

## Interaction of Conduction Electrons and Nuclear Magnetic Moments in Metallic Lithium\*

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The probability density at the nucleus of a metallic lithium conduction electron on the Fermi surface is calculated in the spherical approximation, giving the value  $P_F=0.11\pm 0.01$  atomic unit. This is in good agreement with measurements of the nuclear magnetic resonance shift discovered by Knight and with recent determinations by Schumacher, Carver, and Slichter of the paramagnetic susceptibility.

### I. INTRODUCTION

A NUMBER of years ago Knight<sup>1</sup> discovered a significant difference between the frequencies at which nuclear resonance occurs when a given element is in the form of a metal, on the one hand, and when it is part of a nonmetallic compound, on the other. This shift was attributed by Townes *et al.*<sup>2</sup> to the additional magnetic field at the nucleus,  $\Delta H$ , resulting from a partial alignment of the spins of the conduction electrons. They derived the expression

$$\frac{\Delta H}{H} = \frac{hc\Delta\nu IM}{\mu_I\mu_0(2I+1)} \frac{P_F}{\chi_p P_A}, \quad (1)$$

where the symbols have the following meaning:  $\Delta\nu$  is the hyperfine splitting of the atomic ground state;  $I$  is the nuclear spin;  $M$  is the mass of one atom;  $\mu_I$  is the nuclear magnetic moment;  $\mu_0$  is the Bohr magneton;  $\chi_p$  is the paramagnetic susceptibility per unit mass; and  $P_A$  represents the probability density of the valence electron at the nucleus in the free atom, while  $P_F$  is the same quantity for the metallic conduction electrons, averaged over the Fermi surface.

Subsequently Korringa<sup>3</sup> proposed that the longitudinal relaxation time  $T_1$  is connected with this shift by the following approximate relation:

$$T_1 = \frac{\mu_0^2}{\pi\hbar(kT)\gamma_I^2} \left(\frac{\Delta H}{H}\right)^{-2}, \quad (2)$$

where  $\gamma_I = \mu_I/\hbar I$ .

Since all other quantities are known from independent measurements, knowledge of the Knight shift or of  $T_1$  gives one information about the quantity  $\chi_p(P_F/P_A)$ . In the case of metallic Li, direct measurement of  $\Delta H/H$  by Gutowsky and McGarvey<sup>4</sup> leads to the result

$$\chi_p(P_F/P_A) = 1.73 \pm 0.02 \times 10^{-6} \text{ cgs units}, \quad (3)$$

and preliminary measurements of  $T_1$  by Norberg<sup>5</sup> are in good agreement with this value.

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<sup>1</sup> W. D. Knight, *Phys. Rev.* **76**, 1259 (1949).

<sup>2</sup> Townes, Herring, and Knight, *Phys. Rev.* **77**, 852 (1950).

<sup>3</sup> J. Korringa, *Physica* **16**, 601 (1950).

<sup>4</sup> H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1952).

<sup>5</sup> R. E. Norberg (private communication).

Recent measurements of  $\chi_p$  by Schumacher *et al.*<sup>†</sup> give the value,

$$\chi_p = (3.74 \pm 0.6) \times 10^{-6} \text{ cgs mass units}, \quad (4)$$

which is in good agreement with unpublished calculations by Pines.<sup>‡</sup> Thus these data indicate that

$$(P_F/P_A)_{\text{expt}} = 0.46 \pm 0.07. \quad (5)$$

It is of interest to examine whether the band picture of the metallic electrons in Li can account for this value. Kohn and Bloembergen,<sup>6</sup> using a variational method with certain *s*, *p*, and *d* functions, suggested by perturbation theory, obtained a value of 1.0, in rather bad agreement with (5). In the present paper, we wish to report a more accurate calculation giving a value,

$$(P_F/P_A)_{\text{theor}} = 0.49 \pm 0.05. \quad (6)$$

This value was obtained with the effective potential constructed by Seitz<sup>7</sup> and by replacing the atomic polyhedron by an equivalent sphere. All checks indicate that the remaining calculational errors within the framework of this model are less than 10 percent.

