

## Magnetic Hyperfine Structure of the Ground State of Lithium\*†

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The magnetic hyperfine splitting of the  ${}^2S$  ground state of the lithium atom is calculated. It is shown that the discrepancy between experiment and the value calculated in the traditional Hartree-Fock approximation can be accounted for quantitatively by the exchange polarization effect, which distorts one  $1s$  orbital relative to the other. The present calculation obtains a value within one percent of the experimental value. A general procedure is proposed for evaluating operators that do not commute with the Hamiltonian, when approximate variational methods must be used.

## INTRODUCTION

RECENTLY, several calculations have been reported concerned with *ab initio* evaluation of the electronic contribution to the magnetic hyperfine structure of the  ${}^2S$  ground state of the lithium atom.<sup>1,2</sup> It is found that this effect is considerably underestimated by the traditional Hartree-Fock electronic wave function,<sup>2</sup> but that if allowance is made for the polarization of the  $1s$  orbital due to the unbalanced spin, a significantly better value is obtained. A general discussion of this polarization effect, with special reference to the lithium atom, has been given in an earlier paper.<sup>3</sup> The case of the lithium atom has also been discussed by Pratt.<sup>4</sup>

The present paper reports results of a series of calculations undertaken to see if this exchange polarization effect could account quantitatively for the hyperfine structure of lithium. The calculations reported here followed the procedure of an approximate matrix Hartree-Fock calculation by the method of symmetry and equivalence restrictions,<sup>3</sup> followed by the evaluation of configuration interaction effects by second-order perturbation theory. The single-particle Hamiltonian was taken to be that appropriate to the occupied  $2s$  orbital and the  $1s$  orbital of the same spin.

Both the traditional Hartree-Fock method and the method of symmetry and equivalence restrictions constrain the two  $1s$  spatial orbitals to be identical. This must be compensated for by certain configuration interaction effects that would be absent, to second order in perturbation theory, if the unrestricted Hartree-Fock method were used.<sup>3</sup> The principal result of the present work is to indicate that these specific

configuration interaction effects can account for the hyperfine splitting of lithium to within one percent of the experimental value. Essentially the same result should be obtained by an unrestricted Hartree-Fock calculation, if carried out with sufficient accuracy. Various results are listed in Table I.

The discrepancy between the present results and those of both Sachs<sup>2</sup> and Cohen, Goodings, and Heine<sup>1</sup> can be attributed to the use of a considerably larger set of basis functions of the type  $e^{-\zeta r}$  in the present work than in either of these other calculations. Since the value of the electronic orbitals at the nucleus is zero except for the contribution of basis functions of this type, the hyperfine splitting is sensitive to such functions. This could easily be overlooked since the energy effects involved are very small.

The unrestricted Hartree-Fock function obtained by Sachs<sup>2</sup> contains a  ${}^4S$  component, and cannot be compared directly with the pure  ${}^2S$  atomic state. For this reason only the projected unrestricted function of Sachs, which is a pure doublet, is listed in Table I.

In the  ${}^2S$  state of an atom, the separation of the hyperfine structure levels is given by<sup>5</sup>

$$\Delta E = h\nu = (8\pi/3)\mu_0\mu_I[(2I+1)/I](\rho_+ - \rho_-). \quad (1)$$

Here  $(\rho_+ - \rho_-)$  is the excess of electronic density with positive spin over that of negative spin, measured at the atomic nucleus.

For calculation in terms of the normalized radial factors of electronic orbitals, it is convenient to introduce the radial operator, for an atom with  $N$  electrons,

$$f = \sum_{i=1}^N \frac{2\delta(r_i)}{r_i^2} \sigma_{zi}, \quad (2)$$

such that  $\int_0^\infty 2\delta(r)dr = 1$ , and

$$\langle f \rangle = 4\pi(\rho_+ - \rho_-), \quad (3)$$

evaluated for the state  $M_s = +\frac{1}{2}$ .

For the  $\text{Li}^7$  nucleus, for which  $I = \frac{3}{2}$ , the experimental value of  $\mu_I$  is 3.256310 nuclear magnetons<sup>6</sup> and of  $\Delta\nu$ ,

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<sup>1</sup> M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

<sup>2</sup> L. M. Sachs (to be published).

<sup>3</sup> R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

<sup>4</sup> G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).

<sup>5</sup> E. Fermi, Z. Physik **60**, 320 (1930).

<sup>6</sup> N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), p. 172.

TABLE I. Results of variational calculations.

