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Perturbation theory in $1/Z$ for atoms: First-order pair functions in an l-separated Hylleraas basis set

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For the $1/Z$ perturbation theory of atoms, a partial-wave method is presented for determining first-order pair wave functions. It rests on the fact that the Hylleraas variational principle decouples for the individual partial waves ($l=0,1,2,\dots$) and that all partial waves for $l \gg 1$ are easily representable (Schwartz, 1962). The lth partial wave is approximated in basis functions obtained by projecting the well-known Hylleraas functions (containing the powers of r_{12}) onto $P_l(\cos\theta_{12})$. Results for the $1s^2$ ground state show rapid convergence. The variational value for the (total) second-order $1s^2$ energy, which would be provided by 45 Hylleraas functions, is achieved with 10, 12, 9, 8, 5, and 5 basis functions for $l=0$, 1, 2, 3, 4, and 5, respectively. For any $l \geq 6$, one function is sufficient. Also good convergence is found for three-electron integrals (parts of the second-order lithium energy).

I. INTRODUCTION

This paper deals with the determination of first-order atomic eigenfunctions within the $1/Z$ perturbation theory.[1–3] Using the Hylleraas variational principle[1,2] and taking up suggestions of Schwartz,[4] we will explore the separate variation of the individual "partial waves" of a first-order pair wave function.

Perturbation theory for atoms can be based either on the bare-nucleus Hamiltonian (the $1/Z$ ansatz) or the Hartree-Fock Hamiltonian.[5,6] These two methods differ in an important aspect. This is the strict transferability of components (of eigenfunctions and energies) between small and large atoms, which is afforded only by the $1/Z$ method: The first-order eigenfunction $\Psi^{(1)}(n)$ of an n-electron atom can be composed exactly from a finite number of hydrogenic orbitals and helium pair functions $\Psi^{(1)}(2)$ of different electronic states (Sinanoglu,[7] Chisholm and Dalgarno[8]). Similar exact (de)compositions (or "partitions"), which likewise rest exclusively on components arising from physical states, do also exist for the second- and third-order energies $E^{(2)}(n)$ and $E^{(3)}(n)$ (Ref. 9). On the other hand, there are the well-known, more technically oriented, decompositions of $E^{(2)}(n)$ and $E^{(3)}(n)$ which have frequently been used in calculations for the lithium[8,10,11] and larger atoms up to neon.[12] The components of $E^{(2)}(n)$ then are two-electron energies $E^{(2)}(2)$ and "three-electron integrals"; those of $E^{(3)}(n)$ are two-electron energies $E^{(3)}(2)$ and (third-order) "three- and four-electron integrals." *All of these components* can be expressed in terms of the first-order pair functions $\Psi^{(1)}(2)$. The practical task consists in approximating the $\Psi^{(1)}(2)$ with sufficient accuracy.

Consider now the concrete case of the three-electron ground state [configuration $(1s)^2 2s$]. Let $E^{(2)}(3)=E^{(2)}_{\mathrm{Li}}$ be its second-order energy. (Third-order energies will not be treated in this paper.) The relevant first-order pair functions $\Psi^{(1)}(2)$ then belong to the $(1s)^2$ ground state and the $1s2s$ singlet and triplet states.[8]

The appropriate and mostly applied method of approximating such pair functions is the Hylleraas variational principle.[1,2] Each (entire) pair function $\Psi^{(1)}(2)$ [together with its pair energy $E^{(2)}(2)$] is then determined in one common variation. On the other hand, Schwartz[4(a)] has pointed out (i) the Hylleraas variational principle for $\Psi^{(1)}(2)$ decouples into separate principles for the individual partial waves $\Psi^{(1)}_l(2)$ ($l=0,1,2,\dots,$), so, one large variational problem will be reduced to a series of small ones. (ii) The $\Psi^{(1)}_l$ for $l \gg 1$ are of a simple form (compare Sec. II of this paper). Furthermore, as observed by Knight,[12(a)] (iii) the three-electron integrals of $E^{(2)}_{\mathrm{Li}}$ depend only on the ($l=0$) partial wave of their respective pair function. Therefore, a more compact calculation of these integrals will be possible than if one used a representation for the entire pair function.

