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Calculations on the ^2S Ground State of the Lithium Atom Using Wave Functions of Hylleraas Type

SVEN LARSSON*
Quantum Chemistry Group, Uppsala University, Uppsala, Sweden

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A wave function was obtained for the ^2S ground state of the lithium atom using 60 basis functions of the Hylleraas type, i.e., with interelectronic distance coordinates. The energy obtained was -7.478025 atomic units as compared with the value -7.478069 calculated from experiments. The wave function was used to calculate the Fermi contact term. It was found that this basis set gave the value 2.906, which is in agreement with experiments, when both doublet spin functions were used, but a value that was 4% greater when only one spin function was used. In the first case, 100, and in the latter, 60, linear parameters were varied. The interelectronic distance coordinates are expanded according to a formula by Sack. The final integrals are evaluated analytically, and the resulting formulas, along with a short discussion of their convergence properties, are given in an Appendix.

I. INTRODUCTION

CALCULATIONS of electronic wave functions for atoms can be done by the variation principle. One gets wave functions and upper bounds to the true energy, the accuracy of which depends on the extent of the calculation. So far wave functions of high accuracy have been obtained only for the He atom.[1,2] For atoms with three or more electrons one encounters problems with either slow convergence or computationally difficult integrals. Thus calculations have been made on the lowest ^2S state by Weiss,[3] who used a basis consisting of antisymmetrized products of one-electron orbitals. For 45 configurations he obtained the energy -7.4771 atomic units (a.u.). This corresponds to about 98% of the correlation energy.[4] The same accuracy can be obtained with about 10 configurations of Hylleraas type,[5–7] i.e., functions containing explicitly non-negative powers of interelectronic distance coordinates; but here the integrals are more involved and more time-consuming to calculate.

The present work is an extension of the latter Hylleraas-type calculations. With the help of a formula by Sack[8] it has been possible to write an automatic and fast program for the matrix elements. For a basis of the order 60 an energy has been obtained that is an order of magnitude better than the previous calculations but still not comparable to the calculations on He by Pekeris[1] and Kinoshita.[2]

The wave function has been tested on a calculation of the Fermi contact term, which is responsible for the hyperfine splitting in the $^2S_{1/2}$ ground state. Much attention has been paid to this term, mainly because previous theoretical calculations give widely spread values even for wave functions that have good energies.[9] The unrestricted Hartree-Fock wave function gives about 97% of the correct value for the Fermi contact term, which must be considered a remarkably good value. Owing to the erratic results of calculations of the Fermi contact term, it has been calculated for every step in the extension of the basis set in order to get an idea about the trend. A discussion of the results is given in Sec. V.

II. WAVE FUNCTION

An exact wave function for a $^2S_{1/2}$ state may be written:

$$\psi=\psi_a(\alpha\beta\alpha-\beta\alpha\alpha)+\psi_b(2\alpha\alpha\beta-\beta\alpha\alpha-\alpha\beta\alpha). \qquad (1)$$

ψ_a and ψ_b must be such that ψ is antisymmetric, i.e.,

$$\mathcal{A}\psi=\psi, \qquad (2)$$

where $\mathcal{A}$ is the three-particle antisymmetrizer

$$\mathcal{A}=e-(12)-(13)-(23)+(123)+(132). \qquad (3)$$

The two spin functions $\chi_1=\alpha\beta\alpha-\beta\alpha\alpha$ and $\chi_2=2\alpha\alpha\beta-\beta\alpha\alpha-\alpha\beta\alpha$ span together the spin space in which $S=\frac{1}{2}$ and $S_z=\frac{1}{2}$.

We can construct a trial wave function in the following way:

$$\begin{aligned}\psi&=\mathcal{A}\{\phi^{(1)}\chi_1+\phi^{(2)}\chi_2\}\\&=\mathcal{A}\{\sum_{\mu=1}^{N}(A_{1\mu}\phi_\mu\chi_1+A_{2\mu}\phi_\mu\chi_2)\},\end{aligned} \qquad (4)$$

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where the constants $A_{1\mu}$ and $A_{2\mu}$ may be determined variationally. The N basis functions ϕ_μ are, in principle, general functions of the space coordinates for the three electrons, having S symmetry. Since the operation of projection on the spin space spanned by χ_1 and χ_2 commutes with the operation of antisymmetrization, it is clear that (4) is a ${}^2S_{1/2}$ wave function and can be written in the form (1). Note that all $A_{2\mu}=0$ does not imply that $\psi_b=0$.

