

Hyperfine Splitting of the Lithium Ground State*

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(Received October 12, 1959)

The results of calculations of the hyperfine splitting of the lithium atom ground state are reported. These were done by the Hartree-Fock (HF), unrestricted Hartree-Fock (UHF) and projected UHF approximations to the ground-state eigenfunctions. The exchange polarization effect allowed by the UHF method yields a 34.9% increase in the hyperfine splitting compared to the HF method.

THE hyperfine splitting of the lithium atom ground states results from the Fermi¹ contact interaction between the nucleus and the electrons:

$$H_{eo} = \frac{8\pi}{3} \left(\frac{\beta_n}{I} \right) \left(\frac{\beta_e}{s} \right) \mathbf{I} \cdot \sum_{i=1}^3 \mathbf{s}_i \delta(\mathbf{r}_i), \quad (1)$$

where β_n and β_e are the nuclear and electronic magnetic moments, I and s are the nuclear and electronic spin magnitudes, and $\mathbf{I}$ and $\mathbf{s}_i$ are the nuclear and electronic spin operators.

A rigorous first-order calculation of the hyperfine splitting would require the use of the exact ground eigenstates of a Hamiltonian which included all interactions of lesser order than the magnetic interaction with the nucleus. Since these are inaccessible, it is necessary to use approximate unperturbed wave functions. The most common approximation is that of a single determinantal wave function constructed from variationally determined spin orbitals which are equivalent in pairs in the sense that the (space) orbitals appearing as factors in the occupied spin orbitals are either identical in pairs or mutually orthogonal. This procedure will be henceforth referred to as the Hartree-Fock (HF) approximation. For an electronic configuration $1s^2 2s$, the HF approximation yields the explicit expression for the splitting:

$$\Delta E = (8\pi/3) (\beta_n/I) \beta_e (2I+1) \phi_{20}^2(0), \quad (2)$$

where $\phi_{20}(\mathbf{r})$ is the (real) $2s$ orbital.

Proposals have been made to relax the restriction of equivalence and allow different (space) orbitals for the paired spin orbitals when the variational principle is applied.²⁻⁴ Instead of treating the full degenerate problem, that is, using a linear combination of the determinants possible with the different (space) orbitals, one still assumes a single determinantal wave function. This function is not an eigenfunction of $\mathbf{S}^2$, but is a mixture of the possible spin states. This procedure, known as the unrestricted Hartree-Fock

(UHF) approximation, should lead to a lowering of the energy below that of the HF approximation since the wave function is allowed more freedom. If one uses for the UHF wave function corresponding to the $1s\alpha$, $1s'\beta$, $2s\alpha$ configuration the expression

$$D_2 = A \{ 1s\alpha, 1s'\beta, 2s\alpha \},$$

where A is the antisymmetrizing operator, then the hyperfine splitting resulting from the Hamiltonian (1) is given by

$$\Delta E = (8\pi/3) (\beta_n/I) \beta_e (2I+1) \times [\phi_{10}^2(0) - \phi_{1'0}^2(0) + \phi_{20}^2(0)]. \quad (3)$$

The wave function D_2 is a mixture of doublet and quartet components, whereas the lithium ground state is a doublet. We may project out the doublet component of D_2 by applying to it the projection operator $\mathcal{O}_2$,⁵

$$\mathcal{O}_2 D_2 = \frac{\mathbf{S}^2 - \frac{3}{2}(\frac{3}{2}+1)}{\frac{1}{2}(\frac{1}{2}+1) - \frac{3}{2}(\frac{3}{2}+1)} D_2 = \frac{1}{3} [2D_2 - D_1 - D_3] = \frac{1}{3} \Psi_2, \quad (4)$$

where the subscript on each D refers to the orbital associated with beta spin, the numbers 1, 2, 3 referring to $1s$, $1s'$, and $2s$, respectively. The splitting calculated using Ψ_2 is given by

