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Effect of Correlation on the Hyperfine Interaction in Lithium

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The results of calculations of the hyperfine interaction in the ground state of lithium, using well-correlated wave functions, are reported. An analysis of the wave functions is made in terms of operators which resolve the general doublet function into two components, one of which is characterized by a spatially symmetric core function. The calculations show that this component with the spatially symmetric core can give very good values for both the energy (-7.47630 a. u.) and the hyperfine interaction (98.8% of experiment). The inclusion of the second doublet component and some quartet component in the wave function has very little effect on either the energy or the hyperfine interaction. These results are discussed and compared with those obtained with the unrestricted Hartree-Fock (UHF) method. The conclusion is reached that the usual interpretation of the results obtained for lithium with the UHF method is not entirely acceptable.

INTRODUCTION

WE have calculated the hyperfine interaction (hfi) in the ground state of lithium with several different wave functions obtained with the variational method. Each of these functions takes into account at least some of the correlation of the electrons other than that introduced by antisymmetrization. Our aim was to gain insight into the relation of the hfi with other properties of the wave function.

Lithium has the advantage that it is manageable with a number of different methods, and that many calculations[1–4] and discussions[5–7] have been reported in the literature. We were particularly interested in the comparison of our results with those obtained for lithium from the unrestricted Hartree-Fock (UHF) method,[2,4] which has been used widely, and sometimes with remarkable success, for the calculation of the hfi in a number of different atoms.[4,8,9]

CHOICE OF WAVE FUNCTIONS

As the ground-state configuration, $1s^22s$, of Li contains no angular momentum, the influence of the spin-orbit coupling terms in the Hamiltonian is very small. The ground state is, therefore, to a good approximation, a pure doublet state. We have restricted our variational functions correspondingly, by requiring them to be eigenfunctions of S_z and to be, exactly or approximately, eigenfunctions of $\mathbf{S}^2$ with eigenvalue $\frac{3}{4}\hbar^2$.

The general eigenfunction of S_z with eigenvalue $\frac{1}{2}\hbar$ for a three-electron system is

$$\Psi(1,2,3)=\sum_P(-1)^pP[\varphi(1,2,3)\alpha(1)\beta(2)\alpha(3)]. \tag{1}$$

Here, p is the parity of the permutation, P. The doublet states for such a system are singled out by the requirement that Ψ contains no contributions from the quartet state. The condition that ensures this can be found by operating on Ψ with the operator[10]

$$\mathbf{S}^2=-\frac{N(N-4)}{4}+\sum_{i<j}P_{ij}^{\sigma}, \tag{2}$$

where P_{ij}^{σ} merely permutes the spin variables and N is the number of electrons. One finds that

$$\sum_P(-1)^pP\varphi(1,2,3)=0. \tag{3}$$

This condition follows even more directly, for the three-electron case, by noting that the quartet state has a completely symmetric spin function and therefore, a completely antisymmetric space function. Hence, for the doublet state the antisymmetric part of the space function must vanish.

We define the permutations $P_0\cdots P_5$ in terms of the cyclic notation by

$$\begin{aligned} &P_0=(1)(2)(3), && P_4=(123), && P_5=(132),\\ &P_1=(1)(23), && P_2=(2)(13), && P_3=(3)(12), \end{aligned} \tag{4}$$

and introduce the well-known projection operators

$$e_1=\tfrac{1}{6}\sum_i P_i,\quad e_2=\tfrac{1}{6}\sum_i(-1)^pP_i,\quad e_3=\tfrac{1}{3}(2P_0-P_4-P_5). \tag{5}$$

They satisfy the relations

$$e_ie_j=e_je_i=e_i\delta_{ij},\quad \sum_i e_i=P_0. \tag{6}$$

For a doublet state we have seen that

$$e_2\varphi=0 \tag{7}$$

and we can also require

$$e_1\varphi=0 \tag{8}$$

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[1] J. H. Bartlett, J. J. Gibbons, and R. E. Watson, Phys. Rev. **50**, 315 (1936). This paper was not concerned specifically with the hfi but with the magnetic moment of the Li nucleus.

[2] L. M. Sachs, Phys. Rev. **117**, 1504 (1960).

[3] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).

[4] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[5] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[6] G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).

[7] W. Marshall, Proc. Phys. Soc. (London) **A78**, 113 (1961).

[8] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[9] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **124**, 1124 (1961).