A tractable way to proceed is to have $\phi^{(2)}=0$ and to restrict $\phi^{(1)}$ to the form

$$\phi^{(1)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\Theta(\mathbf{r}_1,\mathbf{r}_2)\vartheta(\mathbf{r}_3). \tag{5}$$

We get

$$\psi=\mathcal{A}\{\Theta(\mathbf{r}_1,\mathbf{r}_2)(\alpha\beta-\beta\alpha)\vartheta(\mathbf{r}_3)\alpha(s_3)\}. \tag{6}$$

This wave function corresponds to the physical picture of the Li atom: a closed shell plus a valence electron. A natural spin-orbital analysis of a wave function of the type (6) gives the result[10] that $\vartheta(\mathbf{r}_3)\alpha(s_3)$ is one of the natural spin orbitals. Wave functions of this type have been calculated by Öhrn and Nordling,[7] with good results. In the present calculation ψ has been constructed in a more general way. The ϕ_μ's are functions of r_1, r_2, r_3, r_{23}, r_{13}, r_{12} of the form

$$\begin{aligned}\phi(r_1,r_2,r_3,r_{23},r_{13},r_{12})&=r_1{}^ir_2{}^jr_3{}^kr_{23}{}^lr_{13}{}^mr_{12}{}^n\\ &\times\exp(-\alpha r_1-\alpha r_2-\gamma r_3)=\{ijklmn\}.\end{aligned} \tag{7}$$

The latter notation is possible since α and γ are determined once and then not varied again. We will always have

$$i,j,k,l,m,n\geq 0. \tag{8}$$

The restriction to the form (5) will be removed by having $N>1$ in (4) and by the introduction of terms containing r_{13} and r_{23} to arbitrary powers and by permitting $A_{2\mu}\neq 0$.

Are there any reasons for mixing in the second spin function at all, i.e., to have $A_{2\mu}\neq 0$? Suppose that the function

$$\psi_1=\mathcal{A}\{\phi(\alpha\beta\alpha-\beta\alpha\alpha)\} \tag{9}$$

belongs to the basis. We can then form other ψ's by permuting the particle indices in ϕ. It is easy to see that the permutation (12) gives back the same basis function ψ_1, while (13) and (132) give a new function ψ', and (23) and (123) give a new function ψ''. We have

$$\psi'=\mathcal{A}\{(13)\phi(\alpha\beta\alpha-\beta\alpha\alpha)\}=-\mathcal{A}\{\phi(\alpha\beta\alpha-\alpha\alpha\beta)\}, \tag{10}$$

$$\psi''=\mathcal{A}\{(23)\phi(\alpha\beta\alpha-\beta\alpha\alpha)\}=-\mathcal{A}\{\phi(\alpha\alpha\beta-\beta\alpha\alpha)\}; \tag{11}$$

ψ_1, ψ', and ψ'', are linearly dependent and as a linearly independent pair we may take ψ_1 and $\psi'-\psi''$,

$$\begin{aligned}\psi_{12}=\psi'-\psi''&=\mathcal{A}\{[(13)-(23)]\phi(\alpha\beta\alpha-\beta\alpha\alpha)\}\\ &=\mathcal{A}\{\phi(2\alpha\alpha\beta-\beta\alpha\alpha-\alpha\beta\alpha)\},\end{aligned} \tag{12}$$

which follows from (10) and (11). If ϕ has (12) symmetry from the beginning we have

$$\psi'=\psi''=-\tfrac{1}{2}\psi, \tag{13}$$

i.e., ψ_{12} vanishes identically. It follows from (12) that instead of introducing a function $\mathcal{A}\{\phi\chi_2\}=\mathcal{A}\{[(13)-(23)]\phi\chi_1\}$, we may introduce, because of the linear dependency, the function $\mathcal{A}\{(13)\phi\chi_1\}$. Evidently, we can, instead of using the spin function χ_2, make the permutation (13) of the particle indices in ϕ and use χ_1.

