PHYSICAL REVIEW A VOLUME 30, NUMBER 1 JULY 1984

Approximate solutions of the momentum-space integral Schrödinger equation for two-electron atoms

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(Received 13 January 1984)

It is demonstrated that correlated Gaussian geminals can be used with the same computational effort as products of Gaussian orbitals in the iterative solution of the two-electron integral Schrödinger equation in momentum space. The most accurate energies $E_{1/2}$ and wave functions ϕ^1 ever constructed directly in momentum space are reported for H^-, He, and Li^+.

I. INTRODUCTION

Quantum-mechanical state vectors in the momentum representation play a pivotal role in the theory of Compton scattering.[1] They are usually obtained by Fourier transformation[2] of the position (coordinate) representation of the state vector because thousands of papers have been published[3] on the computation of approximate solutions of the configuration-space Schrödinger equation for atoms and molecules.

Momentum-space wave functions can also be obtained by direct approximate solution of the integral Schrödinger equation in momentum space. Apparently, less than 20 published papers have dealt with this approach. Since the pioneering work of Fock[4] on the H atom and of McWeeny[5] on H_2^+, a number of studies on the problem of one electron in the field of an arbitrary number of nuclei have appeared.[6] Numerical methods for the solution of the momentum-space Hartree-Fock equations for many-electron systems have also been studied.[7] Actual calculations for many-electron systems have been restricted to the ground states of the helium atom[8–12] and the H_2 and H_3 molecules.[7(c)] All of the work on He uses an iterative procedure for the solution of the momentum-space integral Schrödinger equation first employed by Svartholm[13] in his treatment of nuclear systems.

This paper is concerned with obtaining approximate solutions to the momentum-space integral Schrödinger equation for the two-electron systems He, H^-, and Li^+ using the Svartholm iteration starting from correlated wave functions of high accuracy. A brief outline of the Svartholm iterative procedure is given in Sec. II. The wave functions chosen to start the iteration are described in Sec. III after a motivational summary of previous calculations on He. The calculation of the first-iterated functions and half-iterated energies is described in Sec. IV and numerical results are presented in Sec. V followed by concluding remarks in Sec. VI. Atomic units are used throughout this paper.

II. ITERATIVE METHOD OF SOLUTION

In the nonrelativistic and infinite nuclear mass approximations, the integral Schrödinger equation in momentum space for a two-electron atom with nuclear charge Z may be written[8] as

$$(p_0^2+p_1^2+p_2^2)\phi(\vec{p}_1,\vec{p}_2)=\lambda[ZI_1(\phi)+ZI_2(\phi)-I_{12}(\phi)]\ , \tag{1}$$

where

$$p_0^2=-2E\ , \tag{2}$$

$$\lambda=\pi^{-2}\ , \tag{3}$$

$$I_1(\phi)=\int p^{-2}\phi(\vec{p}_1-\vec{p},\vec{p}_2)d\vec{p}\ , \tag{4a}$$

$$I_2(\phi)=\int p^{-2}\phi(\vec{p}_1,\vec{p}_2-\vec{p})d\vec{p}\ , \tag{4b}$$

$$I_{12}(\phi)=\int p^{-2}\phi(\vec{p}_1-\vec{p},\vec{p}_2+\vec{p})d\vec{p}\ , \tag{4c}$$

and $\phi(\vec{p}_1,\vec{p}_2)$ is the momentum-space wave function with the two-electron spin function having been factored out as usual.

