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Compact and accurate integral-transform wave functions. III. Radially correlated wave functions for the ground state of the lithium atom[*]

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Radially correlated wave functions for the ground state of the lithium atom are constructed using a variant of the integral-transform or generator-coordinate method. The best of these is estimated to be close to the radial limit.

I. INTRODUCTION

We have recently demonstrated[1,2] that a suitable variant of the integral-transform or generator-coordinate method can be used to construct compact and accurate wave functions for few-electron atoms. A set of such wave functions has been presented for the ground[1] and four lowest excited[2] states of the heliumlike ions.

In this paper we apply these methods to a three-electron system—the ground state of the lithium atom. For the sake of simplicity we restrict ourselves to a superposition of configurations ansatz in which the configurations are built up from spherically symmetric orbitals. We refer to such wave functions as purely radially correlated (PRC) wave functions. The best such wave function is the radial limit wave function. The radial limit has been attained for the helium atom by Schwartz[3] and Bunge.[4] The best available PRC wave function for the ground state of the lithium atom is that of Hameed *et al.*[5] Better ones are given in this paper. It is argued that our best wave function is close to the radial limit.

II. THEORETICAL DETAILS

We employ the integral-transform method as described in an earlier paper[1] (hereafter referred to as I). Our variational ansatz for the $^2S_{1/2}$ ground state of the lithium atom is

$$\psi(x_1,x_2,x_3)=(4\pi)^{-3/2}\hat{A}_3\sum_{k=1}^{N}\Phi_k(c_kS_1+d_kS_2)\ , \qquad (1)$$

where $x_i=(\vec{r}_i,\zeta_i)$ is a combined space-spin coordinate for electron i. In the above $\hat{A}_3$ is the three-particle antisymmetrizer,

$$\hat{A}_3=6^{-1/2}[e-(12)-(13)-(23)+(123)+(132)]\ , \qquad (2)$$

and Φ_k is a generator function given by

$$\Phi_k(r_1,r_2,r_3)=\exp(-\alpha_k r_1-\beta_k r_2-\gamma_k r_3)\ . \qquad (3)$$

S_1 and S_2 are spin functions which together span the spin space in which $S=\frac{1}{2}$ and $S_z=\frac{1}{2}$. They can be chosen to be given by[6]

$$\begin{aligned}S_1&=\alpha(\zeta_1)\beta(\zeta_2)\alpha(\zeta_3)-\beta(\zeta_1)\alpha(\zeta_2)\alpha(\zeta_3)\\&=\alpha\beta\alpha-\beta\alpha\alpha\ , \end{aligned}\qquad (4)$$

$$S_2=2\alpha\alpha\beta-\beta\alpha\alpha-\alpha\beta\alpha\ , \qquad (5)$$

where α and β are the usual one-electron spin functions. The linear coefficients $\{c_k\}$ and $\{d_k\}$ are to be found by solving the secular equations.

If both the $\{c_k\}$ and the $\{d_k\}$ are thus determined, then we have included both spin functions and we call the resultant wave function a W^2-type wave function. If we set all the d_k's equal to zero and determine the $\{c_k\}$ variationally, then we have included only one spin function and we call the resultant wave function a W^1-type wave function. The nonlinear parameters are chosen to be the lattice points of a pseudorandom number quadrature formula (scheme P in the notation of I). Specifically the nonlinear parameters are generated by the following equations:

$$\alpha_k=\eta[(A_2-A_1)\langle k(k+1)\sqrt{2}/2\rangle+A_1]\ , \qquad (6a)$$

$$\beta_k=\eta[(B_2-B_1)\langle k(k+1)\sqrt{3}/2\rangle+B_1]\ , \qquad (6b)$$

$$\gamma_k=\eta[(G_2-G_1)\langle k(k+1)\sqrt{5}/2\rangle+G_1]\ , \qquad (6c)$$

for $k=1,2,\ldots,N$. In the above $\langle x\rangle$ is defined to be the fractional part of x. The parameters A_1, A_2, B_1, B_2, G_1, and G_2 define a parallelotope in α-β-γ space and are chosen variationally to minimize the energy. Since we are dealing with bound states, we impose the restrictions that

$$\min_k \alpha_k>0\ , \qquad (7a)$$

$$\min_k \beta_k>0\ , \qquad (7b)$$

$$\min_k \gamma_k>0\ . \qquad (7c)$$

In principle $\eta=1$ but in practice it is chosen to ensure that our wave functions satisfy the virial theorem (see I for a fuller discussion).