In practice one usually chooses ϕ (when multiplied by χ_1) such that the energy lowering is appreciable and such that it gives the correct localization of the electron shells. The exponential parameters will, for instance, be 2.76 for the core and 0.65 for the valence electron. The energy lowering when $\mathcal{A}\{\phi\chi_2\}=\mathcal{A}\{(13)\phi\chi_1\}$ is included will then probably be small, since $(13)\phi$ is very different in shape from ϕ.

For the Fermi contact term, however, adjustments to the wave functions of this kind are known to be very important.[9] The inclusion of terms with the spin function χ_2 does not cause any extra labor for the calculation of matrix elements if one has already included the corresponding term with spin χ_1. The integrals are the same; only the weights are different because of the "integration" over the spin variables. But the resulting secular equation will have a larger dimension. In this paper wave functions will be constructed both with and without terms with the spin function χ_2. A wave function constructed with only the spin function χ_1 will be denoted by ψ_1. If terms with χ_2 are also included the resulting wave function will be denoted by ψ_{12}. As pointed out above a basis function ϕ which is symmetrical in index 1 and 2 will give a vanishing ψ when multiplied by χ_2 and antisymmetrized. The final ψ_{12} is therefore constructed from 100 basis functions; 60 with spin function χ_1 and those 40 which are unsymmetrical in index 1 and 2 (indicated by an asterisk in Table I) with spin function χ_2.

III. CALCULATIONS

The nonrelativistic Hamiltonian for three electrons in the field of a fixed Li nucleus is (in Hartree atomic units)

$$\mathcal{H}=\sum_{i=1}^{3}-\tfrac{1}{2}\nabla_i{}^2-\sum_{i=1}^{3}\frac{3}{r_i}+\frac{1}{r_{23}}+\frac{1}{r_{13}}+\frac{1}{r_{12}}, \tag{14}$$

where the first sum represents the kinetic energy $\mathcal{T}$, and the rest the potential energy $\mathcal{V}$. Since the wave function has no explicit angular dependence it is convenient to transform the kinetic-energy part into the mutually independent distance coordinates r_1, r_2, r_3, $r_{23}=u_1$, $r_{13}=u_2$,

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[10] S. Larsson and V. H. Smith (to be published).

and $r_{12}=u_3$,

$$T=-\tfrac{1}{2}\Bigg[\sum_{i=1}^{3}\left(\frac{\partial^2}{\partial r_i^2}+\frac{2}{r_i}\frac{\partial}{\partial r_i}+2\frac{\partial^2}{\partial u_i^2}+\frac{4}{u_i}\frac{\partial}{\partial u_i}\right)+\sum_{P}\left(\frac{r_i^2+u_k^2-r_j^2}{u_kr_i}\frac{\partial^2}{\partial r_i\partial u_k}+\frac{1}{2}\frac{u_i^2+u_k^2-u_j^2}{u_iu_k}\frac{\partial^2}{\partial u_i\partial u_k}\right)\Bigg]. \qquad (15)$$

The second summation is over the six permutations

$$P=\begin{Bmatrix}1 & 2 & 3\\ i & j & k\end{Bmatrix}.$$

From the variation principle one obtains the matrix eigenvalue problem

$$(\mathbf{H}-E\boldsymbol{\Delta})\mathbf{c}=0, \qquad (16)$$

where the eigenvalues E approximates the eigenvalues of the corresponding Schrödinger equation from above and the matrix elements are

$$H_{kl}=\int\psi_k\mathcal{H}\psi_l d\tau \quad\text{and}\quad \Delta_{kl}=\int\psi_k\psi_l d\tau. \qquad (17)$$

The first step in the calculation is to perform the antisymmetrization and to "integrate" over spin. Then we operate with the Hamiltonian and get as a result a linear combination of integrals.

$$I=\int\prod_{i=1}^{3}\left[r_i^{j_i}u_i^{k_i}\exp(-a_ir_i)r_i^2dr_i\sin\vartheta_i d\vartheta_i d\varphi_i\right]. \qquad (18)$$