[10] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, New York, 1958), 4th ed., p. 222.

because the completely symmetric part of φ does not contribute to Ψ. From Eqs. (6), (7), and (8) it follows that φ can be chosen to satisfy the equation

$$e_3\varphi=\varphi. \tag{9}$$

For the purpose of constructing variational functions that satisfy this requirement, it is of interest to express φ in terms of a function χ on which no conditions of symmetry are imposed. Writing

$$\varphi(1,2,3)=\textstyle\sum_P C_P P\chi(1,2,3), \tag{10}$$

we find that the general solution of Eq. (9) can be written in the form:

$$\varphi=(q_1\Omega_1+q_2\Omega_2)\chi, \tag{11}$$

where

$$\begin{aligned}\Omega_1&=\tfrac{1}{2}(P_0+P_3)-e_1,\\ \Omega_2&=\tfrac{1}{6}[2(P_0+P_1)+2(P_0+P_2)-(P_0+P_3)]-e_1,\end{aligned} \tag{12}$$

and q_1 and q_2 are given in terms of the C_P's, i.e.,

$$q_1=(2C_0-2C_2-C_1+C_5),\quad q_2=3(C_1-C_5).$$

The operators Ω_i satisfy the relations:

$$\begin{gathered}\Omega_1^2=\Omega_1,\quad \Omega_2^2=\Omega_2,\\ \Omega_1\Omega_2=\Omega_2\Omega_1=0,\\ \Omega_1+\Omega_2=e_3.\end{gathered} \tag{13}$$

From Eqs. (13) and (9) it follows that one has

$$\varphi=\Omega_1\varphi+\Omega_2\varphi, \tag{14}$$

which is the decomposition of a doublet function φ satisfying Eq. (9) into parts with symmetry character Ω_1 and Ω_2. By applying $P_0\pm P_3$, one sees that these parts are symmetric and antisymmetric in 1 and 2, respectively.

Equation (14) does not directly provide a decomposition of a *given* doublet function Ψ, because the function φ, while it satisfies Eq. (7), may not satisfy Eq. (8). After a projection $\varphi\rightarrow(P_0-e_1)\varphi$, which does not affect Ψ, the decomposition can, however, be performed, and the resulting decomposed form of Ψ is unique. In the following we define, quite generally, a doublet function of the first type, or of type one (of a three-electron problem) to be a function for which $\Omega_2\varphi=0$. A function with $\Omega_1\varphi=0$ will be called of the second type, or of type two.

The appearance of two homogeneous parameters, q_1 and q_2, corresponds to the fact that the doublet state belongs to the two-dimensional irreducible representation of the permutation group γ_3. The ratio q_1/q_2 therefore cannot be obtained from group-theoretical considerations. Fortunately, the present problem is simple enough to allow an assignment of this ratio for the ground state, which is valid to a high degree of approximation. This can be seen from the approximation described by

$$\varphi_1^{(0)}\propto[a(1)b(2)+b(1)a(2)]c(3). \tag{15}$$

This function can be obtained from Eq. (11) with $\chi=a(1)b(2)c(3)$ and $q_2=0$. For Ψ, one has, from Eq. (1), in terms of Slater determinants

$$\Psi_1^{(0)}\propto\begin{pmatrix}a & b & c\\ \alpha & \beta & \alpha\end{pmatrix}-\begin{pmatrix}a & b & c\\ \beta & \alpha & \alpha\end{pmatrix}. \tag{16}$$

This function was used in a variational calculation of the energy of the ground and several excited states by Ritter, Pauncz, and Appel[11] for the special choice

$$a\propto e^{-\alpha r},\quad b\propto e^{-\beta r}, \tag{17}$$

and c a linear combination of generalized Laguerre functions. The degree to which the ground state is described by this doublet function was also studied by them. They considered the more general variational function

$$\Psi^{(0)}=\Psi_1^{(0)}+\lambda\Psi_2^{(0)}, \tag{18}$$

where

$$\Psi_2^{(0)}\propto\begin{pmatrix}a & b & c\\ \alpha & \beta & \alpha\end{pmatrix}+\begin{pmatrix}a & b & c\\ \beta & \alpha & \alpha\end{pmatrix}-2\begin{pmatrix}a & b & c\\ \alpha & \alpha & \beta\end{pmatrix}. \tag{19}$$

This function is obtained from $\chi=a(1)b(2)c(3)$ with $q_1=0$. Ritter, Pauncz, and Appel found that the generalization (18) gave only a very slight improvement of the energy and that $\lambda=q_2/q_1$ is very small. All of the calculations in reference 11 bear this out. This result can be interpreted to mean that the ground state is to a high degree of approximation of the type with $q_2=0$.

