A Semi-Classical Derivation of the Contact Hyperfine Energy

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In nuclear magnetic resonance (NMR) and high resolution electron spin resonance (ESR) the energy contribution of terms which arise from hyperfine interactions is becoming more significant in its relation to atomic, molecular and crystal structure. Resonance techniques provide a means of measuring quite accurately certain parameters for a comparison with those determined theoretically from a particular quantrum mechanical model of the system.

For example, consider the empirical Hamiltonian of electron-atomic nucleus system in a magnetic field, Plate 1, a[2]. The first term is the electron Zeeman energy, the second is the nuclear Zeeman energy and the third is an energy of interaction between the electron spin and nuclear spin. Further consider the case where S and I are both ½. The energy levels are then as shown in Fig. 1. It has been assumed, as dictated by the physical situation, that the Paschen-Back, or decoupled, representation is valid for the interaction of I and S with the magnetic field. The first and largest splitting is the electron Zeeman effect. The next splitting indicates the removal of the nuclear spin degeneracy by the magnetic field. The electron spin-nuclear spin interaction further shifts the levels by an amount ¼A as indicated in the figure by the dotted lines. (The matrix elements for *I.S.* are listed in Plate I, b.) In ESR the selection rules for absorption of magnetic dipole radiation are for M_s to change by plus or minus one and M_I not change. The frequency for the absorption lines are in Plate I, c. After a measurement the electron g factor and A are the only unknowns and may be determined by solution of the two equations.

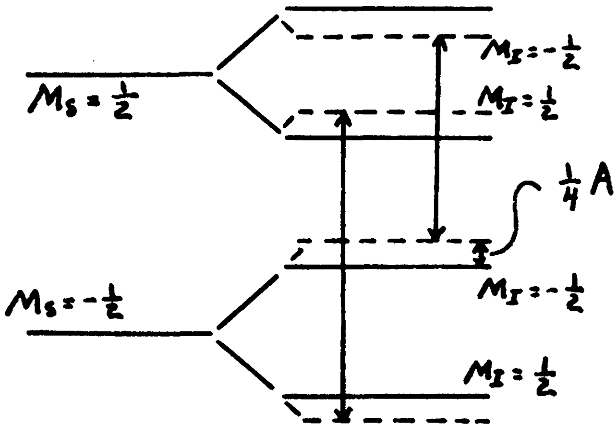

Figure 1

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[2]Formulas could not be printed as part of the text, therefore reference is given to the plates accompanying the article.

In this paper the parameter of interest is A, whose origin it is desired to investigate. One source is the electron spin-nuclear spin dipole-dipole interaction which has the form shown in Plate I, d. The parameter A is related to this expression in the manner indicated in Plate I, e. For an electron in an angular momentum s state the term vanishes when integrated over the angular coordinates (Panofsky and Phillips, 1955).

Another source for A is the "Fermi contact energy" (Fermi, 1930) whose classical origin is not so obvious. This term may be expressed in the form of Plate I, f which is obtained rigorously by the methods of relativistic quantum mechanics (Breit and Doermann, 1930). This term does not vanish for s state electrons but assumes the form in Plate I, g. Here it is particularly obvious why empirical values of A are useful for checking theoretically calculated wavefunctions of the physical system.

In this paper a semi-classical model for obtaining the contact term is proposed. Models of this type are of academic interest because they usually lead to physical insight for expressions which are actually of quantum mechanical origin. The solution of this problem is also of interest from the standpoint of boundary value problems in electro dynamics. It should be pointed out that R. Ferrell (1960) has recently published a semi-classical derivation of this term which assumes a completely different model and method of solution.

The description of the model used in this report is as follows: The atomic nucleus is assumed to be a uniformly distributed charge cloud of radius a, charge density d, and rotating with angular velocity w. The magnetic field of the nucleus will be calculated at all points in space, and then the energy of interaction with the intrinsic magnetic moment of the electron can be determined.

a) $$\mathcal{H} = g_e \beta_e \underline{H} \cdot \underline{S} + g_N \beta_N \underline{H} \cdot \underline{I} + A \underline{I} \cdot \underline{S}$$

b) $$(M_S M_I / \underline{I} \cdot \underline{S} / M_S M_I) = M_S M_I$$

c) $$h\nu = g_e \beta_e H \pm \tfrac{1}{2} A$$

d) $$\mathcal{H}_D = g_e \beta_e g_N \beta_N \left[\frac{\underline{I} \cdot \underline{S}}{R^3} - 3 \frac{(\underline{I} \cdot \underline{R})(\underline{S} \cdot \underline{R})}{R^5} \right]$$

e) $$A \underline{I} \cdot \underline{S} = \int \psi^* \mathcal{H}_D \psi \, d\tau$$

f) $$\mathcal{H}_F = \frac{8\pi}{3} g_e \beta_e g_N \beta_N \underline{I} \cdot \underline{S} \, \delta(\underline{r})$$

g) $$A \underline{I} \cdot \underline{S} = \int \psi^* \mathcal{H}_F \psi \, d\tau = \frac{8\pi}{3} g_e \beta_e g_N \beta_N |\psi(0)|^2 \underline{I} \cdot \underline{S}$$