From the form of wave functions and of the Hamiltonian it follows that $k_i\geq -1$. The interelectronic coordinates are expanded according to a formula by Sack,[8] which is a generalization of the well-known Laplace expansion,

$$u_3^n=r_{12}^n=\sum_{l_3=0}^{\infty}R_{nl_3}(r_1,r_2)P_{l_3}(\cos\vartheta_{12}), \qquad (19)$$

and the same for u_1 and u_2. P_l are Legendre polynomials and ϑ_{12} the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. R_{nl} is a function related to the hypergeometric functions through

$$R_{nl}(r_1,r_2)=\frac{(-\frac{1}{2}n)_l}{(\frac{1}{2})_l}r_>^n\left(\frac{r_<}{r_>}\right)^l\times F\left(l-\tfrac{1}{2}n,\ -\tfrac{1}{2}-\tfrac{1}{2}n,\ l+\tfrac{3}{2};\ \frac{r_<^2}{r_>^2}\right), \qquad (20)$$

$$F(\alpha,\beta,\gamma;\ x)=1+\sum_{s=1}^{\infty}\frac{(\alpha)_s(\beta)_s}{(\gamma)_ss!}x^s. \qquad (21)$$

$(\alpha)_0=1$; $(\alpha)_s=\alpha(\alpha+1)\cdots,\ (\alpha+s-1)$; $r_<=\min(r_1,r_2)$; $r_>=\max(r_1,r_2)$. We see that for odd positive n and for $n=-1$, Eq. (21) breaks off after a finite number of terms. For even positive n, Eq. (21) breaks off for $l\leq\frac{1}{2}n$, and for $l>\frac{1}{2}n$, R_{nl} vanishes because of the term $(-\frac{1}{2}n)_l$. The next step is to integrate over the angles. The Legendre polynomials are expanded in spherical harmonics; for instance:

$$P_{l_3}(\cos\vartheta_{12})=\frac{4\pi}{2l_3+1}\times\sum_{m_3=-l_3}^{l_3}Y_{l_3m_3}{}^*(\vartheta_1,\varphi_1)Y_{l_3m_3}(\vartheta_2,\varphi_2). \qquad (22)$$

The angular integrations are now easy to perform, since the spherical harmonics form an orthonormal set. We get the condition

$$l_1=l_2=l_3=l \qquad (23)$$

and

$$I=\sum_{l=0}\frac{(4\pi)^3}{(2l+1)^2}\int\prod_{i=1}^{3}\left[r_i^{j_i+2}R_{k_il}\exp(-a_ir_i)dr_i\right]. \qquad (24)$$

The integration region is over positive r_i's and to proceed we must divide this region into six parts, each characterized by $0<r_\lambda<r_\mu<r_\nu<\infty$. The convergence of formula (24) and the remaining integrations are discussed in the Appendix. All calculations were done on the CDC 3600 computer at Uppsala University.

The eigenvalue problems are solved by two different methods. One is Löwdin's partitioning technique.[11] This method allows for big matrices since it is possible to split the matrix into two parts and to handle only one part at a time. The other is Givens's method[12]; after $\boldsymbol{\Delta}$ has been triangulated[13] and $\mathbf{H}$ transformed. This transformation is done once for the N-dimensional secular problem and then all the eigenvalue problems can be solved directly of orders from 1 to N, without further triangularization or transformation.

IV. CHOICE OF PARAMETERS; NUMERICAL RESULTS

The eigenvalue problem has been solved for every step in the extension of the basis set. The energies are listed in Table I. The second column is for ψ_{12} with both spin functions included and thus obtained by varying more linear parameters than the number of basis functions listed. The idea is to make the convergence of energy as fast as possible for a basis set with the spin function

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[11] P. O. Löwdin, J. Mol. Spectry. **10**, 12 (1963).

[12] F. Prosser and H. H. Michels, Program 62:1, Quantum Chemistry Program Exchange, Indiana University. Rewritten in double precision by G. Sperber, Quantum Chemistry Group, Uppsala University.

[13] H. H. Michels, C. P. van Dine, and P. Elliot, Program 97, Quantum Chemistry Program Exchange, Indiana University. Rewritten by the present author to allow for large dimensions and in double precision.

