Helium Wave Function in Momentum Space*

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Approximate solutions to the integral Schrödinger equation in momentum space are obtained. The iteration scheme of Svartholm is used to obtain the first iterated wave function and the half-iterated energy. A wave function of the type

$$\phi = \Sigma\, C_{ij}[\exp(-\alpha_i p_1^2 - \alpha_j p_2^2) + \exp(-\alpha_j p_1^2 - \alpha_i p_2^2)]$$

is employed to start the iteration procedure. The best energy value computed using a wave function with three nonlinear parameters is -2.8915 atomic units. This energy is to be compared with the result of a conventional variational calculation using the same wave function in coordinate space, -2.85112 atomic units.

I. INTRODUCTION

THE Schrödinger equation in configuration space for the system of two electrons about a nucleus of charge Z is[1]

$$\left(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\psi(\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{r}_1,\mathbf{r}_2), \quad (1.1)$$

where $\mathbf{r}_i$ is the position vector of the ith electron and $\mathbf{r}_{12}$ is defined by $\mathbf{r}_1 - \mathbf{r}_2$.

The eigenfunction in momentum space is defined by

$$\phi(\mathbf{p}_1,\mathbf{p}_2) = (2\pi)^{-3}\int d\mathbf{r}_1 d\mathbf{r}_2\, \psi(\mathbf{r}_1,\mathbf{r}_2)\, e^{-i\mathbf{p}_1\cdot\mathbf{r}_1 - i\mathbf{p}_2\cdot\mathbf{r}_2}, \quad (1.2)$$

where $\mathbf{p}_i$ is the momentum of the ith electron. Let

$$\lambda = \pi^{-2}, \quad (1.3)$$

$$p_0^2 = -2E. \quad (1.4)$$

The equation in momentum space corresponding to Eq. (1.1) may be written[2]

$$(p_0^2 + p_1^2 + p_2^2)\phi(\mathbf{p}_1,\mathbf{p}_2) = \lambda[ZI_1(\phi) + ZI_2(\phi) - I_{12}(\phi)], \quad (1.5)$$

where

$$I_1(\phi) = \int d\mathbf{p}\, p^{-2}\phi(\mathbf{p}_1 - \mathbf{p}, \mathbf{p}_2),$$

$$I_2(\phi) = \int d\mathbf{p}\, p^{-2}\phi(\mathbf{p}_1, \mathbf{p}_2 - \mathbf{p}), \quad (1.6)$$

$$I_{12}(\phi) = \int d\mathbf{p}\, p^{-2}\phi(\mathbf{p}_1 - \mathbf{p}, \mathbf{p}_2 + \mathbf{p}).$$

We may obtain a series of converging approximations for the ground state solution of Eq. (1.5) by a method due to Svartholm,[3,4] based on the Gauss-Hilbert variational principle and the Kellog method of iterated functions. In the Svartholm method we regard λ as the eigenvalue parameter. We select a starting function, ϕ^0, and form the following integrals:

$$\phi^{r+1} = (p_0^2 + p_1^2 + p_2^2)^{-1}[ZI_1(\phi^r) + ZI_2(\phi^r) - I_{12}(\phi^r)], \quad (1.7)$$

$$W_r = \int \phi^{r+1}(p_0^2 + p_1^2 + p_2^2)\phi^r d\mathbf{p}_1 d\mathbf{p}_2, \quad (1.8)$$

$$T_r = \int \phi^r(p_0^2 + p_1^2 + p_2^2)\phi^r d\mathbf{p}_1 d\mathbf{p}_2. \quad (1.9)$$

If we let

$$\lambda_r = T_r/W_r, \quad (1.10)$$

and

$$\lambda_{r+\frac{1}{2}} = W_r/T_{r+1}, \quad (1.11)$$

then $\lambda_0, \lambda_{\frac{1}{2}}, \lambda_1, \cdots$ is a monotonically decreasing sequence which converges to λ, the smallest eigenvalue of Eq. (1.5). In addition, the sequence $\phi^0, \phi^1, \cdots$ converges to ϕ, the eigenfunction of Eq. (1.5) which corresponds to λ. In general, we cannot make as many iterations as we would like due to the difficulty of evaluating the integrals of Eq. (1.6). We must stop the iteration at some ϕ^s, and some λ_t. The quantity λ_t is a function of p_0 and the parameters of the starting function, ϕ^0. We may first minimize λ_t in the parameters of ϕ^0. Then, because of Eq. (1.3), we must choose p_0 such that

$$\lambda_t = \pi^{-2}. \quad (1.12)$$

It is easily seen that the value of E obtained from this p_0 is an upper bound to the energy of the system.