Before going on to the details of the calculation, we should like to mention the reason for the discrepancy between the present result (6) and the earlier value of Kohn and Bloembergen. It turns out that although the probability of finding the electron in an angular momentum state with  $l > 2$  is less than 1 percent, the boundary conditions cannot even remotely be satisfied with *s*, *p*, and *d* functions only. The higher angular momentum states, in spite of their small amplitude, play an essential role at the surface of the cell boundary. The present calculation includes states up to  $l=6$ .

### II. DETAILS OF THE CALCULATION

#### The Quantity $P_A$

Since we require the ratio  $P_F/P_A$  we began by calculating

$$P_A = |\psi_A(0)|^2, \quad (7)$$

<sup>†</sup> Schumacher, Carver, and Slichter, *Phys. Rev.* **95**, 1089 (1954).

<sup>‡</sup> D. Pines, *Phys. Rev.* **95**, 1090 (1954).

<sup>6</sup> W. Kohn and N. Bloembergen, *Phys. Rev.* **80**, 913 (1951); **82**, 283 (1951).

<sup>7</sup> F. Seitz, *Phys. Rev.* **47**, 400 (1935); for a correction see W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954).

where  $\psi_A$  is the normalized  $2S$  wave function of atomic Li. Using the potential of Seitz,<sup>7</sup> we found

$$(P_A)_{\text{theor}} = 0.223a_0^{-3}, \quad (8)$$

where  $a_0$  is the Bohr radius, while the measured hyperfine splitting of the  $2s$  state<sup>8</sup> leads to

$$(P_A)_{\text{expt}} = 0.231a_0^{-3}. \quad (9)$$

The agreement, to within 4 percent, must be considered excellent and gives one additional confidence in the Seitz potential. Any inaccuracy of this potential, should have a quite negligible effect on the ratio  $P_F/P_A$ .

### The Metallic Wave Function in the Spherical Approximation

We next calculated the quantity  $P_F$ . With an equivalent spherical cell boundary this is the value of  $|\psi_F(0)|^2$ , where  $\psi_F$  is the normalized wave function for any wave vector on the Fermi surface. If we denote the radius of the equivalent sphere by  $r_s$ , we must solve the boundary value problem:

$$(-\nabla^2 + V(r) - E)\psi(r) = 0, \quad r < r_s; \quad (10)$$

$$\psi(r) = e^{2ikr_s \cos\theta} \psi(-r), \quad r = r_s; \quad (11)$$

$$\partial\psi(r)/\partial r = -e^{2ikr_s \cos\theta} \partial\psi(-r)/\partial r, \quad r = r_s; \quad (12)$$

where  $k$  is the magnitude of the wave vector, assumed in the  $z$  direction ( $kr_s = 1.9192$ ), and  $\theta$  is the angle between  $\mathbf{k}$  and  $\mathbf{r}$ , if possible  $\psi(r)$  can be expanded in terms of the  $s, p$ , etc., solutions of (10),

$$\psi(r) = c_0 R_0(r) P_0(\cos\theta) + ic_1 R_1(r) P_1(\cos\theta) + c_2 R_2(r) P_2(\cos\theta) + \dots, \quad (13)$$

where the  $R_l$  are normalized such that  $R_l(r_s) = 1$  and the  $c_l$ , by a simple symmetry argument, are real.

According to the variational theory described in a previous paper,<sup>9</sup> the  $c_l$  are determined by the condition that the surface integral,

$$K \equiv \int_S \frac{\partial\psi(r)}{\partial r} \psi^*(-r) e^{-2ikr_s \cos\theta} \sin\theta d\theta, \quad (14)$$

be stationary. When (13) is substituted in (14) one finds that  $K$  is a quadratic form in the  $c_l$ . The stationary condition leads to a set of linear equations for the  $c_l$ , which are compatible provided that

$$\Delta \equiv \begin{vmatrix} 2L_0 I_{00} & (L_0 + L_1) i I_{01} & (L_0 + L_2) I_{02} & \dots \\ (L_0 + L_1) i I_{01} & -2L_1 I_{11} & (L_1 + L_2) i I_{12} & \dots \\ (L_0 + L_2) I_{02} & (L_1 + L_2) i I_{12} & 2L_2 I_{22} & \dots \\ \vdots & \vdots & \vdots & \ddots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} = 0, \quad (15)$$

<sup>8</sup> M. Fox and I. I. Rabi, Phys. Rev. **48**, 746 (1935).