In order to implement a method, as outlined by (i)—(iii), suitable basis functions are needed which can compactly represent the individual partial waves. Schwartz[4] has pointed out that products of one-particle functions $u_m(r_1)u_n(r_2)$ (the ansatz of configuration interaction) must lead to poor convergence for all of the higher l. Somerville and Stewart,[13] who used products of hydrogenic orbitals, have numerically confirmed this. The basis-function problem has been solved to a certain extent by Byron and Joachain[14] who showed powers of $r_<$ and $r_>$ to yield much better convergence than powers of r_1 and r_2.

In this paper we propose to approximate the particular partial wave $\Psi^{(1)}_l$ in those basis functions which are obtained by projecting, onto the Legendre polynomial $P_l(\cos\theta_{12})$, the well-known Hylleraas functions [the powers of $u=r_{12}$, $s=r_1+r_2$, $t=r_2-r_1$, multiplied by the zeroth-order pair function $\Psi^{(0)}(r_1,r_2)$]. This projection provides sets (of radial functions) which are different for different l. Through the leading Hylleraas function $r_{12}\cdot\Psi^{(0)}$, these sets accord exactly with the known behavior[4] of the asymptotic $\Psi_l^{(1)}$ ($l \gg 1$). We will see (for the two-electron ground state) that these "l-separated Hylleraas functions" have good convergence properties also for the low l.

The theory given in Sec. II of the paper as well as the calculations of Sec. III will deal with the *ground-state* pair function. Our method can be transferred to excited-state pair functions, first to the singlet and triplet 1s2s states, then also to P states.

II. METHOD

We consider the $1/Z$ expansion[1,2(a)] of the ground state of the two-electron atom (in the fixed-nucleus and nonrelativistic approximation):

$$\Psi_{\mathrm{He}}=\Psi_{\mathrm{He}}^{(0)}+Z^{-1}\Psi_{\mathrm{He}}^{(1)}+\cdots\,,\quad \Psi_{\mathrm{He}}^{(0)}=\frac{1}{\pi}e^{-(r_1+r_2)}\,, \tag{1}$$

$$E_{\mathrm{He}}=-1+\tfrac{5}{8}Z^{-1}+E_{\mathrm{He}}^{(2)}Z^{-2}+\cdots\,. \tag{2}$$

(Unit of length $=1/Z$ bohr; unit of energy $=Z^2$ hartree.)

We assume the first-order eigenfunction $\Psi_{\mathrm{He}}^{(1)}$ to be expanded in partial waves (θ_{12} is the angle between the vectors $\vec{r}_1$ and $\vec{r}_2$):

$$\Psi_{\mathrm{He}}^{(1)}=\sum_{l=0}^{\infty}\Psi_l^{(1)}\ \text{ with } \Psi_l^{(1)}=R_l(r_1,r_2)P_l(\cos\theta_{12})\,, \tag{3}$$

$$E^{(2)}=\sum_{l=0}^{\infty}E_l^{(2)}\ \text{ with } E_l^{(2)}=\left\langle\Psi_{\mathrm{He}}^{(0)}\left|\frac{1}{r_{12}}-\frac{5}{8}\right|\Psi_l^{(1)}\right\rangle\,. \tag{4}$$

(i) Then the Hylleraas variational principle decouples into separate principles for each partial wave[4]:

$$E_l^{(2)}\le\widetilde{E}_l^{(2)}=2\left\langle\Psi_{\mathrm{He}}^{(0)}\left|\frac{1}{r_{12}}-\frac{5}{8}\right|\widetilde{\Psi}_l^{(1)}\right\rangle+\langle\widetilde{\Psi}_l^{(1)}\,|\,H^{(0)}+1\,|\,\widetilde{\Psi}_l^{(1)}\rangle\,, \tag{5}$$

where $\widetilde{\Psi}_l^{(1)}$ is some approximation to $\Psi_l^{(1)}$ and

$$H^{(0)}=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-1/r_1-1/r_2\,.$$

(ii) The asymptotic behavior of $\Psi_l^{(1)}$ for large l is[4,15]

$$\Psi_l^{(1)}=\tfrac{1}{2}r_{12}\,|_l\,\Psi_{\mathrm{He}}^{(0)}+\cdots\quad(l\gg 1) \tag{6}$$

where $r_{12}\,|_l$ is the projection of the coordinate r_{12} onto $P_l(\cos\theta_{12})$:

$$r_{12}\,|_l=\left[\frac{1}{2l+3}\frac{r_<^{l+2}}{r_>^{l+1}}-\frac{1}{2l-1}\frac{r_<^{l}}{r_>^{l-1}}\right]P_l(\cos\theta_{12})\quad(\text{valid for } l=0,1,2,\ldots)\,. \tag{7}$$