II. CHOICE OF STARTING FUNCTION

In the case of the ground state of the two-electron atom, the most obvious choice for ϕ^0 is the momentum-

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[1] We work throughout in atomic units (a.u.): the unit of length is the Bohr radius a_0; the unit of energy is e^2/a_0.

[2] R. McWeeny and C. A. Coulson, Proc. Phys. Soc. (London) **A62**, 509 (1949).

[3] N. Svartholm, thesis, Lund, 1945 (unpublished).

[4] I. N. Sneddon, *Fourier Transforms* (McGraw-Hill Book Company, New York, 1951), 1st ed., p. 384.

space equivalent of the Kellner wave function,

$$\phi^0=(p_1^2+a^2)^{-2}(p_2^2+a^2)^{-2}.$$

This function was used by McWeeny and Coulson.[2] They were unable to evaluate either ϕ^1 or $\lambda_{\frac{1}{2}}$. The work of Krauss,[5] Boys,[6] Preuss[7] and others employing Gaussian approximations for wave functions in configuration space is encouraging, and suggests that a coordinate-space Gaussian wave function might be a good starting point. The transformation of such a coordinate-space wave function results in a wave function which is again Gaussian in form. Thus, we are led to consider starting functions of the general type

$$\phi^0=\sum_\mu C_\mu\varphi_\mu, \tag{2.1}$$

where

$$\varphi_\mu=\varphi_{ij}+\varphi_{ji}, \tag{2.2}$$

and

$$\varphi_{ij}=\exp(-\alpha_i p_1^2-\alpha_j p_2^2). \tag{2.3}$$

The subscript μ indicates the pair (i,j). For a function of this type we are able to evaluate ϕ^1 in closed form and can express $\lambda_{\frac{1}{2}}$ in terms of one-dimensional integrals.

III. THE CALCULATION OF ϕ^1

We need consider only a single term. When φ_{ij} is inserted into Eq. (1.7), the integrals which arise are all of the type

$$\mathcal{I}(\alpha,\beta;\mathbf{a},\mathbf{b})=\int d\mathbf{p}\, p^{-2}\exp[-\alpha(\mathbf{a}-\mathbf{p})^2-\beta(\mathbf{b}+\mathbf{p})^2]. \tag{3.1}$$

This integral may be shown to be related to the error function.[8] We have the results:

$$I_1(\varphi_{ij})=2\pi^{\frac{3}{2}}\alpha_i^{-\frac{1}{2}}F(\tfrac{1}{2},\tfrac{3}{2},\alpha_i p_1^2)\varphi_{ij}, \tag{3.2}$$

$$I_2(\varphi_{ij})=2\pi^{\frac{3}{2}}\alpha_j^{-\frac{1}{2}}F(\tfrac{1}{2},\tfrac{3}{2},\alpha_j p_2^2)\varphi_{ij}, \tag{3.3}$$

$$I_{12}(\varphi_{ij})=2\pi^{\frac{3}{2}}(\alpha_i+\alpha_j)^{-\frac{1}{2}}F\left(\tfrac{1}{2},\tfrac{3}{2},\frac{[\alpha_i\mathbf{p}_1-\alpha_j\mathbf{p}_2]^2}{(\alpha_i+\alpha_j)}\right)\varphi_{ij}, \tag{3.4}$$

where

$$F(a,b,z)=\frac{\Gamma(b)}{\Gamma(a)}\sum_{\nu=0}^{\infty}\frac{\Gamma(a+\nu)}{\Gamma(b+\nu)\nu!}z^\nu \tag{3.5}$$

is the confluent hypergeometric function. The total contribution to ϕ^1 from the term φ_μ is

$$\varphi_\mu^1=(p_0^2+p_1^2+p_2^2)^{-1}[ZI_1(\varphi_\mu)+ZI_2(\varphi_\mu)-I_{12}(\varphi_\mu)], \tag{3.6}$$

and the total iterated wave function is then

$$\phi^1=\sum_\mu C_\mu\varphi_\mu^1. \tag{3.7}$$

[5] M. Krauss (private communication).
[6] S. F. Boys, Proc. Roy. Soc. (London) **200**, 542 (1950).
[7] H. Preuss, Boulder Conference, June, 1959 (unpublished).
[8] The derivation is somewhat lengthy. A limited number of copies are available upon request.