The ansatz of Eq. (1) has, to our knowledge, never been used previously. The ansatz of Empedocles[7] is the most similar to Eq. (1) of all those that we have found in the literature. Note that Empedocles used the integral-transform method with a number-theoretic quadrature formula. The numerical methods we use for optimizing the parallelotope parameters and solving the secular equations are those described in I.

III. RESULTS AND DISCUSSION

W^1-type wave functions with $N=5$, 10, and 25 terms were constructed for the ground state of the lithium atom. The parallelotope parameters and the energies are given in Table I. Next we built W^2-type wave functions with $N=5$, 10, and 25 terms. Here we used the parallelotope parameters from the corresponding W^1-type wave function with the same N. However, we reoptimized the linear coefficients $\{c_k\}$ and $\{d_k\}$ as well as η for the W^2-type functions. η values and energies are listed in Table I. For each of these wave functions we also computed the Fermi contact parameter[8] defined by

$$f = 4\pi \left\langle \sum_{i=1}^{3} \delta(\vec{r}_i)\hat{\sigma}_{z_i} \right\rangle , \tag{8}$$

where $\hat{\sigma}_{z_i}$ is a Pauli spin operator and the angular brackets denote an expectation value. f is clearly proportional to the spin density at the nucleus and governs the hyperfine structure of atomic S states.[9,10] The f values are also listed in Table I. All quantities cited in this paper are in atomic units.

A listing of PRC wave functions for Li available in the literature has been given by Empedocles.[7] These and a few others are listed in Table II. A glance at this table shows that four of our functions, the $N=10$ W^1, the $N=10$ W^2, the $N=25$ W^1, and the $N=25$ W^2 functions, give lower energies than the best of the previously available functions. The best energy obtained by us is the $N=25$ W^2 function energy of $-7.448\,312\,5$. To our knowledge, this is the best energy ever obtained for the ground state of the lithium atom from a PRC wave function. From a study of the convergence patterns in Table I we estimate that the radial limit energy is no lower than -7.4486. The above estimate is supported by the facts that an e_1 extrapolation[19] of the three W^1 energies yields $-7.448\,583$, and a similar extrapolation of the three W^2 energies yields $-7.448\,460$. We therefore feel that the $N=25$ W^2 function is close to the radial limit wave function.

TABLE I. Parallelotope parameters, energies and Fermi contact parameters for Li. All quantities are in atomic units.

N	5	10	25
A_1	1.5714	2.3051	1.2276
A_2	3.0758	4.2294	4.0671
B_1	3.1468	2.4344	2.9534
B_2	3.3255	3.7179	5.9102
G_1	0.6504	0.6451	0.3296
G_2	0.7311	0.7049	0.8887
$\eta(W^1)$	1.000 664 88	0.999 994 44	0.999 986 04
$-E(W^1)$	7.446 337 8	7.447 734 0	7.448 262 0
$f(W^1)$	1.618	2.222	2.825
$\eta(W^2)$	0.999 817 38	1.000 170 23	1.000 003 50
$-E(W^2)$	7.446 557 7	$7.447\,930\,2_5$	7.448 312 5
$f(W^2)$	2.796	2.700	2.791

Recall that the total correlation energy is defined[20] to be the absolute difference between the exact and the restricted Hartree-Fock energy. Similarly the radial correlation energy is defined to be the absolute difference between the radial limit and restricted Hartree-Fock energy. The exact[21] nonrelativistic energy of the lithium atom is $-7.478\,069$ and the restricted Hartree-Fock energy[11] is $-7.432\,727$. Thus the total correlation energy is 0.045 342. The correlation energy recovered by our best PRC function is 0.015 585 5 or 34.4% of the total correlation energy. From our estimate of the radial limit energy we estimate the radial correlation energy to be no more than 0.015 873 or 35.0% of the total correlation energy.

Clementi *et al.*[22] proposed a partitioning of the radial correlation energy into the radial promotional correlation energy and the radial nonpromotional correlation energy. Their definition is inseparably linked to the configuration interaction (CI) method. They define the radial nonpromotional correlation energy to be that part of the radial

TABLE II. Comparison of energies of various PRC wave functions for the ground state of the lithium atom.