The above discussion indicates that the use of the operators Ω_1 and Ω_2 to construct trial functions is very suitable to the present problem.

The components $\Omega_1\varphi$ and $\Omega_2\varphi$ are, in general, not orthogonal as vectors in Hilbert space. In the approximation given by Eq. (18) one finds, e.g.,

$$\langle\Psi_1^{(0)}|\Psi_2^{(0)}\rangle\approx\langle c|a\rangle^2-\langle c|b\rangle^2. \tag{20}$$

Of course, this quantity is not zero but it has only a small numerical value in the Ritter *et al.* calculation. From these results one can expect that, more in general, the ground state is mainly of the type generated by Ω_1, i.e., of the first type.

Guided by this argument, we have chosen our variational functions primarily among those with $q_2=0$. As a special function of this kind, we define a shell function of the first type in the strict sense to be a state, Ψ, obtained from

$$\varphi_s=\Phi_A(1,2)\Phi_B(3),\quad \Phi_A(1,2)=\Phi_A(2,1). \tag{21}$$

Φ_A will be called the core function. A nonsymmetric Φ_A would give a function with $\Omega_2\varphi_s\neq0$. We have taken

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[11] Z. W. Ritter, R. Pauncz, and K. Appel, J. Chem. Phys. **35**, 571 (1961). This type of function has been used also by E. A. Burke and J. F. Mulligan, *ibid.* **28**, 995 (1958) and by B. H. Brigman and F. A. Matsen, *ibid.* **27**, 829 (1957).

functions Φ_A and Φ_B in the form originally used by James and Coolidge,[12] i.e.,

$$\Phi_A(1,2)=[a_1+a_2(r_1+r_2)+a_3r_1r_2+a_4(r_1^2+r_2^2)+a_5r_{12}+a_6r_{12}^2]\exp[-\delta(r_1+r_2)], \quad (22)$$

$$\Phi_B(3)=b_1r_3\exp(-\gamma_1r_3)+b_2\exp(-\gamma_2r_3). \quad (23)$$

This allows for correlation of the core to a much greater extent than does the function of Ritter *et al.* It should be noted that the coefficients of r_1 and r_2 in the exponential are identical, whereas the work of Ritter *et al.* suggests a symmetrical form obtained with different exponentials. The polynomial in Eq. (22) more than makes up for this loss of generality as is indicated by the energy values; however, the extreme simplicity of the function of Ritter *et al.* is a very attractive feature.

Going further, but still following James and Coolidge exactly, we have introduced correlation with the "outer" electron by taking

$$\varphi(1,2,3)=\varphi_s+\textstyle\sum_q(c_qf_q+c_q'h_q), \quad (24)$$

where

$$f_q=r_{23}^p\zeta_i(nmk), \quad h_q=P_3f_q,$$
$$p\geq 1, \quad i=1,2, \quad q=(p)(i)(nmk), \quad (25)$$
$$\zeta_i(nmk)=r_1^nr_2^mr_3^k\exp[-\gamma_ir_3-\delta(r_1+r_2)].$$

When one imposes the restriction $c_q=c_q'$ in all terms, φ is symmetric in 1 and 2 and one has $\Omega_2\varphi=0$. When $c_q\neq c_q'$ is allowed, then the doublet state of the second type and the quartet state is mixed in. On the basis of the above discussion, one should not expect to gain much by relaxing the restriction $c_q=c_q'$.

The functions thus obtained from (24) with the restriction $c_q=c_q'$ will be called generalized shell functions of the first type. This class embraces all functions with $q_2=0$ and none other, and contains the strict shell-type functions as a good approximation for the ground state.

THE HYPERFINE INTERACTION

We have calculated the hfi from the contact term

$$\mathcal{H}_C=(8\pi/3)\gamma_N\gamma_e\mathbf{I}\cdot\textstyle\sum\mathbf{s}_i\delta(\mathbf{r}_i). \quad (26)$$

The dipole term in $\mathcal{H}$, which gives zero for a pure doublet state, has been neglected.

