_1\rangle$	1.4015 48539	1.1099 72518
$\langle 1/\rho_{12}\rangle$	0.3924 38253	0.1307 78256
$-\langle\mathfrak{B}\rangle$	2.4106 58825	2.0891 66780
$\langle\mathfrak{T}\rangle\times 10$	5.0037 80598	5.0172 10624
$\lambda_M\times 10$	4.1513 80151	4.8030 73332
$-E_M$	2.9034 42635	2.1748 22905
$-E_{\mathrm{exp}}$	2.903722	2.17526

Both the $1\,{}^1S$ and $2\,{}^3S$ states were treated. For each solution obtained, a value of

$$\bar{\lambda} = -\langle\mathfrak{T}+\tfrac{1}{2}\rangle/\langle\mathfrak{B}\rangle \qquad (5.16)$$

was calculated using Gaussian quadrature. For an exact solution,

$$\bar{\lambda}=\lambda_1=(-2E_1)^{-\frac{1}{2}}. \qquad (5.17)$$

The following results were obtained:

	N	$\bar{\lambda}$	λ_1
$1\,{}^1S$:	14	0.414885	0.414961
	15	0.414899	
$2\,{}^3S$:	15	0.479316	0.479442

In calculating $\lambda_1(1\,{}^1S)$, the value[9] $E(1\,{}^1S)=-2.903722$ a.u. (atomic units) was used. $\lambda_1(2\,{}^3S)$ was calculated from $E(2\,{}^3S)=-2.17526$ a.u. which is the sum of the experimental binding energy,[10] $I(2\,{}^3S)=0.175260$ a.u., and the ground-state energy of He$^+$.

Using the $A(l,n_1,n_2)$ calculated in the $N=15$ cases, the quantities $\langle\mathfrak{B}\rangle$ and $\langle\mathfrak{T}\rangle$ were calculated exactly. Upper bounds on the energies of the two states under consideration were calculated, along with the corresponding values of λ_M, according to Eqs. (2.18) and (2.19). These results are displayed in Table II.

All the calculations indicated above were done on the Naval Ordnance Research Calculator (NORC). One iteration toward a wave function required about five minutes. Seventy-seven iterations were necessary in the ${}^1S$ case and 192 in the ${}^3S$ case. The energy calculations were completed in about three hours.

6. DISCUSSION OF THE RESULTS

The variational calculations which have been done on the helium problem fall into two categories. First, there are the Hylleraas-type calculations in which the basis functions involve the variable r_{12} explicitly. Recent calculations[9–11] using this approach have yielded

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[8] F. B. Hildebrand, *Introduction to Numerical Analysis* (McGraw-Hill Book Company, Inc., New York, 1956), Chaps. 7 and 8.

[9] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[10] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[11] E. A. Hylleraas and J. Mitdal, Phys. Rev. **103**, 829 (1956); J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).

TABLE III. Results of using successively higher Legendre polynomials in the $1\,^1S$ wave function

$$\chi(\rho_1,\rho_2,\theta_{12})=\sum_{l=0}^{l_f}\sum_{n_1=l+1}^{15}\sum_{n_2=l+1}^{15}A(l,n_1,n_2)\times R_{n_1l}(\rho_1)R_{n_2l}(\rho_2)\tilde{P}_l(\cos\theta_{12}),$$

when computing the energy $E=-\frac{1}{4}\langle\mathfrak{V}\rangle^2/\langle\mathfrak{T}\rangle$.