$$\Delta E = (8\pi/3) (\beta_n/I) \beta_e (2I+1) [6 + 3(\phi_{10}, \phi_{1'0})^2 + 3(\phi_{1'0}, \phi_{20})^2]^{-1} [4\phi_{10}^2(0) - 2\phi_{1'0}^2(0) + 4\phi_{20}^2(0) + 5\phi_{10}^2(0)(\phi_{1'0}, \phi_{20}) + 5\phi_{20}^2(0)(\phi_{10}, \phi_{1'0}) - 10\phi_{10}(0)\phi_{20}(0)(\phi_{10}, \phi_{1'0})(\phi_{1'0}, \phi_{20}) - 2\phi_{1'0}(0)\phi_{20}(0)(\phi_{1'0}, \phi_{20}) - 2\phi_{10}(0)\phi_{1'0}(0)(\phi_{10}, \phi_{1'0})], \quad (5)$$

where (a, b) is the inner product of (space) functions a and b .

The case of the lithium atom was discussed in some detail by Pratt⁴ who suggested that the exchange polarization allowed in the UHF method afforded a direct approach to the calculation of hyperfine splitting for systems where the equivalence restriction would give no splitting. Subsequently, Wood and Pratt⁶ applied a simplified form of UHF to the iron atom and

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ E. Fermi, *Z. Physik* **60**, 320 (1930).

² J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 571 (1954).

The explicit formalism which was utilized is given in this letter.

³ G. B. Berthier, *J. chim. phys.* **51**, 363 (1954).

⁴ G. W. Pratt, Jr., *Phys. Rev.* **102**, 1303 (1956).

⁵ P. O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).

⁶ J. H. Wood and G. W. Pratt, Jr., *Phys. Rev.* **107**, 995 (1957).

the manganese divalent ion. Cohen, Goodings, and Heine⁷ have recently calculated the polarization effect in lithium and sodium by a perturbation treatment using the numerical wave functions of Fock and Petrashen.⁸ Having in hand a HF calculation of the ground state of the lithium atom,⁹ we have applied the UHF method to the same problem for comparison.

An analytical expansion of the form

$$\phi_i = \sum_{m,n} \chi_{mn} c_{i;mn}, \quad (6)$$

in terms of Slater-type functions

$$\chi_{mn} = \frac{(2\zeta_m)^{n+\frac{1}{2}}}{[4\pi(2n)!]^{\frac{1}{2}}} r^{n-1} e^{-\zeta_m r} \quad (7)$$

was assumed for the orbitals. The exponents, three being necessary for two orbitals, were adjusted to minimize the total energy using two powers of r . Having ascertained this minimum, the expansion was carried to four

TABLE I. Expansion parameters for the UHF lithium atom ground-state orbitals.^a

mn	ζ_m	$c_{1s;mn}$	$c_{1s';mn}$	$c_{2s;mn}$
11	2.40	0.000000 ^b	0.000000	-0.000000
12		0.395230	0.381699	0.148014
13		-0.102567	-0.087028	-0.036137
14		0.006717	-0.000425	0.033464
21	0.67	0.018164	0.028171	-0.015645
22		-0.017809	-0.027705	-1.071172
23		0.008973	0.014042	0.062361
24		-0.001992	-0.003142	-0.031610
31	4.50	0.485226	0.482485	0.076064
32		0.196046	0.196857	0.022892
33		0.076357	0.078059	0.004458
34		0.034200	0.035873	0.002265

^a These parameters are defined by Eqs. (6) and (7).

^b All numbers are rounded to six decimal places.

powers of r to demonstrate convergence. The expansion coefficients were determined numerically for each basis set utilizing the Roothaan SCF (self-consistent field) procedure.¹⁰ The coefficients resulting from the UHF calculations are listed in Table I, those for the HF calculations were reported at the International Conference on Molecular Quantum Mechanics, 1959, and will appear in a forthcoming publication of the proceedings of that conference.⁹ All calculations were carried out on the IBM-704 computer at Argonne National Laboratory

The expectation value of S^2 for the UHF function D_2 is given by

⁷ M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

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

⁹ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. (to be published).