Svartholm's iterative method[13] for solution of Eq. (1) is based on the Gauss-Hilbert variational principle and the Kellogg theory of iterated functions.[14] In this procedure, λ is regarded as an eigenvalue parameter and an initial function ϕ^0 is chosen. Then for $n=0,1,2,\ldots$ the following objects are formed:

$$\phi^{n+1}=(p_0^2+p_1^2+p_2^2)^{-1}\times[ZI_1(\phi^n)+ZI_2(\phi^n)-I_{12}(\phi^n)]\ , \tag{5}$$

$$W_n=\int \phi^{n+1}(p_0^2+p_1^2+p_2^2)\phi^n d\vec{p}_1 d\vec{p}_2\ , \tag{6}$$

$$T_n=\int \phi^{n}(p_0^2+p_1^2+p_2^2)\phi^n d\vec{p}_1 d\vec{p}_2\ , \tag{7}$$

$$\lambda_n=T_n/W_n\ , \tag{8}$$

and

$$\lambda_{n+1/2}=W_n/T_{n+1}\ . \tag{9}$$

It may be shown that $\lambda_0,\lambda_{1/2},\lambda_1,\ldots$ is a monotonically decreasing sequence which converges to λ, the smallest eigenvalue of Eq. (1). Also, the sequence $\phi^0,\phi^1,\ldots$ converges to ϕ, the eigenfunction of Eq. (1) corresponding to λ. In practice, the number of iterations performed is limited by the difficulties of performing the integrals in Eqs. (5)–(7), and hence the iteration must be stopped at some ϕ^s and some λ_t. Of course, one may also vary parameters in ϕ^0 to minimize λ_t. The quantity λ_t is now a function of p_0^2 and the root of the nonlinear equation

$$\lambda_t(p_0^2)-\pi^{-2}=0 \tag{10}$$

yields, through Eq. (2), an upper bound E_t to the true ground-state energy.

For integer n, the energies E_n are simply the variational energies corresponding to the trial function ϕ^n. However, the energies $E_{n+1/2}$ do not have any counterparts in the usual Rayleigh-Ritz procedure. Thus an advantage of the iterative procedure is that an improved wave function ϕ^n may become available even if neither of the components W_n and T_n that enter into the corresponding variational energy E_n are calculable.

III. CHOICE OF STARTING FUNCTION ϕ^0

One may pass from the position-space representation $\psi(\vec{r}_1,\vec{r}_2)$ of a state vector to its momentum-space representation $\phi(\vec{p}_1,\vec{p}_2)$ via the Dirac-Fourier transform:

$$\phi(\vec{p}_1,\vec{p}_2)=(2\pi)^{-3}\int\psi(\vec{r}_1,\vec{r}_2)\times\exp[-i(\vec{p}_1\cdot\vec{r}_1+\vec{p}_2\cdot\vec{r}_2)]d\vec{r}_1d\vec{r}_2\ . \tag{11}$$

Thus the accumulated expertise about approximate position-space wave functions may help us choose a $\phi^0(\vec{p}_1,\vec{p}_2)$ with which to begin the iteration.

McWeeny and Coulson[8] used the momentum-space counterpart of the product of two 1s Slater orbitals as their starting function:

$$\phi^0=(p_1^2+a^2)^{-2}(p_2^2+a^2)^{-2}\ , \tag{12}$$

which is variationally optimal for $a=Z-\frac{5}{16}$ and corresponds to $E_0=-a^2$. They were unable to evaluate either ϕ^1 or $\lambda_{1/2}$. Since that time, progress has been made[10–12] with this ϕ^0 only by introduction of simplifying assumptions about the Hamiltonian. Schreiber[10] and Lombardi[12] have obtained ϕ^1 by approximating the Coulombic interelectronic repulsion operator by the leading monopole term of its Laplace expansion in position space. This is equivalent to the assumption that the wave function is purely radial: $\phi(\vec{p}_1,\vec{p}_2)=\phi(p_1,p_2)$ and $\psi(\vec{r}_1,\vec{r}_2)=\psi(r_1,r_2)$. Such an assumption leads to an integral equation different from Eq. (1). Monkhorst and Szalewicz[11] have applied the Svartholm iteration to the momentum-space Hartree-Fock equations[7] using the ϕ^0 of Eq. (12) as their starting function. They were able to obtain both the first and second iterated functions in a sequence that converges to the Hartree-Fock wave function instead of the exact wave function.