Plate I

a) $$\varphi_{R<r} = \sum F_n R^n P_n(\cos\theta) \qquad \varphi_{R>r} = \sum G_n \left(\frac{1}{R}\right)^{n+1} P_n(\cos\theta)$$

a) $$H = -\nabla\varphi$$

c) $$R = r \qquad (B_{R>r})_{\hat{\varphi}} - (B_{R<r})_{\hat{\varphi}} = 0$$

c) $$(H_{R>r})_{\hat{\theta}} - (H_{R<r})_{\hat{\theta}} = \frac{4\pi}{c} K_{\hat{\varphi}}$$

c) $$K_{\hat{\varphi}} = dj \cdot dr = dw\, r \sin\theta$$

d) $$F_1 = -\frac{8\pi}{3}\frac{dw}{c} r\, dr \qquad G_1 = -\frac{1}{2} r^3 F_1$$

b) $$(H_{R<r})_{\hat{\theta}} = -F_1 \sin\theta \qquad (H_{R>r})_{\hat{\theta}} = \frac{F_1}{2}\left(\frac{r}{R}\right)^3 \sin\theta$$

b) $$(H_{R<r})_{\hat{r}} = F_1 \cos\theta \qquad (H_{R>r})_{\hat{r}} = F_1\left(\frac{r}{R}\right)^3 \cos\theta$$

e) $$R < a \qquad H_{\hat{\theta}} = \frac{8\pi}{3}\frac{dw}{c} \sin\theta \left[\frac{6}{5} R^2 - \frac{1}{2} a^2\right]$$

e) $$H_{\hat{r}} = \frac{8\pi}{3}\frac{dw}{c} \cos\theta \left[-\frac{3}{10} R^2 + \frac{1}{2} a^2\right]$$

f) $$H_{\hat{z}} = \frac{10\mu_w}{a^5}\left[\frac{1}{2} a^2 - \frac{3}{10} R^2 - \frac{3}{10} R^2 \sin^2\theta\right]$$

e) $$R > a \qquad H_{\hat{\theta}} = \frac{4\pi}{15}\frac{dw}{c}\frac{a^5}{R^3} \sin\theta$$

e) $$H_{\hat{r}} = \frac{8\pi}{15}\frac{dw}{c}\frac{a^5}{R^3} \cos\theta$$

f) $$H_{\hat{z}} = \frac{\mu_w}{R^3}\left[2 - 3\sin^2\theta\right]$$

e) $$\mu_w = \frac{4\pi}{15} a^5 \sigma \frac{w}{c}$$

f) $$E = -\mu_e \cdot H \qquad \mu_e = -g_e \beta_e$$

f, g) $$\bar{E} = \int_0^\infty \psi^* E \psi\, d\tau = \int_0^a \psi^* E_{R<a} \psi\, d\tau + \int_a^\infty \psi^* E_{R>a} \psi\, d\tau$$

f) $$\psi = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-\frac{Z}{a_0} r}$$

h) $$\bar{E} = -\frac{8\pi}{3}\mu_e \mu_w |\psi(0)|^2$$

Plate II

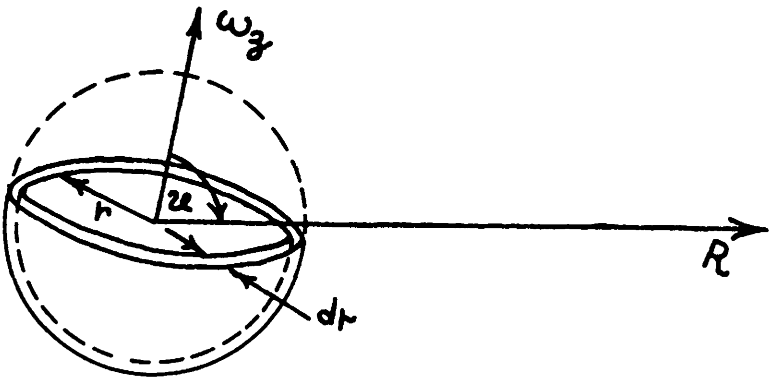

Figure 2

The spherical charge cloud may be divided into concentric shells of radius r and thickness dr, Fig. 2. The magnetic scalar potential at the field point R due to the rotating shell may be expanded in a series of Legendre polynomials, Plate II a. The F's and G's are determined by the boundary conditions at the surface of the shell, Plate II, c: 1) the normal component of the magnetic induction must be continuous and 2), the tangential component of the magnetic field changes by the surface current density. From the symmetry of the shell, the surface current has only one component. From equations of Plate II, b and II, c it is found that all F's and G's vanish except first order, Plate II, d. The magnetic field for the whole nucleus can be found by integrating H over the range of $r=O$ to a, Plate II, e. The nuclear magnetic moment is obtained from the behavior at large R.

The expression for the contact energy follows directly, Plate II, f. When the average value of E is found from integrating with the wavefunction, the z component is the only one that does not vanish. Also the contribution from the electron distribution outside the nucleus vanishes, Plate II, g. In the calculations a typical s wavefunction is used, and the final result is that of Plate II, h.

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