TABLE I. The energies and the Fermi contact term for various numbers of basis functions. The asterisk indicates that two spin functions are possible.

No.	$\{ijklmn\}$	−Energy (a.u.) ψ_1	−Energy (a.u.) ψ_{12}	Fermi contact term (a.u.) ψ_1	Fermi contact term (a.u.) ψ_{12}
1	001000	7.417907	7.417907	2.041	2.041
2*	101000	7.417823	7.417889	2.237	3.165
3	111000	7.430033	7.430046	2.823	3.240
4*	201000	7.444700	7.444731	3.845	3.101
5	001001	7.472382	7.472405	3.605	2.964
6	001002	7.473999	7.474021	3.516	2.917
7	000000	7.474831	7.474840	2.859	2.572
8*	000100	7.476320	7.476350	3.071	2.666
9	002000	7.476786	7.476826	3.013	2.818
10*	010100	7.476996	7.477033	3.207	2.882
11	001003	7.477144	7.477185	3.238	2.909
12*	001100	7.477267	7.477287	3.321	2.919
13	003000	7.477363	7.477377	3.289	2.962
14*	101001	7.477439	7.477455	3.287	2.961
15*	301000	7.477562	7.477579	3.231	2.914
16	001004	7.477581	7.477598	3.224	2.921
17	221000	7.477586	7.477602	3.226	2.920
18	111001	7.477665	7.477683	3.155	2.911
19*	201001	7.477747	7.477765	3.122	2.900
20*	301001	7.477800	7.477817	3.170	2.870
21	000200	7.477819	7.477841	3.147	2.868
22*	000110	7.477826	7.477847	3.129	2.865
23*	020100	7.477832	7.477856	3.176	2.861
24*	110100	7.477835	7.477860	3.208	2.857
25	004000	7.477848	7.477869	3.199	2.865
26	000001	7.477849	7.477870	3.184	2.860
27	002001	7.477885	7.477905	3.157	2.875
28*	100000	7.477885	7.477914	3.156	2.875
29*	102000	7.477888	7.477923	3.161	2.884
30*	000101	7.477901	7.477935	3.162	2.887
31*	010200	7.477915	7.477957	3.211	2.893
32*	011100	7.477916	7.477957	3.199	2.893
33*	000300	7.477918	7.477963	3.208	2.892
34*	001200	7.477927	7.477967	3.185	2.891
35	001005	7.477931	7.477971	3.187	2.892
36*	401000	7.477938	7.477978	3.167	2.889
37*	401001	7.477945	7.477984	3.146	2.887
38*	501000	7.477945	7.477984	3.147	2.894
39*	101002	7.477945	7.477984	3.147	2.893
40*	201002	7.477945	7.477985	3.147	2.894
41*	101003	7.477966	7.478006	3.173	2.895
42	110000	7.477968	7.478009	3.147	2.896
43	112000	7.477982	7.478010	3.096	2.898
44*	200000	7.477987	7.478010	3.049	2.899
45*	202000	7.478002	7.478015	3.001	2.898
46*	100001	7.478003	7.478016	2.998	2.899
47*	102001	7.478003	7.478017	2.999	2.900
48*	200001	7.478004	7.478018	2.976	2.900
49*	021100	7.478005	7.478018	2.986	2.901
50*	030100	7.478006	7.478019	3.003	2.903
51*	201003	7.478006	7.478019	3.003	2.903
52	005000	7.478006	7.478019	3.004	2.903
53*	211000	7.478006	7.478020	3.008	2.903
54	001006	7.478008	7.478021	3.007	2.904
55*	302000	7.478008	7.478021	3.007	2.904
56*	300000	7.478008	7.478022	3.008	2.907
57*	000400	7.478009	7.478024	3.009	2.907
58*	100100	7.478009	7.478024	3.010	2.907
59*	311000	7.478009	7.478024	3.012	2.906
60*	301002	7.478010	7.478025	3.019	2.906

χ_1. The matrix elements are simultaneously calculated for the spin χ_2 since this, as has already been pointed out, gives no new integrals.

