

## Letters to the Editor

**PUBLICATION** of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is five weeks prior to the date of issue. No proof will be sent to the authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not exceed 600 words in length and should be submitted in duplicate.

### Calculation of the $g$ Factor of Metallic Sodium\*

Y. YAFET

Department of Physics, University of California,  
Berkeley, California

(Received December 12, 1951)

WE calculate here the effect of spin-orbit coupling on the electronic  $g$  value expected in a spin-resonance experiment on metallic Na in a field  $H$ . On account of the strong coupling between electronic spins, it is assumed that in most of the transitions only the component of the total spin along  $H$  changes. Correlation and exchange effects do not affect the energies of such transitions and since we will not attempt to calculate line widths,<sup>1</sup> we may neglect such effects and use a sum of one-electron Hamiltonians,

$$\mathcal{H} = \sum_j [(\hbar^2/2m)(-i\nabla + \alpha)^2 + V(\mathbf{r}) + \lambda(\mathbf{r})\mathbf{l}_j \cdot \mathbf{s}_j]; \quad (1)$$

$$\alpha = e\mathbf{H} \times \mathbf{r}/2\hbar c; \quad \lambda(\mathbf{r}) = (\hbar^2/2m^2c^2r)[dV(\mathbf{r})/dr].$$

The sphere approximation was made, and the Prokofjew field of the free ion used for  $V(\mathbf{r})$ . The result is not sensitive to the effect of a correlation hole around the electron. Nuclear spin-electron spin interactions, not included above, are comparable to the spin-orbit effect only at temperatures low enough to have a large nuclear alignment; that is, when  $T < 1^\circ\text{K}$ .

The approximation (1) allows us to treat the absorption in terms of one-electron spin flips. Since  $k$  is conserved, only electrons at the top of the Fermi distribution need be considered. Because of the quenching of orbital angular momentum by the motion through the lattice, one expects  $g$  to be close to  $g_{\text{spin}} = 2.0023$ . The spin-orbit interaction can be treated as a perturbation, the unperturbed states being  $\psi_{\mathbf{k}}(\mathbf{r})\alpha$  and  $\psi_{\mathbf{k}}(\mathbf{r})\beta$ , with the spin quantized along  $H$ . Let  $\theta_0$  be the angle  $\mathbf{H}$ ,  $\mathbf{k}$ ;  $\theta$ ,  $\varphi$  and  $\theta'$ ,  $\varphi'$  be the polar angles from  $\mathbf{k}$  and  $\mathbf{H}$ , respectively. The calculation is done by a development<sup>2</sup> of the Bardeen method<sup>3</sup> rather than calculate matrix elements, we solve the nonhomogeneous linear equation of the first order in the spin-orbit parameter and satisfy the proper boundary condition at the surface of the atomic sphere by adding a solution to the homogeneous equation. We have,

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}} = [u_0(\mathbf{r}) + u_1(\mathbf{r}) + \dots]e^{i\mathbf{k} \cdot \mathbf{r}}$$

where the functions  $u_n(\mathbf{r})$  have a  $\cos^n\theta$  dependence on angle for an  $s$ -band. The series in the  $u_n$ 's converges rapidly only for small  $k$ . Near the top of a band,  $k$  is not small, but still each  $u_n$  for  $n \neq 0$  is small compared to  $u_0(\mathbf{r})$  because of the smallness of  $\nabla u_0(\mathbf{r})$  over most of its domain. Since the  $3p$  states are energetically  $\sim 10$  or more times closer to the  $3s$  state than the higher states, it has seemed reasonable to retain terms only up to  $u_1(\mathbf{r})$ .

Let  $\chi_{\alpha}(\mathbf{r}) = \{[u_{\mathbf{k}}(\mathbf{r}) + \varphi_{\mathbf{k}}(\mathbf{r})]\alpha + \eta_{\mathbf{k}}(\mathbf{r})\beta\}e^{i\mathbf{k} \cdot \mathbf{r}}$  be the first-order solution;  $\eta_{\mathbf{k}}(\mathbf{r})$  is unimportant for the calculation and may be neglected. The functions  $u_0(\mathbf{r})$  and  $u_1(\mathbf{r})$  are given in reference 3, and the resulting equation for  $\varphi_{\mathbf{k}}$  is, in atomic units,

$$-\frac{1}{2}(\nabla^2 + 2i\mathbf{k} \cdot \nabla)\varphi_{\mathbf{k}} + V(\mathbf{r})\varphi_{\mathbf{k}} - \frac{1}{2}k \sin\theta_0\lambda(\mathbf{r})[r^{-1}P(\mathbf{r})\sin\theta\sin\varphi + ikr\{r^{-1}P(\mathbf{r}) - ru_0(\mathbf{r})\}\sin\theta\cos\theta\sin\varphi] = E_0\varphi_{\mathbf{k}},$$

$r^{-1}P(\mathbf{r})$  being the radial  $p$  function denoted by the same symbol in reference 3, and  $E_0 = -0.6$  Ry. The  $p$  part of  $\varphi_{\mathbf{k}}$  is given by the nonhomogeneous term with angular dependence  $\sin\theta\sin\varphi$ .