(iii) Consider the second-order energy $E_{\mathrm{Li}}^{(2)}$ for the ground state of the lithiumlike atom[8]:

$$E_{\mathrm{Li}}^{(2)}=E_{\mathrm{He}}^{(2)}+\tfrac{1}{2}E_{\mathrm{He}'}^{(2)}+\tfrac{3}{2}E_{\mathrm{He}''}^{(2)}+4M_1-2M_2-M_3-M_4+\tfrac{1}{2}M_5+\tfrac{3}{2}M_6\,, \tag{8}$$

where the three heliumlike energies belong to the ground and the singlet and triplet 1s2s states, respectively, and $M_1,\ldots,M_6$ are "three-electron integrals." From the latter, M_1, M_2, and M_3 are expressed in the first-order *ground* state $\Psi_{\mathrm{He}}^{(1)}$ from Eq. (1). Using the partial-wave expansion (3), M_1 to M_3 are seen[12(a),16] to depend only on $\Psi_{l=0}^{(1)}$.

Our procedure for evaluating M_1 to M_3 will be the following. Their definition[8] is

$$M_1=\left\langle\Psi_{\mathrm{He}}^{(1)}(1,2)b(3)\left|\frac{1}{r_{13}}\right|a(1)a(2)b(3)\right\rangle\,, \tag{9a}$$

$$M_2=\left\langle\Psi_{\mathrm{He}}^{(1)}(1,2)b(3)\left|\frac{1}{r_{13}}\right|b(1)a(2)a(3)\right\rangle\,, \tag{9b}$$

$$M_3=\left\langle\Psi_{\mathrm{He}}^{(1)}(1,2)b(3)\left|\frac{1}{r_{13}}\right|a(1)b(2)a(3)\right\rangle\,, \tag{9c}$$

where a and b are the 1s and 2s orbitals of hydrogen. In Eqs. (9a)–(9c) $\Psi_{\mathrm{He}}^{(1)}$ is assumed to fulfill the normalization condition

$$\langle\Psi_{\mathrm{He}}^{(1)}\,|\,\Psi_{\mathrm{He}}^{(0)}\rangle=0\,. \tag{10}$$

One integration in each of (9a)–(9c) is carried out to give, for example,

$$M_1=\langle\Psi_{\mathrm{He}}^{(1)}(1,2)\,|\,\omega_1(1,2)\rangle\,, \tag{11}$$

where

$$\omega_1(1,2)=\frac{1}{r_1}\left[1-(1+\tfrac{3}{4}r_1+\tfrac{1}{4}r_1^2+\tfrac{1}{8}r_1^3)e^{-r_1}\right]a(r_1)a(r_2) \tag{12}$$

is independent of the angle θ_{12}. So, $\Psi_{\mathrm{He}}^{(1)}$ in Eq. (11) can be replaced by $\Psi_{l=0}^{(1)}$. Our numerical evaluation will start from this expression for M_1 and similar ones for M_2 and M_3. The auxiliary functions (12), etc., have been given by Cohen.[17]

For carrying out the separate variations (5) we express the radial function $R_l(r_1,r_2)$ as a linear combination of basis functions to be constructed in the following way. The well-known Hylleraas basis functions[1,2,4(a),12(a)] used for representing the total $\Psi_{\mathrm{He}}^{(1)}$ are the powers of $r_{12}=u$, $r_1+r_2=s$, and $r_2-r_1=t$ multiplied by the zeroth-order wave function:

$$F_{pqr}=u^p s^q t^r\Psi_{\mathrm{He}}^{(0)},\quad p,q\in\{0,1,2,\ldots\},\quad r\in\{0,2,4,\ldots\}\,. \tag{13}$$

By expanding each of these F_{pqr} in partial waves similar to (3), a specific set of radial functions is obtained for each $l=0,1,2,\ldots$; the first three Hylleraas functions u, s, and u^2, for example, have the following partial-wave projections:

$$u\Psi_{\mathrm{He}}^{(0)}\,|_l=r_{12}\,|_l\Psi_{\mathrm{He}}^{(0)} \tag{14}$$

with $r_{12}\,|_l$ from Eq. (7),

$$s\Psi_{\mathrm{He}}^{(0)}\,|_l=s\Psi_{\mathrm{He}}^{(0)}\delta_{l,0}\,, \tag{15}$$

$$u^2\Psi_{\mathrm{He}}^{(0)}\,|_l=[(r_1^2+r_2^2)\delta_{l,0}-2r_1r_2P_1(\cos\theta_{12})\delta_{l,1}]\Psi_{\mathrm{He}}^{(0)} \;. \tag{16}$$