The first function may be considered as an approximation to the Hartree-Fock function and the energy -7.4179 atomic units (a.u.) is fairly close to the HF energy -7.4327 a.u.[9] This function is first improved in the core as in the work by James and Coolidge,[5] with the functions 2–6. So far we have still a wave function of the type core-geminal–valence-orbital. The next three terms are included to give more flexibility to the valence electron and to take into account the correlation between this electron and the core.

TABLE II. Variation of the parameter α at nine basis functions (one spin function).

α	−Energy (a.u.)
2.70	7.476749
2.80	7.476766
2.90	7.476576

In order to determine the parameters α and γ the calculation with nine basis functions was done with $\alpha=2.70$, 2.80, 2.90 and $\gamma=0.65$. These values were deduced from earlier calculations. The result is given in Table II. A simple interpolation gave the best value $\alpha=2.76$. After this minimization the scale factor

$$\eta=-\frac{\langle\mathcal{V}\rangle_{\text{av}}}{2\langle\mathcal{T}\rangle_{\text{av}}} \tag{25}$$

was calculated.[14] The value was very near to 1 (1.00019). Therefore $\alpha=2.76$ and $\gamma=0.65$ could be accepted and were kept fixed during the remaining calculations.

The next basis functions were chosen mainly by trial and error. When some new functions had been introduced they were ordered after contribution to the total energy; those which gave only a small energy improvement were deleted. Next functions related to the best of the previous ones and also new ones were tried. The process was continued until almost all conceivable combinations had been tried. To some extent it is possible to predict beforehand if a configuration will be good or bad. We may, for instance, compare the terms $\mathcal{A}(\{010100\}\chi_1)$ and $\mathcal{A}(\{100100\}\chi_1)$. The first one contains the factor r_2r_{23} and therefore describes the situation when electron 1 is near the nucleus and electron is 2 farther out. Because of the factor r_{23} it will not come too near the valence electron. The second term does not have this feature since instead it contains the factor r_1r_{23}. The first thus describes the repulsion between the core and the valence electron in a much better way and also gives a much greater energy contribution.

The procedure described is of course not unique. One function may give a large or small contribution to the energy depending on the preceding functions of the set. The method cannot be applied when the basis is large, since every step in the extension is then rather time-consuming.

The energy value calculated from experiments by subtracting relativistic and finite nuclear mass effects[15]

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[14] P. O. Löwdin, J. Mol. Spectry. **3**, 46 (1959).

[15] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

is -7.478069. If this value is correct it can be seen that the convergence is rather bad at the end of the expansion. A possible way to improve it is perhaps to use terms with other exponential functions. The inclusion of the second spin function partly has this effect.

The scale factor η was calculated for all the wave functions. It was between 1.0000 and 1.0001 in most cases. The values given in Table I for energy and Fermi contact term are those obtained from a scaled wave function. (This explains why one basis function in Table I actually gives better energy than two basis functions.)

V. FERMI CONTACT TERM

The wave functions were used to calculate the expectation value of the Fermi contact term[16]

$$f=\langle 4\pi\sum_{i=1}^{3}\delta(\mathbf{r}_i)\sigma_{z_i}\rangle, \tag{26}$$

where we have

$$\sigma_{z_i}\alpha(i)=\alpha(i),\quad \sigma_{z_i}\beta(i)=-\beta(i). \tag{27}$$

Because of the δ function, f is a "one-point" property of the wave function, and may therefore be expected to vary considerably for different wave functions.

In a Hartree-Fock calculation[9] (restricted or unrestricted) or a natural expansion of more accurate wave functions,[10] one obtains f as the difference between almost equal and large contributions from the two core orbitals plus a small contribution from the valence orbital. This fact will cause the Fermi contact term to be still more dependent on occasional inadequacies of the wave function.