IV. THE CALCULATION OF $\lambda_{\frac{1}{2}}$

From Eqs. (1.8) and (1.9) we have

$$W_0=\sum_\mu\sum_\nu C_\mu C_\nu\int d\mathbf{p}_1 d\mathbf{p}_2\,\varphi_\mu^1(p_0^2+p_1^2+p_2^2)\varphi_\nu=\sum_\mu\sum_\nu C_\mu C_\nu W_{\mu\nu}, \tag{4.1}$$

$$T_1=\sum_\mu\sum_\nu C_\mu C_\nu\int d\mathbf{p}_1 d\mathbf{p}_2\,\varphi_\mu^1(p_0^2+p_1^2+p_2^2)\varphi_\nu^1=\sum_\mu\sum_\nu C_\mu C_\nu T_{\mu\nu}, \tag{4.2}$$

where μ denotes the pair (i,j) and ν denotes the pair (k,l). A comparison of Eqs. (1.11), (4.1), and (4.2) shows that the minimization of $\lambda_{\frac{1}{2}}$ with respect to the linear parameters, C_μ, leads to an ordinary secular equation

$$|W_{\mu\nu}-\lambda_{\frac{1}{2}}T_{\mu\nu}|=0. \tag{4.3}$$

We define

$$J_m(i,j;k,l)=\int d\mathbf{p}_1 d\mathbf{p}_2\,\varphi_{ij}I_m(\varphi_{kl}), \tag{4.4}$$

$$K_{m,n}(i,j;k,l)=\int d\mathbf{p}_1 d\mathbf{p}_2(p_0^2+p_1^2+p_2^2)^{-1}\times I_m(\varphi_{ij})I_n(\varphi_{kl}). \tag{4.5}$$

The subscripts m and n may be 1, 2, or 12. In terms of these definitions, the matrix elements defined by Eq. (4.1) and Eq. (4.2) may be written

$$W_{\mu\nu}=2Z\sum J_1(i,j;k,l)-2J_{12}(i,j;k,l)-2J_{12}(i,j;l,k), \tag{4.6}$$

$$T_{\mu\nu}=2\sum[Z^2K_{1,1}(i,j;k,l)+Z^2K_{1,2}(i,j;k,l)-ZK_{1,12}(i,j;k,l)-ZK_{1,12}(k,l;i,j)]+2K_{12,12}(i,j;k,l)+2K_{12,12}(i,j;l,k). \tag{4.7}$$

The summation is over the four possible permutations, $(i,j;k,l)$, $(j,i;k,l)$, $(i,j;l,k)$, and $(j,i;l,k)$. These integrals have been either evaluated or reduced to one-dimensional integrals.[8] If we let

$$\kappa=\alpha_1 p_0^2, \tag{4.8}$$

then it is possible to define the following pair of functions, each of which is independent of p_0;

$$\bar{W}_{\mu\nu}=\tfrac{1}{2}p_0^{-7}(\kappa^7\pi^{-9})^{\frac{1}{2}}W_{\mu\nu}, \tag{4.9}$$

$$\bar{T}_{\mu\nu}=\tfrac{1}{4}p_0^{-6}\kappa^3\pi^{-6}e^{-\kappa}T_{\mu\nu}. \tag{4.10}$$

If we let $\bar{\lambda}$ denote the smallest root of the equation

$$|\bar{W}_{\mu\nu}-\bar{\lambda}\bar{T}_{\mu\nu}|=0, \tag{4.11}$$

then

$$\lambda_{\frac{1}{2}}=(4\pi^3\kappa e^{2\kappa})^{-\frac{1}{2}}p_0\bar{\lambda}. \tag{4.12}$$

The entire dependence of $\lambda_{\frac{1}{2}}$ on p_0 is then displayed explicitly by Eq. (4.12). Once $\bar{\lambda}$ has been found, the

TABLE I. Best computed energies, in atomic units.