Parameters $\zeta$	Restricted Hartree-Fock		Configuration interaction	
	$E$ , a.u.	$\langle f \rangle$ , $a_0^{-3}$	$E$ , a.u.	$\langle f \rangle$ , $a_0^{-3}$
5.0	-7.427893	2.50517	...	...
6.0	-7.428477	2.53131	...	...
7.0	-7.428745	2.54454	-7.428834	3.25263
8.0	-7.428771	2.54897	-7.428860	3.23853
9.0	-7.428627	2.54758	...	...
1.75, 3.5, and 7.0	-7.431765	2.26782	-7.431849	2.86996
2.00, 4.0, and 8.0	-7.431608	2.29215	-7.431693	2.87223
Traditional Hartree-Fock <sup>a</sup>				2.0945
Unrestricted Hartree-Fock, by perturbation method <sup>b</sup>				2.70
Projected unrestricted Hartree-Fock <sup>a</sup>				2.5665
Experimental value				2.9062

<sup>a</sup> See reference 2.

<sup>b</sup> See reference 1. Since this result is for a wave function that contains a quartet admixture it is not strictly comparable to the other results tabulated, which are all for pure doublet wave functions.

803.512 Mc/sec.<sup>7</sup> With fundamental constants from the compilation by Cohen et al.,<sup>8</sup> the experimental value of  $\langle f \rangle$  is

$$\langle f \rangle_{\text{exp}} = 2.9062a_0^{-3}. \quad (4)$$

#### DESCRIPTION OF CALCULATIONS

A series of preliminary calculations, not listed in Table I, indicated that configuration interaction with configurations containing  $p$  or  $d$  orbitals, or with configurations other than those specifically identified with the exchange polarization effect, had a negligible effect on the hyperfine splitting. It is important to emphasize that these configurations, which are the dominant terms in a calculation of the correlation energy, have little effect on the hyperfine splitting. Since the energy contributed by different excited configurations is additive in the second order of perturbation theory, it follows that the total energies given in Table I could be greatly improved by adding in the effect of such configurations. But this would have no significant effect on the value of the hyperfine splitting.

The configurations which do have a significant effect on the hyperfine splitting have a very small effect on the total energy. They represent a modification of the  $1s$  orbitals near the nucleus, so as to compensate for the unsymmetrical exchange interaction with the singly-occupied  $2s$  orbital. Even though the energy differences are small, all integrals needed for the matrix Hartree-Fock and configuration interaction calculations were evaluated to an accuracy on the order of one percent of the calculated differences in energies. This justifies the variational procedure used, since the energy minima found are numerically significant.

All of the calculations listed in Table I used a basis of  $s$  orbitals that included three normalized radial functions proportional to

$$e^{-2.757r}, \quad e^{-1.0r}, \quad \text{and} \quad re^{-0.700r}. \quad (5)$$

<sup>7</sup> P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

<sup>8</sup> E. R. Cohen, J. W. M. DuMond, T. W. Layton, and J. S. Rollett, Revs. Modern Phys. **27**, 363 (1955).

The numerical Hartree-Fock orbitals<sup>9</sup> can be expanded to reasonable accuracy in terms of these three functions. In addition, either one or three functions of the form  $e^{-\zeta r}$  were added to the set, as indicated in the table.

The matrix Hartree-Fock calculation was repeated for different values of the parameter  $\zeta$ , with only one function  $e^{-\zeta r}$  added to the set of Eq. (5). A limited configuration interaction calculation, using only the configurations identified with the exchange polarization effect, was carried out for the two values of  $\zeta$  (7.0 and 8.0) for which the Hartree-Fock energy took its lowest values.

The basis set was then augmented by addition of orbitals with exponents  $\zeta/2$  and  $\zeta/4$ , and the same calculations carried out. From the variational principle, the effect of increasing the orbital basis set in this manner can only be to improve the wave function, with a first order effect on any operator not commuting with the Hamiltonian. The fact that the two augmented sets (with  $\zeta=7.0$  and  $8.0$ , respectively) lead to values of the hyperfine splitting closer to each other after configuration interaction than before, and closer to the experimental value than any of the other results in the variational sequence, indicates that the present result is not fortuitous. However, it could only be checked by a more accurate calculation of the same nature.

An attempt was made to vary the parameter  $\zeta$  for a series of augmented sets (six independent radial functions). The computer programs used could not work accurately with functions as nearly linearly dependent as in the augmented set with  $\zeta < 7.5$ , so results for lower values of  $\zeta$  are not available. A range of values of  $\zeta$  between 7.0 and 12.0 gave values of  $\langle f \rangle$  between 2.87 and 3.03.<sup>10</sup> The energy variation was very small in this range, but the two lowest energies are those in Table I.