The results are given in Table I. We see that the wave function constructed with only one spin function gives remarkably bad values. Even after 42 basis functions have been introduced and we have obtained 99.8% of the correlation energy, the discrepancy from the experimental value 2.906[17] is as much as 8%. Just as remarkable is the good agreement obtained with ψ_{12}. Here we obtain, after 100 basis functions (60+40), complete numerical agreement with the experimental value. Several explanations for this may be given. The most obvious of course is that we have varied more linear parameters in ψ_{12}. Another is that when a basis function is multiplied by χ_2 this corresponds to (13) change in the function ϕ and therefore introduces another exponential decrease and acts as a fine adjustment in the wave function. The f values from ψ_1 are larger than the experimental value in general, while the f values from ψ_{12} are slightly smaller than the experimental value between 20 and 40 basis functions. This may be attributed to the fact that we have not included terms containing factors of the type $r_{ij}/(r_i+r_j)$ and $(r_i-r_j)/r_{ij}$. Such terms were introduced by Kinoshita in his He calculation.[2] According to him a Hylleraas expansion may still be complete, even though terms of the type above are not included. Probably we could even have avoided terms with the power 0 on all the r_i's, and still have had a complete set. Such a cutoff of terms would, however, give the Fermi contact term equal to zero. In our case we have still a number of terms which have a nonzero value at the origin of the respective electron coordinates and the effect should therefore be small and decreasing for an increasing basis.

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APPENDIX

After the interelectronic coordinates have been expanded according to Sack's formula[10] and the angular intergrations performed, we are left with the sums

$$J_P=\sum_{\kappa=0}^{\infty}\frac{1}{(2\kappa+1)^2}\int_{\Omega_P}\prod_{i=1}^{3}\left[r_i^{j_i+2}R_{k_i\kappa}\exp(-a_ir_i)dr_i\right]. \tag{28}$$

The integration region Ω_P is given by $0<r_\lambda<r_\mu<r_\nu<\infty$, where $\{\lambda,\mu,\nu\}$ is the permutation P of $\{1,2,3\}$. The function R is defined by (20) and (21). From the form of R it follows that the series is infinite only when all k_i's are odd. It will be shown below that the convergence of the infinite series is as for

$$\sum_{\kappa=1}^{\infty}\frac{1}{\kappa^6}$$

or better. In general ten terms are enough to obtain 10 significant figures.

After the expression for the R's has been inserted, every term in (28) breaks down to integrals of the fol-

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[16] E. Fermi, Z. Physik **60**, 320 (1930).

[17] The experimental value is calculated from the formula [see, e.g., Blinder (Ref. 9)]

$$f=\frac{9}{4}\frac{a}{g_I}\frac{1}{\mu_0 g\mu_N}C=2.9062\text{ a.u.}$$

Here, g=electronic g factor=2.0023; μ_0=the Bohr magneton $=0.92731\ 10^{-20}$ erg G^{-1} (Cohen *et al.*); μ_N=the nuclear magneton $=0.50504\ 10^{-23}$ erg G^{-1} (Cohen *et al.*); a=the measured space factor=401.756 Mc/sec (Kusch and Taub); g_I=the measured nuclear g factor=3.256310 (Ramsey); C=factor for conversion to atomic units$=0.981726\times10^{-45}$ a.u. sec (Mc/sec)$^{-1}$ erg^2 G^{-2}. E. R. Cohen, J. W. M. Du Mond, J. W. Layton, and J. S. Rollett, Rev. Mod. Phys. **27**, 363 (1954); P. Kusch and H. Taub, Phys. Rev. **75**, 1477; N. F. Ramsey, in *Molecular Beams* (Oxford University Press, New York, 1956), p. 172.

lowing kinds:

$$A(k,\alpha)=\int_0^\infty x^k e^{-\alpha x}dx=\frac{k!}{\alpha^{k+1}}, \tag{29}$$

$$V(k,l,\alpha,\beta)=\iint_{0<x<y<\infty} x^k y^l e^{-\alpha x}e^{-\beta y}dydx, \tag{30}$$

$$W(k,l,m,\alpha,\beta,\gamma)=\iiint_{0<x<y<z<\infty} x^k y^l z^m \times e^{-\alpha x}e^{-\beta y}e^{-\gamma z}dzdydx. \tag{31}$$