Table I shows how the first 12 Hylleraas functions contribute to the various partial waves. The number of nonzero projections reduces with increasing l. In some instances there is a linear dependence between projections. Thus for a particular l, the number of basis functions which derive from a given finite set of Hylleraas functions reduces further. Resulting from the two categories of Hylleraas functions (those containing even and odd powers of u, respectively), there are two types of radial functions differing in their behavior at $r_1=r_2$; infinitely differentiable functions like (15) and (16) and functions still having continuous second derivatives like (14). We note that the similar but more elementary functions $r_<^m r_>^n \Psi_{\mathrm{He}}^{(0)}$ which were used by Byron *et al.*,[14] for general m and n, are merely continuous and, so, individually are less suitable to represent a $\Psi_l^{(1)}$ wave function.

The simplest one among the so defined basis sets is, for each l, just the single function (14). Thus

$$\Psi_l^{(1)}=c_l r_{12}\,|_l\Psi_{\mathrm{He}}^{(0)} \tag{17}$$

with c_l to be optimized. This approximation has been discussed by Schwartz.[4] Because of the asymptotic behavior (6), (17) becomes exact (together with $c_l\to\frac{1}{2}$) for large l. Owing to the variable parameter c_l, the range of validity of (17) extends down to smaller l values than that of Eq. (6) itself. (Numerical values will be given in Sec. III.) We will call (17) the "one-function approximation."

TABLE I. l projection of the Hylleraas functions. The projections marked by × form the basis set for the specific l.

Hylleraas function[a]	u	s	u^2	us	s^2	t^2	u^3	u^2s	us^2	ut^2	s^3	st^2	[c]
$l=0$	×	×	×	×	×	[b]	×	×	×	×	×	[b]	[c]
$l=1$	×		×	×			×	×	×	×			[c]
$l\geq 2$	×			×			×		×	×			[c]

[a] Compare Eq. (13).

[b] This projection is linearly dependent of the preceding ones.

[c] The functions of the fourth degree $u^4,u^3s,\ldots,t^4$ provide 6,5,4,3 linearly independent projections for $l=0,1,2,\geq 3$, respectively.

III. CALCULATIONS

The evaluation of the functional (5) for the basis functions (14)—(16), etc., is straightforward and leads to sums of James-Coolidge integrals[18,10(a)]

$$V_{m,n}(\alpha,\beta)=\int\int_{0<x<y<\infty} x^m y^n e^{-\alpha x-\beta y}dx\,dy$$

$$m=0,1,2,\ldots;\quad m+n=-1,0,1,2,\ldots\;. \tag{18}$$

The numerical values of the $V_{m,n}$ are computed conveniently via the recursion formulas of Refs. 18(a) and 10(a). For reaching high values of m ($m\geq 25$ while $m+n\leq 10$) we used double-precision arithmetic (on a Control Data Corporation Cyber-170 computer). The final step in the evaluation of $E_l^{(2)}$ is the solution of the system of linear equations corresponding to (5).

TABLE II. Partial-wave contributions $E_l^{(2)}$ to the second-order energy of the two-electron atom. Variational results for three basis sets of different size. All entries in 10^{-6} a.u.

l	A[a]	B[b]	C[c]	Byron *et al.*[d]
0	−124 694	−125 331.2	−125 333.2	−125 334
1	−24 782	−26 471.9	−26 489.9	−26 495
2	−3833	−3895.6	−3903.1	−3906
3	−1070.2	−1076.8	−1077.5	−1077
4	−404.9	−405.3	−406.0	−405
5	−184.7	−184.8	−185.0	−183
6	−95.7			−94
7	−54.4			−53
8	−33.1			−32
9	−21.3			−21
10	−14.3			−14
$l\geq 11$	−43.8[e]			−42
Sum $E^{(2)}$[f]	−155 231	−157 628[g]	−157 657[g]	−157 656

[a] One basis function for each l.

[b] 5, 7, 5, 5, 2, 2 basis functions for $l=0,1,2,3,4,5$, respectively.

[c] 10, 12, 9, 8, 5, 5 basis functions for $l=0,1,2,3,4,5$, respectively.

[d] Reference 14 (variational calculations using 30 basis functions for each l).

[e] From the asymptotic formula (21).