Henderson and Scherr[9] used the Fourier transform of a sum of products of spherical Gaussian orbitals as their starting function:

$$\phi^0=(1+P_{12})\sum_k C_k\exp(-\alpha_k p_1^2-\beta_k p_2^2)\ , \tag{13}$$

where P_{12} is a permutation operator that interchanges the coordinates of the two electrons. They were able to obtain ϕ^1 in terms of confluent hypergeometric functions, as well as numerical values of $\lambda_{1/2}$ using only one-dimensional quadratures. No simplifications of the Hamiltonian were necessary in their work.

The correlated ϕ^0 chosen in this paper is more accurate than that of Henderson and Scherr,[9] but it will be shown in Sec. IV that it is nonetheless possible to obtain ϕ^1 and $\lambda_{1/2}$ with an effort comparable to theirs. Our starting functions are chosen to be of the form

$$\phi^0(\vec{p}_1,\vec{p}_2)=(2\pi^3)^{-1/2}(1+P_{12})\sum_{k=1}^{N}d_k\phi_k(\vec{p}_1,\vec{p}_2)\ , \tag{14}$$

where

$$\phi_k(\vec{p}_1,\vec{p}_2)=\exp[-\Delta_k^{-1}\zeta_k(\eta_k p_1^2+\eta_k^{-1}p_2^2-2\theta_k\vec{p}_1\cdot\vec{p}_2)]\ , \tag{15}$$

in which

$$\Delta_k=4\zeta_k^2(1-\theta_k^2) \tag{16}$$

and $\zeta_k>0$, $\eta_k>0$, and $-1<\theta_k<+1$ to ensure square integrability. The ϕ^0 of Eq. (14) is the Dirac-Fourier transform of the following position-space wave function:

$$\psi^0(\vec{r}_1,\vec{r}_2)=(2\pi^3)^{-1/2}(1+P_{12})\sum_{k=1}^{N}C_k\psi_k(\vec{r}_1,\vec{r}_2)\ , \tag{17}$$

where

$$\psi_k(\vec{r}_1,\vec{r}_2)=\exp[-\zeta_k(\eta_k r_1^2+\eta_k^{-1}r_2^2+2\theta_k\vec{r}_1\cdot\vec{r}_2)] \tag{18}$$

and

$$C_k=d_k\Delta_k^{3/2}\ . \tag{19}$$

ψ^0 is a superposition of the correlated Gaussian geminals first advocated by Boys[15] and Singer.[16] An extensive bibliography on Gaussian geminals may be found in a recent paper.[17] Note that in the special case where all the $\theta_k=0$, our ϕ^0 reduces to that of Henderson and Scherr.[9]

IV. CALCULATIONS OF ϕ^1 AND $\lambda_{1/2}$

Inserting the ϕ^0 of Eq. (14) into Eq. (5) leads, after some algebra,[18] to the following ϕ^1:

$$\phi^1(\vec{p}_1,\vec{p}_2)=2^{1/2}(p_0^2+p_1^2+p_2^2)^{-1}(1+P_{12})\times\sum_{k=1}^{N}d_kg_k^{-1/2}\phi_k(\vec{p}_1,\vec{p}_2)\chi_k(\vec{p}_1,\vec{p}_2)\ , \tag{20}$$

where

$$\chi_k(\vec{p}_1,\vec{p}_2)=Z\eta_k^{-1/2}f[g_k\eta_k^{-1}(\eta_k\vec{p}_1-\theta_k\vec{p}_2)^2]+Z\eta_k^{1/2}f[g_k\eta_k(\theta_k\vec{p}_1-\eta_k^{-1}\vec{p}_2)^2]-(a_k+b_k)^{-1/2}f[g_k(a_k+b_k)^{-1}(a_k\vec{p}_1-b_k\vec{p}_2)^2]\ , \tag{21}$$

in which

$$g_k=\Delta_k^{-1}\zeta_k,\ a_k=\eta_k+\theta_k,\ b_k=\eta_k^{-1}+\theta_k \tag{22}$$

and

$$f(x)=F(\tfrac{1}{2},\tfrac{3}{2},x)=\int_0^1\exp(xu^2)du \tag{23}$$

TABLE I. Energies for several wave functions.