In (29), (30), and (31) we have $k\geq 0$, $k+l\geq -1$, $k+l+m\geq -2$. We can easily obtain recursion formulas for these integrals if we write them in iterated form and integrate partially. The recursion formulas are given by James and Coolidge.[5] The case k, l, $m\geq 0$ is trivial and we obtain immediately expressions convenient for programming. In the case of either $l<0$ or $m<0$, but not both, (31) can be evaluated in terms of logarithms and rational expressions of α, β, and γ. In the case of both $l<0$ and $m<0$ we get in addition exponential integrals. In general the rational part is just the first terms in the Taylor expansion of the logarithms or exponential integrals in question. This leads to a loss of significant figures which is difficult to handle in an automatic program. Instead a scheme was developed which is similar to that by Öhrn and Nordling.[18]

From the recursion formulas we obtain

$$W(k,l,m,\alpha,\beta,\gamma)=\sum_{\mu=1}^{M}\frac{\alpha^{\mu-1}k!}{(k+\mu)!} \times V(k+\mu+l,\, m,\, \alpha+\beta,\, \gamma)+R(M), \tag{32}$$

$$R(M)=[k!/(k+M)!]\alpha^M W(k+M,\, l,\, m,\, \alpha,\, \beta,\, \gamma), \tag{33}$$

$$V(k,l,\alpha,\beta)=\sum_{\nu=1}^{N}\frac{\alpha^{\nu-1}k!}{(k+\nu)!}A(k+\nu+l,\, \alpha+\beta)+R'(N), \tag{34}$$

$$R'(N)=[k!/(k+N)!]\alpha^N V(k+N,\, l,\, \alpha,\, \beta). \tag{35}$$

We want to estimate R'. For $l<0$ we have from (30)

$$V(k+N,\, l,\, \alpha,\, \beta)=\int_{0<x<y} x^{k+N+l}(x/y)^{-l}e^{-\alpha x}e^{-\beta y}dydx\leq\int_{0<x<y} x^{k+N+l}e^{-\alpha x}e^{-\beta y}dydx =\frac{1}{\beta}\int_0^\infty x^{k+N+l}e^{-(\alpha+\beta)x}dx=\frac{1}{\beta}\frac{(k+N+l)!}{(\alpha+\beta)^{k+N+l+1}}. \tag{36}$$

Thus for large N, (34) converges as a geometrical series with the quotient $\alpha/(\alpha+\beta)$. In a similar way one can show that (32) converges as a geometrical series with the quotient $\alpha/(\alpha+\beta+\gamma)$. It is then obvious that (32) and (34) or their corresponding recursion formulas provide a general and accurate method by which to calculate W and V. In our calculations we always have

$$\alpha/(\alpha+\beta+\gamma)<\tfrac{1}{2},$$

and we therefore need about three steps or terms in (5) for each significant figure to calculate W. For the calculation of V we need more terms but here fewer operations are involved.

By looking at the leading term in (34) we see that $V(k,l,\alpha,\beta)$ behaves like $1/k$ for k increasing with $k+l$ constant. Then it follows from (32) that $W(k,l,m,\alpha,\beta,\gamma)$ behaves like $1/k^2$ for k increasing with $k+m$ and l constant. In (28) we have a product of three R functions which contain the factors $(r_</r_>)^{\frac{1}{2}}$. We get W functions in (28) of the kind $W(k+2\kappa,\, l,\, m-2\kappa)$ and thus these behave like $1/\kappa^2$ when κ tends to infinity. If we now examine (20) and (21) we see first that the 1 is the dominating part of the hypergeometric function when $l(=\kappa)$ tends to infinity. We also have (for n odd)

$$\left|\frac{(-\frac{1}{2}n)_\kappa}{(\frac{1}{2})_\kappa}\right|\approx\frac{1}{\kappa^{(n+1)/2}}\quad\text{for large }\kappa.$$

There are three such factors and it turns out that for our choice of wave functions the product of them converges as $1/\kappa^2$ or better (in the case when the series does not break off). It is then clear that the series (28) converges as

$$\frac{1}{(2\kappa+1)^2}\frac{1}{\kappa^2}\frac{1}{\kappa^2}\approx\frac{1}{\kappa^6}$$

or better. The total time required to calculate an integral with ten significant figures of the kind (18) in the most difficult case, i.e., with all k_i's odd, was about 4 sec on a CDC 3600 computer.

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[18] Y. Öhrn and J. Nordling, J. Chem. Phys. 39, 1864 (1963).