With Ψ of the form in Eq. (1) where φ satisfies Eq. (3), we find from Eq. (26)

$$\Delta_E=(8\pi/3)\gamma_N\gamma_e[(2I+1)/I]Q,$$

$$Q=N^{-1}\left\{\int\int[\varphi^2(1,2,3)+\varphi^2(3,1,2)-\varphi^2(1,3,2)+\varphi(2,3,1)\varphi(1,3,2)-2\varphi(3,1,2)\varphi(2,1,3)]dr_1^3dr_2^3\right\}_{r_3=0}, \quad (27)$$

$$N=\int\int\int[\varphi^2(1,2,3)-\varphi(1,2,3)\varphi(3,2,1)]dr_1^3dr_2^3dr_3^3.$$

When φ is symmetric in its first two arguments, as is the case when $c_q=c_q'$ for all terms in Eq. (24), the second term of Eq. (27) cancels against the third. This means that with a function of the first type there will be no contribution to Q from pure core terms. The contributions from the last two terms in Eq. (27) may or may not be small, depending on the extent to which the functions involved are orthogonal.

From Eq. (27) one obtains, for the function $\Psi_1^{(0)}$ of Eq. (16),

$$Q_1^{(0)}=N_0^{-1}\{c^2(0)[1+\langle a|b\rangle]^2+\tfrac{1}{2}[a(0)\langle c|b\rangle+b(0)\langle c|a\rangle]^2-a(0)c(0)[\langle c|a\rangle+\langle c|b\rangle\langle a|b\rangle]-b(0)c(0)[\langle c|b\rangle+\langle c|a\rangle\langle b|a\rangle]\}, \quad (28)$$

$$N_0=1+\langle a|b\rangle^2-\tfrac{1}{2}[\langle c|a\rangle^2+\langle c|b\rangle^2]-\langle a|b\rangle\langle a|c\rangle\langle b|c\rangle.$$

We note here that for the UHF-type function, which is of the form

$$\Psi_{\mathrm{UHF}}\propto\begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix}, \quad (29)$$

one has

$$Q_{\mathrm{UHF}}=\{c^2(0)+a^2(0)-b^2(0)[1-\langle a|c\rangle^2]-2a(0)c(0)\langle c|a\rangle\}[1-\langle a|c\rangle^2]^{-1}, \quad (30)$$

and it is customary to force $\langle a|c\rangle=0$ so that the expression reduces further. Comparing Eq. (28) with Eq. (30), one sees that in $Q_1^{(0)}$ those contributions from the core orbitals which are proportional to $a^2(0)$ and $b^2(0)$ are multiplied with the squares of the orthogonality integrals, $\langle c|b\rangle^2$ and $\langle c|a\rangle^2$, respectively, which are very small, whereas in Q_{UHF} their difference appears with the coefficient unity. This allows for an entirely different interpretation of the results obtained with the two methods and we shall discuss this later.

RESULTS

The James and Coolidge wave functions were used with fixed values of the nonlinear parameters, viz., with $\delta=3$, $\gamma_1=0.65$, and $\gamma_2=1.5$. The secular equation for the linear parameters was obtained with the use of the matrix elements which were kindly supplied to us by Professor James. The wave function corresponding to its lowest eigenvalue was scaled in the usual manner by replacing r_i by ηr_i, in order to correct for slight deviations from the virial theorem.

Results were obtained with the symmetric shell-type function of Eq. (21) and by cumulative addition, according to Eq. (24), of various terms as indicated by the following scheme:

q	p	i	n	m	k
9	1	1	0	0	0
10	1	2	0	0	0
11	1	1	0	0	1

The coefficients c_q and c_q' were first restricted by $c_q=c_q'$. The results of this calculation are given in

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[12] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

Table I. Next, we allowed $c_q \neq c_q'$, and the results of this calculation are given in Table II.

TABLE I. The hyperfine interaction with James and Coolidge wave functions. $c_q = c_q'$. f and h terms describe the interaction between the inner and outer electrons.

Number of terms	$-E$(a.u.)	$4\pi Q$	% of experimental value	Terms added to each preceding function
8	7.47476	2.648	91.1	separate shell-type wave function of Eq. (21)[a]
9	7.47606	2.828	97.3	$c_9(f_9+h_9)$
10	7.47621	2.813	96.8	$c_{10}(f_{10}+h_{10})$
11	7.47630	2.872	98.8	$c_{11}(f_{11}+h_{11})$

[a] In the calculations, following James and Coolidge, we omitted certain of the terms arising from the product of the right-hand sides of Eqs. (22) and (23). Reference 12 should be consulted for an explanation of this.