ϕ^0	E_0	$E_{\frac{1}{2}}$	E_0-E_{exp}[a]	$E_{\frac{1}{2}}-E_{\text{exp}}$	$(1-E_0E_{\text{exp}}^{-1})^{\frac{1}{2}}$	$(1-E_{\frac{1}{2}}\cdot E_{\text{exp}}^{-1})^{\frac{1}{2}}$
Eq. (5.1)	−2.3010	−2.5995	0.6027	0.3042	0.4556	0.3237
Eq. (5.2)	−2.5566	−2.7815	0.3471	0.1222	0.3458	0.2051
Eq. (5.3)	−2.8511[b]	−2.8915	0.0526	0.0122	0.1346	0.0648

[a] $E_{\text{exp}} = -2.9037$ a.u.
[b] H. Preuss, preliminary results presented at Boulder Conference, June, 1959 (unpublished).

value of E which satisfies Eq. (1.12) is given directly by

$$E=-2\kappa e^{2\kappa}\pi^{-1}\bar{\lambda}^{-2}. \tag{4.13}$$

We must now make a contour map in the appropriate number of dimensions in order to optimize E with respect to the nonlinear parameters. It is convenient to replace the parameters α_n by the reduced parameters

$$\sigma_n=\alpha_n/\alpha_1. \tag{4.14}$$

The large number of one-dimensional integrals required were evaluated by the use of a seven-point Newton-Cotes integration formula. The entire range of integration was spanned by 97 points. The calculations were performed on the Remington Rand 1103 located at Southern Methodist University in Dallas.

V. RESULTS AND DISCUSSION

We present here the results of the application of the analysis to three different ϕ^0 of the type of Eq. (2.1). They are, in order of increasing complexity and accuracy, the simple "closed-shell" type,

$$\phi^0=\varphi_{11}; \tag{5.1}$$

the simple "open-shell" type,

$$\phi^0=\varphi_{12}+\varphi_{21}; \tag{5.2}$$

and the general type using three nonlinear parameters,

$$\phi^0=\sum_{i=1}^{3}\sum_{j=1}^{3}C_{ij}\varphi_{ij}. \tag{5.3}$$

Because of the symmetry restriction, Eq. (2.2), this latter ϕ^0 is a six-term wave function.

The ordinary configuration-space energy, E_0, computed from these wave functions is listed in the second column of Table I. The energy $E_{\frac{1}{2}}$, computed from $\lambda_{\frac{1}{2}}$ and Eqs. (4.12) and (4.13), is listed in the third column of Table I. For the energies computed from ϕ^0 of equations (5.1) and (5.2), we have listed the optimized energies and, in Table II, the corresponding parameters. For the energy computed from the ϕ^0 of Eq. (5.3), we have listed in the table our best directly computed point. The corresponding parameters are shown in Tables II and III. Three-point Lagrangian interpolation into a three-dimensional grid of 27 points indicated a minimum energy of −2.8965 a.u. corresponding to

$$\alpha_1=0.216,$$
$$\alpha_2=0.860,$$
$$\alpha_3=0.033.$$

The fourth and fifth columns of Table I compare the absolute errors in the computed energies, and the last two columns tabulate a quantity which should be a measure of the error in the appropriate wave function. Strictly, $E_{\frac{1}{2}}$ is not the energy corresponding to ϕ^1 (that would be E_1, the energy computed from λ_1), but is an upper limit to E_1. That is, ϕ^1 is at least as good as is indicated by $E_{\frac{1}{2}}$, and, in fact, necessarily better.

TABLE II. The nonlinear parameters.

ϕ^0	α_1	α_2	α_3
Eq. (5.1)	0.2991		
Eq. (5.2)	0.6621	0.1356	
Eq. (5.3)	0.1729	0.7781	0.0259

TABLE III. The linear parameters for Eq. (5.3).

i \ j	1	2	3
1	0.07632	0.9263	0.01132
2		1.0000	0.06031
3			0.00008

It is interesting to notice that the improvement in the energy is the greater the better the initial wave function is. Thus, the absolute error due to the use of ϕ^0 of Eq. (5.1) is reduced by a factor of about one-half; of Eq. (5.2), by about two-thirds; and of Eq. (5.3), by about three-quarters. Since it seems clear from a consideration of Eq. (3.4) that most of the improvement is due to the explicit introduction of electron correlation, then the trend may not be applicable for wave functions which already contain r_{12}.

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