Source	Reference	$-E$ (a.u.)
Froese-Fischer	11	7.432 727
$N=5$ (W^1)	a	7.446 337 8
$N=5$ (W^2)	a	7.446 557 7
Weiss	12	7.447 20
Brown-Fontana	13	7.447 22
Heikes-Gallup	14	7.447 33
Hardcastle-Keown	15	7.447 485
Lunell	16	7.447 536
Empedocles	7	7.447 54
Goddard	17	7.447 56
Kaldor-Harris	18	7.447 565
Goddard[b]	5	7.447 703 4
Kaldor-Harris[b]	5	7.447 707
Musher *et al.*	5	7.447 707 6
$N=10$ (W^1)	a	7.447 734 0
$N=10$ (W^2)	a	$7.447\,930\,2_5$
$N=25$ (W^1)	a	7.448 262 0
$N=25$ (W^2)	a	7.448 312 5

[a] This work.

[b] Recomputed by Hameed *et al.* (Ref. 5).

correlation energy that can be obtained by a CI expansion that includes only the restricted Hartree-Fock (RHF) determinant and determinants obtained from it by substitution of one or more RHF orbitals by spherically symmetric orbitals with the same nodal structure as the orbitals being replaced. The remainder of the radial correlation energy is called the radial promotional correlation energy. As Clementi *et al.* point out in a footnote,[22] this partitioning is meaningless because the configurations yielding the nonpromotional part of the radial correlation energy can always be expanded in an orthogonal set. We wish to point out that the reverse is also possible. All our orbitals have the same nodal structure and hence all the radial correlation energy that we have obtained is *nonpromotional.* Clearly the radial limit is attainable with our basis. This shows that it is also possible for the radial correlation energy to be considered totally *nonpromotional.* Although the above discussion shows that this sort of partitioning is ill-defined from the point of view of analysis of the correlation energy, it could, of course, be useful in an operational sense; that is useful in building wave functions by *conventional* CI techniques.

An enormous body of literature has grown up around the calculation of the Fermi contact parameter. References to this literature may be found in certain articles.[10,16,23–25] A detailed analysis of our f values is beyond the scope of this work. We restrict ourselves to two brief comments.

Our first comment concerns the quality of our f values. The RHF value[11] of f is 2.093 and the experimental value[27] is 2.9062. Our $N=25$ functions yield f values of 2.825 and 2.791 for W^1 and W^2 types, respectively. An examination of the comparative studies of Lunell,[16] Larsson and Smith,[24] and some more recent f values[11,15,17,18] shows that our values are reasonably good in the sense that many other wave functions give poorer values. The Hylleraas-type function of Larsson[28] and the associated best-overlap and first natural determinants[24] and perhaps the open-shell three-determinant function of Lunell[16] are the only functions that give markedly better values of f than our $N=25$ functions. This supports Ishida's claim[26] that a wave function with adequate radial correlation should yield a decent f value.

Our second comment concerns the basis set dependence of our f values. Table I shows that when N is small (5 or 10) the inclusion of both spin functions is essential in obtaining a decent f value. Larsson[28] found similar phenomena for Hylleraas-type functions. For $N=25$ the f value is virtually the same for both W^1- and W^2-type functions. A good discussion of the use of one as opposed to two spin functions has been given by Slater.[6] Shanks e_1 extrapolation[19] of the f values given by the W^2-type functions yields 2.747. This fact and an examination of the convergence patterns in Table I lead us to estimate the radial limit f value to be 2.80 ± 0.05.

IV. SUMMARY

Our 25 term W^2-type function gives an energy of $-7.448\,312\,5$ which is the best energy ever obtained from a PRC wave function for the ground state of the lithium atom. It also gives a decent value (2.791) of the Fermi contact parameter. We estimate that the radial limit energy is no lower than -7.4486 and that the radial limit f is 2.80 ± 0.05.

These results are rather encouraging. We feel it would be worthwhile to construct a Hylleraas-type function from a basis set obtained as the tensor product of our basis set and some explicit powers of interelectronic coordinates. Hopefully the parallelotope parameters need not be reoptimized.

For other many-electron systems explicitly correlated integral-transform wave functions are not feasible because of the tremendous amounts of computer time that would be required. A retreat to superposition of configurations and even Hartree-Fock functions will be necessary. In this connection the ideas of Somorjai and Grimaldi[29] and Kukulin[30] may prove useful. The "even-tempered" scheme of Raffenetti and Ruedenberg[31] should also be studied for possible adaptation in an integral-transform context. We feel that such studies would be worthwhile.

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