TABLE II. The hyperfine interaction with James and Coolidge wave functions. $C_q \neq C_q'$

Number of terms	$-E$(a.u.)	$4\pi Q$	% of experimental value	Terms added to φ_s in Eq. (24)
9	7.47526	2.552	87.8	$c_9 f_9$
10	7.47608	2.867[a]	98.7	$c_9' h_9$
11	7.47618	2.778	95.6	$c_{10} f_{10}$
12	7.47622	2.840	97.7	$c_{10}' h_{10}$
13	7.47631	2.871	98.8	$c_{11} f_{11}$
14	7.47631	2.883	99.2	$c_{11}' h_{11}$

[a] This quantity has also been calculated by Bartlett *et al*. See reference 1.

TABLE III. Summary of the results in various approximations.

Wave function	$-E$(a.u.)	$4\pi Q$	% of experimental spin density
Restricted Hartree-Fock[a]	7.432727	2.095	72.1
Unrestricted Hartree-Fock[a]	7.432751	2.825	97.2
Ritter *et al.*[b]	7.4450	2.802	96.4
Configuration interaction (Nesbet)[c]	7.43169	2.872	98.8
Separate shells $\varphi_s(123) = \Phi_A(12)\Phi_B(3)$	7.47476	2.648	91.1
Best wave function, present calculation	7.47631	2.883	99.2
Experimental value	7.47906[d]	2.906[c]	

[a] From reference 2.
[b] From reference 11.
[c] From reference 3.
[d] Relativistically corrected value. See, e.g., A. Fröman, Preprint No. 63, Uppsala Quantum Chemistry Group (unpublished).

Finally, in Table III we give various results reported in the literature, as indicated, and also those we obtained with the Ritter *et al.* function and the best James and Coolidge function.

DISCUSSION

The quality of the wave function of Li can be judged from the following properties:

(1) the energy, which is fundamental in the variational method;

(2) the value of Q, which can be compared to experiment;

(3) the absence of quartet state admixture, which should be complete when the spin-orbit coupling is neglected.

As a further criterion one has that the ground state is, to a good approximation, of the first type. This follows from the work of James and Coolidge, that of Ritter *et al.*, and from the foregoing analysis, which shows that this type can be characterized generally, irrespective of the approximation, by the condition $\Omega_2\varphi = 0$.

Looking first at the energy, one sees from Table III that the improvement of UHF over RHF is very small. This we attribute to the inflexible way in which the quartet state, with its high energy, is mixed in by this method. The doublet part of the UHF function is not of the first type, i.e., it is a mixture of states of type $\Psi_1^{(0)}$ and $\Psi_2^{(0)}$ of Eqs. (16) and (19), but without the benefit of a mixing parameter like that in Eq. (18). This circumstance will also have an adverse effect on the energy. The very simple variational function of Ritter *et al.* gives a good improvement of the energy. It also gives a reasonable value of Q. These characteristics suggest that it is of the "right" general type.

The Ritter *et al.* wave function, as well as those of James and Coolidge, shows that a substantial improvement of the energy is obtained by allowing for correlation, as was to be expected. The fact that the functions of James and Coolidge give a better result for the energy than does the Ritter *et al.* function we interpret to mean that the correlation is more complete in the former functions than in the latter. This might be expected since the James and Coolidge functions are rather complex and allow for angular as well as radial correlation, whereas the Ritter *et al.* function is quite simple and allows only radial correlation. Correlation of the outer electron with the core gives a further improvement but, as the table shows, little is gained by allowing, to some extent, states of the second type or quartet states to be mixed in. This was already observed by James and Coolidge.

The table shows that the energy obtained by Nesbet with configuration interaction is actually worse than the RHF energy. Nesbet was not interested in improving the energy so he selected those configurations which he knew would affect the hfi. Unfortunately, it is not possible to determine the contribution of any one configuration to the exact wave function until one has included all configurations. We feel, therefore, that Nesbet's approach is not entirely justified, especially since he is working so far away from the correct energy.

The improvement in Q does not go parallel with the improvement of E, as is to be expected. However, in those cases where the energy is already good, the fluctuations in Q are generally small. We consider first our results with the James and Coolidge wave functions. The first line in Table I shows the results using a strict shell type of function as given by Eq. (21), i.e., with a symmetric core. This value of Q, like the energy, is already considerably better than that given by the RHF method. The succeeding lines in Table I show the results obtained with wave functions of the type given by Eq. (24) with $c_q = c_q'$ which we have called modified shell functions of the first type. These functions are all eigenfunctions of $\mathbf{S}^2$ and we see that the values of Q are quite good.