[f] The exact value is $-157\,666.40\times 10^{-6}$ a.u. [Ref. 12(a)].

[g] For $l\geq 6$ the (almost converged) values of column A have been used.

For each $l \leq 5$ we have applied three basis sets A,B,C of different dimensions. Set A contains only the function (17). In B and C this set is extended by subsequent functions according to Table I. In each case the projections of the Hylleraas functions (13) of a certain polynomial degree $p+q+r$ have been included completely. Our largest calculation is one for $l=1$ with 12 functions ($p+q+r \leq 4$). For $l \geq 6$ set A (the "one-function approximation") is found to be sufficient (see below). The numerical results are collected in Table II.

Comparing for different l the convergence of the energy $E_l^{(2)}$ with increasing basis set, relatively slow convergence is found for $l=1$ and 2, a more rapid one for $l=0$ and an increasingly rapid convergence for $l=3,4,5,\ldots$. From the previously calculated $E_l^{(2)}$ values,[14,19,20] the best ones are those of Byron *et al.*[14]: See the last column of our Table II. These are variational results using basis functions $r_<^m r_>^n \Psi_{\mathrm{He}}^{(0)}$, namely, a rigid set of 30 such functions (including negative exponents n) for any l. For $l=0$, 1, and 2 our calculation C lies behind Ref. 14 by 9×10^{-6} in total. Here our basis sets of 10, 12, and 9 functions, respectively, are too small yet. For all $l \geq 3$, however, the superiority of the l-specific Hylleraas projections over a rigid radial basis set becomes more and more apparent. Taking, for each l, the lowest $E_l^{(2)}$ value of Table II (i.e., Ref. 14 for $l \leq 2$ and C or A, respectively, for the remaining l), these sum to a total $E^{(2)}$ of $-157\,666.1\times10^{-6}$. Comparing this with the exact $E^{(2)}$ (Knight[12(a)])

$$E_{\mathrm{exact}}^{(2)} = -157\,666.40\times10^{-6} \tag{19}$$

in a.u., we conclude that each of the aforementioned $E_l^{(2)}$, within the number of digits given, should be nearly converged. So, the remaining error in our best total $E^{(2)}$ (see last line in Table II) should be almost entirely due to the $l \leq 2$.

Furthermore, our $E^{(2)}$ (total) can be compared with direct calculations using the (entire) Hylleraas functions. Such results for various numbers of functions are reported in Schwartz's paper [Table I of Ref. 4(a)]: In order to obtain our $E^{(2)}$ values of the cases A,B,C, about 6, 30, and 45 Hylleraas functions, respectively, would be required.

The asymptotic region ($l \geq 6$) deserves a further discussion. We have seen that in this region the "one-function approximation" [Eq. (17) and column A in Table II] is sufficient for an accuracy of the total $E^{(2)}$ of better than 10^{-6} a.u. Equation (17) yields $E_l^{(2)}$ as the quotient of two sums of James-Coolidge integrals (18) for $\alpha=\beta=2$ which can readily be evaluated. Actually this expression for $E_l^{(2)}$ can be transformed into a very simple formula proposed by Schwartz.[4] We expand $V_{m,n}$ (2,2) according to

$$V_{m,n}(2,2) = \frac{(\sigma+1)!}{m+1} 2^{-2\sigma-3}\left(\tfrac{1}{2}+R_2+R_3+R_4+\cdots\right), \tag{20}$$

where $\sigma = m+n$ and

$$R_i = \frac{1}{2^i} \frac{(\sigma+2)(\sigma+3)\cdots(\sigma+i)}{(m+2)(m+3)\cdots(m+i)} .$$

Subsequently, using the terms of (20) up to R_7, the quotient of $E_l^{(2)}$ is expanded in powers of $\lambda = 2/(2l+1)$ to give

$$E_l^{(2)} = -\tfrac{45}{256}\lambda^4[1-\tfrac{5}{4}\lambda^2+\tfrac{183}{64}\lambda^4+O(\lambda^6)] . \tag{21}$$

The first two terms of (21) agree with Schwartz's formula [in its extended version as communicated in footnote 8(a) of Ref. 14]. The difference between (21) and the exactly evaluated $E_l^{(2)}$ quotient is very small; for $l=6$ it is 10^{-8} a.u., and less for higher l. The expression (21) can be summed analytically over l (Ref. 21) and yields -43.8×10^{-6} a.u. for $l \geq 11$ as given in Table II. Certainly, for a desired accuracy of $E^{(2)}$(total) of 10^{-6} a.u., the one-function approximation, and so formula (21), could be applied already for $l=6$.