Let  $\varphi_{\mathbf{k}}(\mathbf{r}) = [f(\mathbf{r})/r]\sin\theta\sin\varphi$ . The equation for  $f(\mathbf{r})$  becomes

$$-\frac{1}{2}(d^2f/dr^2 - 2f/r^2) + V(\mathbf{r})f - \frac{1}{2}k \sin\theta_0\lambda(\mathbf{r})P(\mathbf{r}) = E_0f,$$

where  $k = 0.485a_0^{-1}$ . This equation was solved numerically by Störmer's method<sup>4</sup> for the solution  $f(0) = (0)$ ; the boundary condition is  $f = 0$  at the surface of the cell. The fact that the  $1/r^3$  dependence of  $\lambda(\mathbf{r})$  is not meaningful in the immediate vicinity of the origin may seem to invalidate the physical meaning of the procedure. However, it can be shown that because of the fact that  $r = 0$  is a singular point of the homogeneous equation, the details of the cutoff for  $\lambda(\mathbf{r})$  do not affect the solution in a discontinuous way.

From  $\chi_{\alpha}$  it is required to show that  $\Delta g = 2\int_{\text{cell}} \chi_{\alpha}^* L_z \chi_{\alpha} d\tau / \int_{\text{cell}} \chi_{\alpha}^* \chi_{\alpha} d\tau$ . This relation is not obvious when  $\chi_{\alpha}$  is an arbitrary Bloch function, and it seemed worthwhile to establish it. The proof consists of expressing  $\chi_{\alpha}$  as a sum of bound functions,  $\chi_{\alpha} = \sum_l \phi_{\mathbf{k}}(\mathbf{r} - \mathbf{r}_l)e^{i\mathbf{k} \cdot \mathbf{r}_l}$  where the  $\phi_{\mathbf{k}}$  are determined essentially by a method by Wannier,<sup>5</sup> making a gauge transformation<sup>6</sup> and summing over the lattice in a way that yields the required result.

The answer is  $\Delta g = -3.7 \times 10^{-4} \sin^2\theta_0$ , and the strongest absorption occurs for  $\theta_0 = 90^\circ$ , so that  $g_{\text{max}} \approx 2.0019$ .

I wish to thank Professor C. Kittel for suggesting the problem and for many helpful discussions, and Professor J. Bardeen for kindly furnishing tables for the wave functions.

\* This research has been assisted in part by the ONR.

<sup>1</sup> A. W. Overhauser, to be published; thesis, Berkeley (1951).

<sup>2</sup> I am indebted to Dr. Conyers Herring for suggesting the possibility of this line of attack.

<sup>3</sup> J. Bardeen, J. Chem. Phys. 6, 367 (1938).

<sup>4</sup> Nat. Res. Council Bulletin 92, 81 (1933).

<sup>5</sup> G. H. Wannier, Phys. Rev. 52, 191 (1937).

<sup>6</sup> F. London, J. phys. et radium 8, 397 (1937).

### The Nuclear Magnetic Resonance of Titanium and Arsenic

C. D. JEFFRIES, H. LOELIGER, AND H. H. STAUB

Physikalisches Institut, University of Zürich, Zürich, Switzerland

(Received December 18, 1951)

BY using a recording radiofrequency spectrometer similar to that described by Proctor,<sup>1</sup> we have observed<sup>2</sup> a nuclear magnetic resonance signal in liquid  $\text{TiCl}_4$ , and in an aqueous solution of  $\text{H}_2\text{TiF}_6$ . This resonance occurs at a frequency of about 2.39 Mc in a magnetic field of 10,000 gauss and may be ascribed to either  $\text{Ti}^{47}$  or  $\text{Ti}^{49}$ , which are believed to be present in our samples in their natural abundance of 7.5 percent and 5.5 percent, respectively. The resonance signal in  $\text{TiCl}_4$  is not simple, but appears to consist of two partially resolved lines, symmetrically spaced about a central line, the width of the total structure being about 7 gauss. The ratio of the resonance frequency of the central line to the resonance frequency of protons in  $\text{H}_2\text{O}$  in the same magnetic field has been found to be

$$\nu_{\text{Ti}}/\nu_{\text{H}} = 0.05638 \pm 0.00001. \quad (1)$$

The nature of the structure is not yet understood, but it may be due to chemical effects or a mechanism previously observed by Proctor and Yu<sup>3</sup> and by Gutowsky and McCall;<sup>4</sup> however, if the structure were due to this latter mechanism, 13 lines would be expected instead of the 3 observed. The resonance signal from the  $\text{H}_2\text{TiF}_6$  sample is a single normal one and indicates a negative magnetic moment. Also it occurs at a frequency lower than that in  $\text{TiCl}_4$  by about 0.1 percent; this is presumably a "chemical shift."<sup>5</sup> In attempts to measure the spin we have compared the amplitude and width of the Ti resonance signals in  $\text{H}_2\text{TiF}_6$  with those of  $\text{N}^{14}$  in  $\text{HNO}_3$ . However, our  $\text{H}_2\text{TiF}_6$  samples appear to be unstable and to exhibit variable quadrupole broadening depending on slight variations in the method of preparation. This indicates that the degree of dissociation into symmetric  $(\text{TiF}_6)^{-}$  ions depends sensitively upon chemical factors. Using the  $\text{H}_2\text{TiF}_6$  sample showing least quadrupole broadening and assuming that there is nearly complete dissociation, our measurements give a