Atom	Wave function	$-E_0$		$-E_{1/2}$
He	HS1[a]	2.3010		2.5995 (2.5942)
	HS2[a]	2.5566		2.7815 (2.7755)
	HS3[a]	2.8511		2.8915 (2.8818)
	1 term[b]	2.5709		2.7730
	2 term[b]	2.8163		2.8760
	16 term[b]	2.90340		2.90369
	Exact[c]		2.90372	
H^-	16 term[b]	0.52759		0.52773
	Exact[c]		0.52775	
Li^+	16 term[b]	7.27941		7.27987
	Exact[c]		7.27991	

[a] Superposition of products of Gaussian orbitals, Eq. (13), from Ref. 9. The values in parentheses are the $E_{1/2}$ values calculated in this work using the linear and nonlinear parameters reported in Ref. 9 for these three wave functions.

[b] Superposition of correlated Gaussian geminals, Eq. (14). This work.

[c] K. Frankowski and C. Pekeris, Phys. Rev. **146**, 46 (1966).

is a confluent hypergeometric function.[19] Note that when all the $\theta_k=0$ the above ϕ^1 reduces to that given by Henderson and Scherr.[9] An algebraic formula for W_0 can be obtained[18] and the calculation of T_1 can be reduced[18] to a single one-dimensional quadrature. In the special case that all the $\theta_k=0$, the formulas for W_0 and T_1 reduce to those given by Henderson.[9(b)] However, the computational effort involved in numerical work with ϕ^1 and $\lambda_{1/2}$ is essentially the same whether or not the θ_k's are zero.

V. RESULTS

As a first step, the computations of Henderson and Scherr[9] were repeated[18] for each of the three ϕ^0's of the form (13) for which they tabulated linear and nonlinear parameters. Their "interpolated" nonlinear parameters were not used because no corresponding linear parameters were given. As can be seen from Table I, our calculated values of $E_{1/2}$ lie between 5 and 10 millihartrees above their $E_{1/2}$ values. These discrepancies can be attributed partly to the less-accurate quadrature used by them and partly to a small algebraic error on their part.[20]

Table I also reports E_0 and $E_{1/2}$ for 1-, 2-, and 16-term ϕ^0's of the form (14) for He. These ϕ^0's were variationally optimized[18] with respect to all the $(C_k,\zeta_k,\eta_k,\theta_k)$ parameters to minimize E_0. Originally we had planned to use the Fourier transform of the best 16-term wave function reported by Poshusta,[21] but we discovered that his parameters had not been properly optimized. Therefore we performed a careful optimization with repeated and alternating use of the conjugate direction method of Powell[22] and the quasi-Newton method of Fletcher.[23] Precautions to

TABLE II. 16-term wave functions for helium. In this and all subsequent tables the parameters serve to define ϕ^0 via Eqs. (14)–(16) and (19), ψ^0 via Eqs. (17) and (18), and ϕ^1 via Eqs. (15), (16), and (19)–(23). σ is a scale factor which ensures that ψ^0 satisfies the virial theorem, and the requisite factor of σ^3 has already been incorporated in the C_k. The notation $A(-n)$ means $A\times10^{-n}$ in this and all subsequent tables. $\sigma=1.000023157773$.

ζ_k/σ^2	η_k	θ_k	C_k
23.142	1.0000	−9.1316(−1)	−1.751783181217(−1)
17.297	37.974	2.2808(−3)	1.979673096630(−1)
15.142	8.8235	9.6287(−4)	5.076369840966(−1)
12.762	2.2128	1.2932(−1)	6.340978907610(−1)
4.5716	16.483	2.0879(−3)	2.007585069357(−1)
4.1201	1.1206	−7.1306(−1)	−2.055838800345(−1)
4.0864	5.2673	6.2901(−3)	6.901086242048(−1)
3.6280	1.7395	7.9803(−2)	9.965723414332(−1)
1.5280	9.4714	4.4024(−4)	1.117496479693(−1)
1.4694	3.8294	9.9758(−3)	5.497096714246(−1)
1.3279	1.5803	5.2959(−2)	8.968829761697(−1)
1.1818	1.1394	−5.7116(−1)	−9.263129489482(−2)
5.9431(−1)	3.6160	−2.7228(−3)	1.676512602867(−1)
5.8169(−1)	1.5507	5.1985(−2)	3.992914766678(−1)
2.9556(−1)	1.8840	3.0430(−1)	−2.949136827473(−2)
2.7406(−1)	1.7537	1.3495(−1)	7.834309794628(−2)