In Table II, we show the results of introducing functions with $\Omega_2\varphi \neq 0$ and with quartet character, as explained in the preceding section. Comparison of the second line of this table with the second line of Table I shows a lowering of the energy by a very small amount and a change in the hyperfine interaction by 1.4%. Comparison of line 4 of Table II with line 3 of Table I shows a similar result, and, finally, the comparison of line 6 of Table II with line 4 of Table I shows that the effect of destroying the symmetry of the core in our best function is to change the hfi by only 0.4%. Thus, relaxing the condition $\Omega_2\varphi = 0$, or adding some quartet state, gives no appreciable improvement in the hfi.

We want to draw attention here to the first two rows of Table II because they illustrate clearly one of the problems encountered in calculating the hfi. In going from the first to the second row, the energy has been improved very little and yet the value of Q has changed rather significantly. It should be noted, however, that in going from the first to the second line, we have balanced our treatment of up and down spins. The f terms take into account the interaction of the outer electron with one of the core electrons and the h terms treat the interaction with the other core electron of opposite spin orientation. Thus, if an f term of a given form is added, it is apparently quite important to add an h term of the same form.

We feel that these results, along with that obtained with the Ritter *et al.* function, show that, as far as Q is concerned, the improvement of the wave function by adding correlation is very important because it assures a proper behavior of the outer electron with respect to the core. Furthermore, they show that by adding correlation a very satisfactory value of the energy and of Q can be obtained with a doublet state of the first type which will always have a symmetrical core. We note here that the RHF lithium function is also of the first type, but, of course, it does not allow for correlation.

In much of the literature, however, values of the hfi (for lithium and other atoms) are calculated with the UHF functions. The reasons are in part of a practical nature, based on the fact that the method is manageable for a many-electron system and does not require an elaborate group theoretical analysis, and in part empirical, based on the fact that in a number of atoms the resulting values of Q come close to the experimental values. However, there are many other cases in which the method fails to be quantitatively reliable, e.g., $N(2p^3, {}^4S)$, neutral iron series atoms, etc. (see reference 8). As reasons of a more fundamental nature for choosing this particular class of functions are not available, one has appealed to physical intuition to argue that the flexibility of the wave function in the UHF method allows it to develop a tendency in the "right direction." From the above discussion it appears that, for Li, the development of the wave function is not in the right direction, notwithstanding the excellent result for Q.

It is of interest to consider the difference in the mathematical structure of Q_{UHF}, as found in Eq. (30) and of Q_{RHF}. The former, with the additional choice $\langle a|c\rangle = 0$ which is usually imposed on the orbitals, takes the form

$$Q_{\mathrm{UHF}} = a^2(0) - b^2(0) + c^2(0), \qquad (31)$$

where a and b are the two core orbitals, and c is orthogonal to the orbital which represents the electron with the same spin orientation as the outer electron. The value in the RHF method is simply

$$Q_{\mathrm{RHF}} = c^2(0). \qquad (32)$$

The result, Eq. (28) and its generalization Eq. (27), with $\varphi(123) = \varphi(213)$, is much more closely related to Eq. (32) than to Eq. (31), in that the direct contribution from the inner orbitals appears multiplied with the square of a small orthogonality integral. As we have given strong arguments in favor of the use of the first type doublet functions, the excellent value obtained for Li with Eq. (31) is either fortuitous or should be attributed to a hidden mathematical identity. The intuitive arguments, to which we have referred above, might indicate the direction in which such an identity could be found. We think that this is not the case, however. We have come to this conclusion on the basis of the following analysis of the Li case.

The physical meaning of Eq. (31) is habitually expressed in terms of the concept of "spin polarization," i.e., of polarization of the core due to exchange terms in the variational expression for the energy. We doubt that, within the framework of the UHF method, the concept of spin polarization of the core through the exchange interaction has been well defined. In any case, for the concept of "spin polarization," and, indeed, even of "core" to have, besides a mathematical definition, a physical meaning, they should apply to a much wider class of Ψ functions which are relevant to the physical system. An important point lies in the question of what constitutes a core.