<sup>9</sup> W. Kohn, Phys. Rev. **87**, 472 (1952).

where

$$L_l = \left[ \frac{dR_l}{dr} / R_l \right]_{r=r_s}, \quad (16)$$

$$I_{ij} = \int_0^\pi e^{-2ikr_s \cos\theta} P_i(\cos\theta) P_j(\cos\theta) \sin\theta d\theta.$$

In practice, the determinant is truncated after a finite number, say  $\bar{l}$ , of rows and columns and evaluated for a series of energies  $E$  which enter only through the  $L_l$ . (The latter were found by numerical integration and, for high  $l$ , by cruder perturbation methods.) In this way the  $E$  for which  $\Delta$  vanishes is found and the  $c_l$  are then evaluated by solving the set of equations which lead to (15). Finally,  $P_F$  is given by

$$P_F = c_0^2 R_0^2(0) / \sum_{l=0}^{\bar{l}} c_l^2 N_l, \quad (17)$$

$$N_l = \frac{4\pi}{2l+1} \int_0^{r_s} R_l^2(r) r^2 dr. \quad (18)$$

The results are given in Table I.

It will be noted that if one stops at  $l=2$ ,  $P_F$  is much too small.<sup>10</sup> At  $l=3$  no solution at all is found. However, at  $l=6$ ,  $P_F$  appears to have settled down to within less than 10 percent of its true value.

We have made two checks on this result. If the wave function satisfied the boundary condition (11) exactly we should have, at all angles,

$$\frac{c_1 P_1(\cos\theta) + c_3 P_3(\cos\theta) + \dots}{c_0 P_0(\cos\theta) + c_2 P_2(\cos\theta) + \dots} / \tan(kr_s \cos\theta) = 1. \quad (19)$$

Following is a table of this ratio for  $\bar{l}=5$  and 6 (Table II). Again an accuracy of about 5 percent is indicated.

As a second check we have substituted the function (13), with 7 undetermined coefficients into the boundary conditions (11) and (12) at the arbitrarily selected angles,  $\theta=30^\circ, 60^\circ, 75^\circ, 90^\circ$ , and determined  $E$  from the condition that the equations be compatible. The  $c_l$  and  $P_F$  were then evaluated, the result for the latter being  $0.116a_0^{-3}$ , agreeing within 6 percent with the best variational result. We tend to favor the latter

TABLE I. Successive variational approximations.

$\bar{l}$	$E(\text{ry})$	$P_F \times a_0^3$
2	-0.4272	0.046
3	(-0.4065) <sup>a</sup>	
4	-0.4347	0.075
5	-0.4308	0.114
6	-0.4313	0.110

<sup>a</sup>  $\Delta$  has no zero but a minimum at this energy.

<sup>10</sup> The value 0.22 of Kohn and Bloembergen was obtained with  $s, p$ , and  $d$  functions which did not satisfy (10) but were suggested by a perturbation expansion for small  $k$ .

TABLE II. Accuracy of variational functions.

$\theta$	$0^\circ$	$30^\circ$	$60^\circ$	$75^\circ$
$l=5$	1.06	1.04	0.99	0.82
$l=6$	1.04	0.92	0.98	1.05

slightly, since it does not depend on arbitrarily chosen angles.

Combining the last entry of Table I and Eq. (9), and taking into account the error indicated by our checks, we arrive at the result quoted in (6).