TABLE III. 16-term wave functions for H^-. See the heading to Table II for further explanation. $\sigma = 1.000\,017\,094\,531$.

ζ_k/σ^2	η_k	θ_k	C_k
2.8798	1.0635	−8.5174(−1)	2.677 383 327 376(−2)
2.5834	9.7931	2.4075(−2)	−3.320 430 356 170(−2)
2.4141	51.040	−7.6145(−3)	−1.231 589 642 926(−2)
9.6528(−1)	2.1210	1.8354(−1)	−5.661 629 089 259(−2)
7.3289(−1)	8.0306	1.2070(−2)	−3.813 148 584 167(−2)
6.1039(−1)	30.728	1.4973(−3)	−9.051 876 416 704(−3)
5.4738(−1)	1.2002	−6.3871(−1)	2.640 970 814 876(−2)
2.9736(−1)	1.7140	1.3637(−1)	−5.898 343 498 764(−2)
2.7521(−1)	4.8645	2.1178(−2)	−4.134 837 501 070(−2)
2.2471(−1)	14.861	−2.1259(−3)	−9.869 661 031 178(−3)
1.5182(−1)	1.2909	−4.5030(−1)	1.181 921 355 115(−2)
1.1325(−1)	1.5640	7.5911(−2)	−3.059 306 620 704(−2)
1.0764(−1)	3.6857	2.3514(−2)	−2.118 219 070 958(−2)
9.3527(−2)	8.6037	−9.7138(−4)	−6.854 177 628 108(−3)
4.4447(−2)	1.7871	1.1862(−1)	−3.666 679 948 966(−3)
4.2778(−2)	4.2127	−6.1919(−3)	−3.963 989 030 906(−3)

avoid numerical instabilities arising from approximate linear dependence were taken.[18] We were able to obtain a variational energy $E_0 = -2.903\,4048$ which is about a millihartree lower than the variational energy $E_0 = -2.902\,446$ obtained by Poshusta.[21] Ironically enough, Poshusta[21] had presented his own parameters as a reoptimization of the parameters of Longstaff and Singer,[24] who had obtained a variational energy $E_0 = -2.902\,33$. This experience with the 16-term wave function should serve as a forceful demonstration of the fact that multidimensional global minimization is a very difficult process and that none of the numerical algorithms currently available[25] can guarantee convergence to a global minimum. We do *not* make any claim that our parameters correspond to a global minimum. Since this optimization is a difficult process, we have considered it worthwhile to report the parameters for the 16-term ϕ^0 for He in Table II. Note that a scale factor σ that ensures that ψ^0 satisfies the virial theorem has already been incorporated in the C_k but not in the ζ_k. σ is given separately for inclusion in the ζ_k to avoid having to tabulate the latter to 13 significant figures. Similar 16-term wave functions for H^- and Li^+ are reported in Tables III and IV, respectively. These parameters serve to define ϕ^0 via Eqs. (14)—(16) and (19), ψ^0 via Eqs. (17) and (18), and ϕ^1 via Eqs. (15), (16), and (19)—(23).

Returning to Table I, it can be seen that the more accurate the E_0, the greater the relative improvement $(E_0 - E_{\text{exact}})/(E_{1/2} - E_{\text{exact}})$ obtained by a half-iteration. Note further that the ϕ^1 functions defined by Eq. (20) and the parameters in Tables II—IV are even more accurate than is indicated by the $E_{1/2}$ values reported in Table I. This is so because the variational energies E_1 corresponding to ϕ^1 are necessarily lower than $E_{1/2}$. It is also important to note that *no* optimization of any of the parameters to minimize $E_{1/2}$ was carried out, unlike in the work

TABLE IV. 16-term wave functions for Li^+. See the heading to Table II for further explanation. $\sigma = 0.999\,989\,837\,049\,0$.