l_f	$\langle 1/\rho_{12}\rangle$	$\langle 2/\rho_1+2/\rho_2\rangle$	$\langle\mathfrak{T}\rangle$	$-E_M$
0	0.412023142	2.80666963	0.497958538	2.87892030
1	0.394908265	2.80331125	0.499958414	2.90044371
2	0.393108101	2.80313631	0.500245151	2.90269480
3	0.392667464	2.80311071	0.500325607	2.90322771
4	0.392519315	2.80310244	0.500358421	2.90337423
5	0.392464504	2.80309959	0.500370988	2.90342650
6	0.392444967	2.80309796	0.500376246	2.90343911
7	0.392439664	2.80309733	0.500377679	2.90344204
8	0.392438488	2.80309715	0.500377987	2.90344265
14	0.392438253	2.80309708	0.500377806	2.90344263

ground-state energies which are essentially in agreement with experiment.[12] The $2\,^3S$ state problem has also been studied from this point of view.[13] In this case the calculated binding energy agrees with experiment to about 0.02%. Teutsch and Hughes[14] have used the Huang wave function to calculate the hyperfine splitting in this state of the He^3 atom and obtain a value which is about 0.07% from the experimental value[15] of 6739.71±0.05 Mc/sec.

The second type of variational calculation uses trial functions which are generally described as superpositions of configurations (SOC).[16] The best value of the ground-state energy obtained using this method is that of Watson. He quotes the result $E(1\,^1S)=-2.902738$ a.u.

The calculation presented in the last section can be considered as an SOC calculation in which the coefficients are determined by an iteration method. Our $1\,^1S$ result is 0.0007 a.u. lower than that of Watson and gives added evidence that the SOC approach can be used to obtain accurate solutions to many electron problems.

Using the wave function obtained for the $2\,^3S$ state, we have calculated the hyperfine splitting. With the anomalous moment and reduced mass corrections calculated by Teutsch and Hughes[14] we get $\nu=6664$ Mc/sec, which is lower than the experimental value by about 1%.

Examination of Table II shows that the numerical iteration method yields a $1\,^1S$ energy that is about 2.5 times more accurate than the $2\,^3S$ energy. The method is expected to be more accurate for the ground state because there is only one scale factor involved. Physically, the difference in effective Z's seen by the two electrons in the $2\,^3S$ case is not taken into account in the exponential factors as it is in the variational calculations.

In Table III we have listed the results of computing the $1\,^1S$ energy from the wave function

$$\chi(\rho_1,\rho_2,\theta_{12})=\sum_{l=0}^{l_f}\sum_{n_1=l+1}^{15}\sum_{n_2=l+1}^{15}A(l,n_1,n_2)\times R_{n_1l}(\rho_1)R_{n_2l}(\rho_2)\tilde{P}_l(\cos\theta_{12})\quad(6.1)$$

for successively higher values of l_f. It is clear that values of l greater than $l=8$ do not contribute more than 10^{-8} a.u. to the total energy. Furthermore, contributions from $l\geq 5$ did not increase the accuracy appreciably. Green[17] has given as a lower bound on the $l_f=0$ energy the value -2.8792 a.u. which is about 0.0003 a.u. lower than our value. These facts suggest that in order to obtain a ground-state energy with an accuracy comparable to the experimental accuracy it would be necessary to improve the radial least-squares approximations by using more radial functions for a given l. This would also require using more radial points to preserve the orthogonality of the expansion functions over the discrete space. The added labor involved would be partially compensated by the fact that the higher l values can be neglected.

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[12] See S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955), reference 12.

[13] E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930); S. Huang, Astrophys. J. **108**, 354 (1948).

[14] W. B. Teutsch and V. W. Hughes, Phys. Rev. **95**, 1461 (1954).

[15] G. Weinreich and V. W. Hughes, Phys. Rev. **95**, 1451 (1954).

[16] E. A. Hylleraas, Z. Physik **48**, 469 (1928); C. Eckart, Phys. Rev. **36**, 878 (1930); G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. **38**, 154 (1952); L. C. Green, *Proceedings of the National Science Foundation Conference on Stellar Atmospheres*, p. 72, 1954 (unpublished); P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); R. E. Watson, Quarterly Progress Report of Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1956 (unpublished), p. 38.

[17] L. C. Green *et al.*, Phys. Rev. **93**, 273 (1954).