¹⁰ C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

TABLE II. Magnitude of orbitals at the origin.

Orbital	HF ^a	UHF	$\phi_{\text{UHF}} - \phi_{\text{HF}}$
$\phi_{10\alpha}(0)$ a.u.	2.61282	2.61891	0.03186
$\phi_{20\alpha}(0)$ a.u.	0.40826	0.40482	-0.00280
$\phi_{1'0\beta}(0)$ a.u.	2.61282	2.60725	-0.02908

^a These values were obtained from a calculation which yielded a slightly lower energy than that obtained in reference 9.

$$\begin{aligned} (D_2|S^2|D_2) &= (D_2|(7/4)D_2 + D_1 + D_3) \\ &= (7/4) - (\phi_{10}, \phi_{1'0})^2 - (\phi_{1'0}, \phi_{20})^2 \\ &= (7/4) - (0.99999075)^2 - (-0.00166552)^2 \\ &= 0.75001573. \end{aligned} \quad (8)$$

For lithium the UHF procedure thus yields almost a pure doublet.

The values of the orbitals at the origin resulting from the HF and UHF calculations¹¹⁻¹³ are listed in Table II and it is these values which were utilized for the hyperfine splittings listed for this calculation in Table III.

Using the value $\beta_n(\text{Li}^7) = 3.256310$ nuclear magnetons¹⁴ and the fundamental constants as given by Cohen, DuMond, Layton, and Rollett,¹⁵ one obtains for Li^7 the numerical constant $(8\pi/3)\beta_n\beta_e(2+I^{-1}) = 3474.38a_0^3$ Mc/sec which is used to compute the entries of Table III.

As is evident from Table III, the UHF procedure yields a total electronic energy only very slightly below that of the HF, the difference coming in the sixth significant figure. The UHF hyperfine splitting is in much better agreement with experiment, yielding 97% of the experimental value compared to 72% for the HF. This substantial increase was predicted by Cohen, Goodings, and Heine⁷ in their perturbation calculation of the exchange polarization effect. As they point out,

TABLE III. Comparison of hyperfine splittings and total energies for Li^7 .

Method	Reference	Total energy (atomic units)	ΔE (Mc/sec)	$\Delta E/\Delta E_{\text{exp}}$
HF	Fock and Petrashen ⁸	-7.21	573	0.713
HF	This calculation	-7.432727	579.10	0.721
HF	Nesbet ¹¹	-7.43259	585.813	0.729
UHF by perturbation	Cohen, Goodings, and Heine ⁷	...	747	0.930
UHF	This calculation	-7.432751	781.10	0.972
Projected	This calculation	...	709.59	0.883
UHF				
Configuration interaction	Nesbet ¹²	-7.431849	793.493	0.988
Experimental	Kusch and Taub ¹³	-7.478	803.512	1.000

¹¹ R. K. Nesbet, Quarterly Progress Report No. 21, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished). Nesbet, reference 12, reports a better HF value, viz., $\Delta E = -627.005$; this value, however, corresponds to a higher energy, $E = -7.431765$.

¹² R. K. Nesbet, Quarterly Progress Report No. 22, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

¹³ P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

¹⁴ N. F. Ramsey, *Nuclear Moments* (Oxford University Press, New York, 1956), p. 172.

¹⁵ E. R. Cohen, J. W. M. DuMond, T. W. Layton, and J. S. Rollett, Revs. Modern Phys. **27**, 363 (1955).

the improvement is obtained by taking cognizance of the different Hamiltonians for particles of opposite spins. They do not, however, list the individual differences of the separate orbitals, but only note the over-all change at the origin. The self-consistent field calculation carried out shows that the increase over the HF value is not due to a change in the $2s$ orbital, which remains virtually the same, but is in fact due to the net magnetic moment set up by the difference in the inner orbital charge densities as may be seen by Table II.