Using the partial wave $\Psi_{l=0}^{(1)}$ as determined in our variational calculations A, B, and C (compare first line of Table II) the *three-electron integrals* (9a)—(9c) have been evaluated. Again one is led to sums of James-Coolidge integrals (18), here for different (α,β) combinations. The results are shown in Table III. The accuracy of the sum $4M_1-2M_2-M_3$ appearing in Eq. (8) is seen to be determined by that of M_3. In each of the cases A,B,C, the M_3 is somewhat more accurate than the respective $E^{(2)}$(total); compare the last line of Table II.

IV. DISCUSSION

In this paper we have defined a method of l-separated Hylleraas basis functions to be used for the variational determination of first-order pair functions for atoms (within the $1/Z$-perturbation theory). The method has been tested for the ground state of the heliumlike atom. It is found to yield, in compact calculations, accurate values for the second-order quantities: the pair energy $E_{\mathrm{He}}^{(2)}$ and the three-electron integrals M_1,M_2,M_3 (which belong to the energy $E_{\mathrm{Li}}^{(2)}$ of the lithiumlike atom). The results are in more detail.

(i) The l-separated Hylleraas functions give rapid convergence for the individual partial-wave energies $E_l^{(2)}$ for all l. In the asymptotic region of large l (this is $l \geq 6$ for an accuracy of 10^{-6} a.u.) one basis function per l suffices. For $E_{\mathrm{He}}^{(2)}$ (the sum of the $E_l^{(2)}$) the value of $-0.157\,657$ a.u. was obtained by using 10, 12, 9, 8, 5, 5, functions for $l=0,1,2,3,4,5$, respectively. To reach the same accuracy in a direct calculation would require 45 of the original Hylleraas functions. We estimate that Knight's[12(a)] very exact $E_{\mathrm{He}}^{(2)}$ [obtained in 100 Hylleraas functions, Eq. (19)] would be reached in the l-separated method by using about 25 functions for the $l=1$ partial wave and about 20 for those of the remaining low l.

TABLE III. Three-electron integrals M_1,M_2,M_3 (parts of the second-order energy of the three-electron atom) evaluated in the ($l=0$) partial wave from variational calculations A,B,C (which used 1, 5, and 10 basis functions, respectively). All entries in 10^{-6} a.u.

	A	B	C	Exact value[a]
M_1	-5124	-5058.3	-5057.73	-5057.704
M_2	-6368	-6243.2	-6243.46	-6243.572
M_3	$-22\,784$	$-23\,802$	$-23\,755.8$	$-23\,758.968$

[a] Chisholm and Dalgarno, Ref. 8.

(ii) The ansatz in one basis function which is valid for large l has been shown to go over into Schwartz's asymptotic formula.[4,14] Therefore, while retaining the same method, one can deal very simply with the whole asymptotic l region.

(iii) The convergence of the three-electron integrals M_1 to M_3 is similar to that found for the $E_l^{(2)}$ of the low l.

It appears to us worthwhile to try these l-separated pair functions for the calculation of third-order energies. Particularly accurate pair functions are then required. For the third-order lithium energy $E_{\mathrm{Li}}^{(3)}$ the work of Yung, Sanders, and Knight[11] has shown that the variation of the entire pair functions provides a good $E_{\mathrm{Li}}^{(3)}$ only with extreme effort.

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[19] For comparison we give some of the older $E_l^{(2)}$ values which have been obtained through a (configuration-interaction-like) product ansatz for $\Psi_l^{(1)}(r_1,r_2)$. Such calculations have been done in Ref. 13 and in part of Ref. 14. In Ref. 13 (table, p. 100, parameter $t=16$) the following $E_l^{(2)}$ for $l=0$, 4, and 9 have been calculated (using more than 80 basis functions per l): $-125\,298$, -279, -0.3 $(\times 10^{-6}$ a.u.). In Ref. 14 (table, p. 3, case III) a different choice of 20 product functions yielded $-125\,031$, -292, -9 $(\times 10^{-6}$ a.u.) for $l=0$, 4, and 9, respectively.

[20] J. I. Musher and J. M. Schulman, Phys. Rev. 173, 93 (1968), have calculated $\Psi_l^{(1)}$ by numerical solution of its differential equation. Their $E_l^{(2)}$ values (Table II of Musher and Schulman) are less accurate than the variational ones of Ref. 14.

[21] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965), pp. 806—808.