There is little doubt that, in atoms in general, this is a useful physical concept, i.e., that in the true ground state it can be defined in a good approximation. Within the class of functions constructed from three orbitals, it is tempting to speak of a core when two of the orbitals have much smaller radii than the third. However, in a variational calculation, the radial dependence is usually not fixed. If it were left completely free, as in a Hartree-Fock calculation, the "sizes" would be a result and not input information. With this criterion, a RHF lithium function and also $\Psi_1^{(0)}$ would develop a core but it is doubtful that this would be true for $\Psi_2^{(0)}$. Although we have not attempted to verify this, it seems plausible that $\Psi_2^{(0)}$ with radial functions a, b, and c would approximate a function corresponding to the configuration $(1s)(2s)(3s)$ with small admixtures of $(1s)^2(2s)$, etc. Unfortunately, the situation with the UHF function is not clear because it is a mixture of doublet and quartet states. However, it seems likely that one is quite safe in speaking of a core so long as the admixture of the doublet component of type two and of quartet components is small.

In order to ascribe further physical properties, such as polarization, to the core in a function as it develops in a variational calculation, the function should not be subject to conditions which are at variance with known properties of the state which it is supposed to approximate. For this simple reason, the properties of a core developed by a function of type $\Psi_1^{(0)}$ (but with unrestricted analytical form of the radial functions a, b, and c) can be trusted more than those of a core obtained with a single-determinant (UHF) function which is neither of the first type nor free of quartet components.

With this discussion in mind, we shall now indicate schematically how the polarization of the core presumably comes about in the UHF calculations. The procedure is as follows:

$$\Psi_{\mathrm{RHF}} \propto \begin{pmatrix} a & a & c \\ \alpha & \beta & \alpha \end{pmatrix},$$

where Ψ_{RHF} is of the first type, i.e., the core is spatially symmetric; when we "let exchange interaction destroy symmetry," it becomes

$$\Psi_{\mathrm{UHF}} \propto \begin{pmatrix} a & b & c \\ \alpha & \beta & \alpha \end{pmatrix},$$

where Ψ_{UHF} contains type one, type two, and quartet components and the core is asymmetrical; and the results are a very small lowering of the energy and a large asymmetry (polarization) of the core which gives a large change in Q attributed to the core polarization. Our calculations show that we can carry out exactly the same procedure with wave functions which have correlation and get quite different results. Thus, for example, Ψ is of the first type and well correlated; when we "let exchange interaction destroy symmetry," Ψ becomes a mixture of type one, type two, and quartet components, the core being asymmetrical; and the results are a very small lowering of the energy, a small asymmetry of the core, and a small improvement in Q. The mechanism which supposedly produces the polarization is exactly the same in both cases, i.e., the exchange interaction, but the result is quantitatively and qualitatively different. As we have established several reasons for preferring the latter calculation, we may conclude that the effect of exchange or spin polarization, *as it is introduced by the* UHF *method*, is not a physical effect. It cannot, therefore, be used as an argument to explain why Q_{UHF} for Li comes out so well.

However, we have good reasons for contending that it is not the exchange interaction which produces the asymmetry in either of the above cases. James and Coolidge were convinced by their calculations that the nature of the state of the outer electron affected the core very little. The same conclusion appears from the work of Ritter *et al.* on the excited states of Li which shows that the splitting of the inner shell in their calculations is almost completely independent of the value of n in the $(1s)^2ns$ notation. We conclude that the outer electron does not influence the splitting which, evidently, is due partially to core correlation and hence the name "correlation splitting" which is frequently used. Much of the splitting in the Ritter *et al.* calculations is due simply to an improved analytical approximation of the RHF $1s$ orbital as can be seen by writing their wave function in a configuration interaction form.[13]

We wish to speculate on the effect actually introduced by the UHF method in lithium. The UHF lithium function is a mixture of doublet and quartet components. Minimization of the energy expression given by the function will result in a compromise between the tendency to lower the energy because of the Coulomb correlation introduced and the tendency to raise the energy introduced by the inclusion of the quartet component. The correlation contribution just dominates and so there is a small lowering of the energy; however, the quartet component should contribute substantially to the spin density—hence part of the improvement over RHF which is found to result. Part of the improvement in the hfi is due to the correlation in the doublet component. This interpretation is supported by the results of projecting out a UHF lithium function *after* energy minimization. It is then found that the hfi is worse than before projection but it is still better than the RHF value. The projection has removed the quartet component but allowed some of the correlation in the doublet components to remain. Of course, after projection, the parameters do not minimize the doublet component and the wave function is not of pure type one. As greater flexibility is built into the trial function, the variation procedure will cause the effect of the quartet component to become less important until finally, if one had the exact ground state wave function of lithium, the quartet component would be completely absent; but then the doublet function would be completely correlated and, evidently, almost entirely of the first type, i.e., with a symmetric core.