### III. ADDITIONAL REMARKS

#### Effect of Actual Cell Boundary

One of the remaining uncertainties of the calculation is the effect of replacing the true cell boundary by an equivalent sphere. Since the required quantity is  $|\psi_F(0)|^2$  averaged over the Fermi surface one would expect the equivalent sphere model to give a good approximation, provided that the true  $|\psi_F(0)|^2$  does not vary too much over the true Fermi surface. We have the following two indications that the variation is in fact moderate. Kohn and Rostoker<sup>7</sup> have calculated the energy band of metallic Li, using the actual atomic polyhedron. They find that the energies on the Fermi surface, relative to the energy of the  $k=0$  state, differ by only 3 percent in the (1,0,0) and (1,1,1) direction. As a second check we have extracted the variational wave functions consisting of  $s$ ,  $p$ , and  $d$  states from the calculation of Kohn and Rostoker and have computed  $|\psi(0)|^2$  both in the (1,0,0) and (1,1,1) direction. Their ratio is 1.14, indicating a rather moderate variation over the Fermi surface. This result must, however, be viewed with some caution as we have seen that the true wave function cannot be adequately expressed in terms of  $s$ ,  $p$ , and  $d$  functions only.<sup>11</sup>

#### Nature of the Wave Function on the Fermi Surface

Returning to our "spherical" calculation, let us write the wave function in the form,

$$\psi = \sum_{l=0}^{\infty} a_l \varphi_l, \quad (20)$$

where  $\varphi_l$  is a wave function corresponding to angular momentum  $l$ , normalized over the equivalent sphere; and let  $\psi$  itself be normalized to unity so that

$$\sum_{l=0}^{\infty} |a_l|^2 = 1. \quad (21)$$

<sup>11</sup> The absolute values of  $|\psi_E(0)|^2$  obtained with these functions is very large giving  $P_F/P_A \sim 1.3$ .

Our variational calculation gives the following results, which agree with those obtained by fitting the boundary conditions at the selected angles within a few percent:

$$|a_0|^2 = 0.20; \quad |a_1|^2 = 0.73; \quad |a_2|^2 = 0.06; \quad (22)$$

$$|a_l|^2 = 0.00, \quad l > 2.$$

The preponderance of the  $p$  function is noteworthy. This is in line with a recent calculation by Schiff<sup>12</sup> who has calculated the wave function at some points on the Brillouin zone boundary and finds that it has  $p$  character. Since  $|\psi(0)|^2$  therefore vanishes at the zone boundary, Jones and Schiff<sup>13</sup> have anticipated a rather small value of  $P_F$  (the Fermi surface is quite close to the zone boundary), a fact which the present calculation bears out.

#### Perturbation Theory

As first suggested by Bardeen,<sup>14</sup> it is possible to expand the wave function corresponding to the spherical problem (10)–(12) in a power series in  $k$ . We do not know any good *a priori* reason why such an expansion should converge well on the Fermi surface. However, this is in fact the case for the energy  $E = E_0 + E_2 k^2 + E_4 k^4 + \dots$ <sup>14</sup> Keeping two terms gives, in atomic units,  $E = -0.423$ , three terms give  $E = -0.427$ , which should be compared with our best variational result of Table I,  $E = -0.431$ . One can similarly expand  $|\psi(0)|^2$  in powers of  $k$  (see reference 2). In this way, one finds, in atomic units,

$$|\psi(0)|^2 = 0.4247 - 0.9006 k^2, \quad (23)$$

if higher terms are neglected. This expansion is certainly good for small  $k$ . Further it predicts that  $|\psi(0)|^2$  vanishes at  $k = 0.6868$ . The calculation of Schiff<sup>12</sup> shows that  $|\psi(0)|^2$  vanishes at the zone boundary which in our spherical model corresponds to  $k = 0.7533$ . Thus the expansion (23) gives good results for  $k \approx 0$  and slightly low results for  $k$  near the zone boundary. On the Fermi surface where  $k = 0.5979$  we find

$$|\psi_F(0)|_{\text{pert}}^2 = 0.103, \quad (P_F)_{\text{pert}}/P_A = 0.46, \quad (24)$$

which is in remarkably good agreement with the variational result (6) but, as expected, slightly too low.

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<sup>12</sup> B. Schiff, Proc. Phys. Soc. (London) A67, 2 (1954).

<sup>13</sup> H. Jones and B. Schiff, Proc. Phys. Soc. (London) A67, 217 (1954).

<sup>14</sup> J. Bardeen, J. Chem. Phys. 6, 367 (1938); R. Silverman and W. Kohn, Phys. Rev. 80, 912 (1950); 82, 283 (1951).