ζ_k/σ^2	η_k	θ_k	C_k
52.705	42.408	1.0260(−3)	−6.588 257 693 390(−1)
49.061	9.9546	7.7226(−4)	−1.744 788 642 473
41.813	1.0397	−8.9049(−1)	5.454 566 337 362(−1)
40.690	2.2667	7.4682(−2)	−2.454 997 368 340
14.035	17.617	2.3727(−3)	−7.264 727 500 107(−1)
13.511	5.7121	2.9386(−3)	−2.428 456 590 900
11.488	1.7564	6.7759(−2)	−3.702 152 587 673
7.6137	1.1162	−7.2536(−1)	4.536 483 235 045(−1)
5.4079	3.9475	1.0815(−3)	−2.150 403 006 886
4.6347	9.7742	1.7035(−3)	−4.609 152 227 833(−1)
4.1646	1.5897	4.2559(−2)	−3.959 544 794 961
2.3786	3.7194	9.0124(−3)	−1.133 930 352 454
1.8660	1.3660	−1.6997(−1)	2.072 147 338 137
1.7953	1.4680	−5.1822(−2)	−4.180 091 584 050
1.0866	3.2998	−4.8325(−4)	−1.836 948 144 148(−1)
7.8096(−1)	1.5028	3.9765(−2)	−3.277 403 114 080(−1)

of Henderson and Scherr.[9] Finally, it is interesting to note that while the 16-term ϕ^0 decreases in accuracy as Z is increased ($E_0 - E_{\text{exact}} \simeq 0.16$, 0.32, and 0.50 millihartree, respectively, for H^-, He, and Li^+), the 16-term ϕ^1 performs somewhat more uniformly with Z ($E_{1/2} - E_{\text{exact}} \simeq 0.02$, 0.03, and 0.04 millihartree, respectively, for H^-, He, and Li^+).

VI. CONCLUDING REMARKS

It has been shown that the use of correlated Gaussian geminals of the form (14) presents no computational difficulties greater than those encountered with the sum of products of Gaussian orbitals (13) when one attempts to solve the two-electron momentum-space integral Schrodinger equation (1) by the Svartholm iteration (5). The 16-term half-iterated energy $E_{1/2}$ obtained for He is by far the most accurate value[26] ever obtained directly in momentum space, and the 16-term ϕ^1 is likely the most accurate momentum-space wave function for He ever constructed by any technique. The $E_{1/2}$ and ϕ^1 reported for H^- and Li^+ are of similar accuracy and represent the first such calculations done directly in momentum space.

Extension of this work to two-electron multinuclei systems such as H_2 and $H_3{}^+$ in the Born-Oppenheimer approximation is straightforward. The prospects for a fully nonadiabatic treatment of three-particle systems such as the positronium anion $e^-e^+e^-$ also seem good. Both these possibilities are under active study in our laboratory.

ACKNOWLEDGMENTS

The continuing support of the Natural Sciences and Engineering Research Council of Canada (NSERCC) has made this work possible. One of the authors (P.E.R.) thanks NSERCC for a postgraduate scholarship.

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[20] The statement below Eq. (4.12) of Ref. 9(a) seems to be incorrect in that their $\bar{\lambda}$ is *not* independent of p_0. This mistake can be traced to Appendix C of Ref. 9(b), in which it is claimed that the p_0 dependence of certain $K_{m,n}$ integrals can be factored out completely.

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[25] Reviews of optimization methods include M. J. D. Powell, SIAM Rev. **12**, 79 (1970); ACM Trans. Math. Software **1**, 97 (1975).

[26] The previous best energy for He obtained directly in momentum space was −2.8933, as reported by Lombardi[12(b)]