Note added in proof. In a private communication, Dr. A. W. Weiss has informed us of the results for the hfi which he has obtained with his configuration interaction wave functions. He obtains values of Q which are too low by about 10%. While it is true that this result is disappointing it is, perhaps, not too surprising

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[13] We want to thank J. Linderberg for pointing this out to us.

in light of our own experience with the James and Coolidge wave functions.

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Positronium Decay in Teflon. Influence of Lattice Transitions

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The decay of positronium in Teflon has been investigated at temperatures between −200 and +280°C and in greater detail in the region of lattice transitions around room temperature. It is found that the long lifetime τ_2 increases sharply in the interval between 20 and 50°C, while the probability of formation of positronium shows a drop around 20°C. Evidence of the reversibility of the lattice transitions results from the decay features of positronium.

The decay of positrons in Teflon has been investigated by several authors[1] with the help of different techniques and in a wide range of temperature, up to 300°C. Teflon is considered to be a suitable material for checking the validity of the theory of pickoff annihilation of positrons bound in orthopositronium, because both the τ_2 lifetime and the probability of positronium formation were found to be smooth functions of temperature. This seems to indicate that the well-known temperature effects can be rather accurately described in terms of the "excluded volume" effect.[2]

However, remarkable differences in the values of the τ_2 lifetime around room temperature were found with different samples and are reported in the literature. The occurrence of lattice transitions involving changes of density (at 19 and 30°C) might be thought to be responsible for these differences, though a search for changes in the τ_2 decay due to the lattice transitions was reported to be negative.[3]

In the measurements described here, differently processed specimens from a number of suppliers were used, the τ_2 lifetime at 20°C proving different from specimen to specimen, in the range between 1.8×10^{-9} sec and 3.3×10^{-9} sec. Moreover, it was noticed that τ_2 increases remarkably after short thermal treatments such as the ones usually performed to obtain commercial Teflon in the shape of rods or plates. Systematic measurements of positronium decay were consequently carried out with a method already described,[4] the specimens being in the shape of cylinders, 10 mm long and 8 mm in diameter, obtained with pure powder[5] compacted at room temperature. Pure powder was chosen for the final measurements because it exhibits the shortest τ_2 lifetime at 20°C, according to preliminary results.

Figure 1 shows the τ_2 lifetime vs temperature for such specimens, and the percentage of positrons decaying through τ_2 is given as a function of temperature in

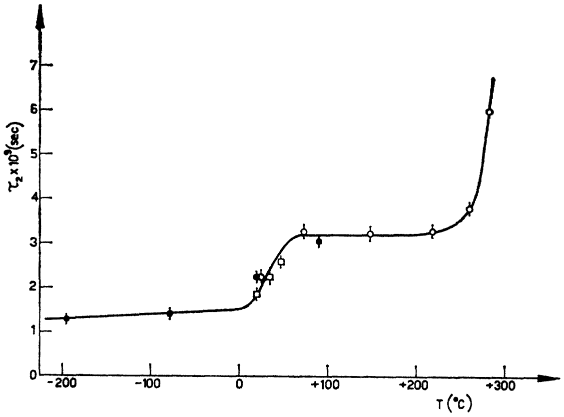

Fig. 1. The long lifetime (τ_2) of positronium vs temperature. The results obtained with three specimens are plotted.

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[1] R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953); R. L. de Zafra and W. T. Joyner, *ibid.* **112**, 19 (1958); A. Bisi, A. Fasana, E. Gatti, and L. Zappa, Nuovo Cimento **22**, 266 (1961).

[2] W. Brandt, S. Berko, and W. W. Walker, Phys. Rev. **120**, 4 (1960).

[3] G. P. Furukawa, R. E. McCoskey, and G. J. King, J. Res. Natl. Bur. Std. **49**, 273 (1952).

[4] C. Cottini, G. Fabri, E. Gatti, and E. Germagnoli, J. Phys. Chem. Solids **17**, 65 (1960).

[5] Kindly supplied by Firm Montecatini.