<sup>9</sup> V. Fock and M. J. Petrashen, Physik Z. Sowjetunion **6**, 368 (1934); **8**, 547 (1935).

<sup>10</sup> R. K. Nesbet, Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1956 (unpublished), p. 47.

## DISCUSSION

The present calculations exemplify a practical problem that can occur in any attempt to calculate a physical property other than the energy of a system of more than a very small number of particles. In such cases variational methods must be used, with the goal of obtaining a wave function sufficiently close to an eigenfunction of the Hamiltonian that mean values of other operators, not necessarily commuting with the Hamiltonian, will be close to the values obtained for a true eigenfunction. If the wave function depends on a number of parameters, ordinarily one would proceed by a steepest descent calculation to approach a stationary value of the energy, expressed as a function of these parameters. By carrying such a calculation through to its limit, eventually any property of the system other than the energy would approach its correct value.

As shown in the present calculations, it can happen that certain changes in parameters have a large effect on the energy with only a small effect on the mean value of some operator other than the Hamiltonian, and conversely. Under these circumstances the error in the calculated value of such an operator is not necessarily small, even though the error in the energy is small.

This difficulty can be dealt with by a slight modification of the method of steepest descent. If parameters have been varied sufficiently that further energy variations are small, a final sequence of variations should be carried out along the path, in the parameter hyperspace, determined by the gradient of the mean value of the auxiliary operator under consideration. The energy should be made stationary along this path. This process ensures that any further variation of the energy will be along a path in the parameter hyperspace orthogonal to that of greatest change of the auxiliary operator. The auxiliary operator is itself stationary for such variations.

The calculations reported here followed this general procedure, simplified by the fact that different contributions to the total energy are additive, in second-order perturbation theory, so that a large class of variations that do not appreciably affect the auxiliary operator can be neglected.

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## Total Neutron Cross Sections of Helium, Neon, Argon, Krypton, and Xenon

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The total neutron cross sections of the noble gases helium, neon, argon, krypton, and xenon have been measured for neutron energies from 120 keV to 6.2 MeV and from 12.1 MeV to 19.8 MeV by a transmission experiment. The neutrons were produced using the  $\text{Li}^7(p,n)\text{Be}^7$ , the  $\text{T}(p,n)\text{He}^3$ , the  $\text{D}(d,n)\text{He}^3$ , and the  $\text{T}(d,n)\text{He}^4$  reactions in the appropriate energy intervals. A Van de Graaff accelerator was the source of the protons or deuterons. In general, the results obtained agree with previous work where such work exists. A previously unobserved S-wave scattering resonance was found in neon at about 500 keV, indicating the presence of an excited state in  $\text{Ne}^{21}$  with  $J = \frac{1}{2}$  and even parity. The results for argon, krypton, and xenon exhibit general agreement with the cross sections of neighboring elements, as would be expected from the previously observed smooth variation of the  $\sigma(A,E)$  surface.

## I. INTRODUCTION

IN the present experiment, total neutron cross sections of helium, neon, argon, krypton, and xenon were obtained from 120 keV to 6.2 MeV, and from 12.1 to 19.8 MeV. Results have previously been published by other investigators for some of these elements at energies within these intervals. The total neutron cross section of helium has been reported up to about 6.1 MeV and from 12.5 MeV to 20.5 MeV.<sup>1-6</sup> Previous

measurements of the neon cross section extend from 0.8 MeV to 3.5 MeV,<sup>7-8</sup> and results for argon have been

<sup>1</sup> J. H. Coon, Bondelid, and Phillips, quoted in J. H. Coon, E. R. Graves, and H. H. Barschall, *Phys. Rev.* **88**, 562 (1952).

<sup>2</sup> R. B. Day and R. L. Henkel, *Phys. Rev.* **92**, 358 (1953).

<sup>3</sup> J. H. Coon, quoted in J. D. Seagrave, *Phys. Rev.* **92**, 1222 (1953).

<sup>4</sup> Unpublished Los Alamos work, results given in *Neutron Cross Sections*, compiled by D. J. Hughes and R. Schwartz, Brookhaven National Laboratory Report BNL-325 (Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 1958), 2nd ed.

<sup>5</sup> C. P. Sikkema, *Nuclear Phys.* **3**, 375 (1957).

<sup>6</sup> H. O. Cohn and J. L. Fowler, *Phys. Rev.* **114**, 194 (1959).

<sup>1</sup> T. A. Hall and P. G. Koontz, *Phys. Rev.* **72**, 196 (1947).

<sup>2</sup> S. Bashkin, F. P. Mooring, and B. Petree, *Phys. Rev.* **82**, 378 (1951).