The results clearly indicate that the UHF approximation is considerably better than the HF approximation for the calculation of hyperfine splittings. The improvement is sufficient to outweigh the drawback of inequivalent orbitals and the resulting unaesthetic

lack of symmetry of the total UHF wave function. In this connection, it should be noted that the inner product of the UHF inner orbitals is still virtually unity. It is of particular interest to note that if one attempts to restore the over-all symmetry by projecting out the doublet, Ψ_2 , a much poorer value for the hyperfine splitting is obtained.

ACKNOWLEDGMENTS

The author would like to express his thanks to Dr. T. L. Gilbert and Professor P. G. Lykos for suggesting this line of investigation and for stimulating discussions during the course of the work, and to Professor C. C. J. Roothaan for his able introduction to the SCF formalism.

PHYSICAL REVIEW

VOLUME 117, NUMBER 6

MARCH 15, 1960

Evaluation of the Interaction Effect in n - p Capture*

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(Received October 8, 1959)

Recent information about the nuclear force has been used to recalculate the thermal n - p capture cross section, and a value of 0.303 ± 0.012 b is obtained. The comparison of this number with the experimental cross section of 0.3315 ± 0.0017 b indicates an "interaction" magnetic dipole moment contribution of 0.028 ± 0.012 b.

I. INTRODUCTION

AN earlier paper under the above title¹ discussed the accuracy with which the thermal n - p capture cross section could be computed from the usual phenomenological theory, the theory which ignores all "interaction effects." Interaction effects are those modifications of the two-body magnetic moment operator which are caused by the mesic nature of the nuclear interaction; in their absence the magnetic moment operator in n - p capture is the sum of the spin magnetic moments of two free nucleons. Meson theory predicts a small value for the interaction effects, but it gives very little more information than that. However, further information is available from the n - p capture experiment, the difference between the observed cross section and the predicted phenomenological cross section being a measure of the interaction effect. The present paper continues the task of assessing the accuracy which can be achieved by the theory.

In I it was concluded that an interaction effect indeed could be detected, and that it gave rise to an $8 \pm 5\%$ increase in the cross section. This determination was of

marginal accuracy. It seemed sufficiently in disagreement with the one-percent effect Sugawara found from meson theory,^{2,3} that he was led to criticize the values and errors chosen for the effective ranges in I. His choices for these quantities considerably increased the estimated error of the prediction and slightly decreased the discrepancy with experiment. Further discussion of the effective ranges will be given in the present paper in an attempt to settle the disagreement. For the sake of background it is interesting to note at this point that other experiments with the two-body system also point to large interaction effects; these effects also conflict with meson theory predictions, so a similar conflict in the present case need not seem surprising. The experiments in question concern deuteron photodisintegration and the deuteron magnetic moment. The photodisintegration seems at first sight to be in excellent agreement with the meson theory. Thus a negligible interaction modification of the medium-energy photodisintegration was found by Pearlstein and Klein,⁴ and careful phenomenological calculations⁵ show that this

² M. Sugawara (private communication).

³ L. Hulthén and M. Sugawara, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. 39. This article effectively summarizes Sugawara's work on the two-nucleon system.

⁴ L. D. Pearlstein and A. Klein, *Bull. Am. Phys. Soc.* 4, 268 (1959); also *Phys. Rev.* (to be published).

⁵ J. J. de Swart and R. E. Marshak, *Phys. Rev.* 111, 272 (1958).

* Work done at the Sarah Mellon Scaife Radiation Laboratory and assisted by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.

† National Science Foundation Cooperative Graduate Fellow.

¹ N. Austern, *Phys. Rev.* 92, 670 (1953). Henceforth this paper will be denoted I.