

### 335(6): Effect of Discarding the Dirac Approximation on the Spin-Orbit Hyperfine Interaction of NMR.

Consider the interaction energy between the magnetic dipole moment  $\underline{m}_s$  of an electron in an atom or molecule with the nuclear magnetic field  $\underline{B}(\underline{I})$  of the atom or molecule:

$$E_h = -\underline{m}_s \cdot \underline{B}(\underline{I}) \quad - (1)$$

In the usual Dirac approximation:

$$\underline{m}_s = \frac{e}{m_e} \underline{S} \quad - (2)$$

where  $\underline{S}$  is the spin angular momentum of the electron and  $e$  and  $m_e$  is charge and mass respectively. As in Note 334(2), discarding the Dirac approximation produces:

$$\underline{m}_s = 2 \left( \frac{\gamma^2}{1+\gamma^2} \right) \frac{e}{m_e} \underline{S} \quad - (3)$$

The nuclear magnetic dipole moment is defined conventionally as:

$$\underline{m}_N = g_N \frac{e}{2m_p} \underline{I} \quad - (4)$$

where  $g_N$  is the nuclear g factor,  $m_p$  the nuclear mass or proton mass in the case of atomic H, and  $\underline{I}$  the nuclear spin angular momentum.

In a fully rigorous theory  $\underline{m}_N$  must also be corrected, but that is highly non-trivial. So in the first approximation the definition (4) is used.

The nuclear magnetic field is:

$$\underline{B}(\underline{I}) = -\frac{\mu_0}{4\pi r^3} (\underline{m}_N - 3 \underline{\hat{r}} \underline{\hat{r}} \cdot \underline{m}_N) \quad (5)$$

here:

$$\underline{\hat{r}} = \underline{r} / r \quad (6)$$

Therefore:

$$H_{\text{int}} = \left( \frac{\gamma^2}{1+\gamma} \right) \frac{\mu_0 e^2 g_N}{4\pi m_e m_p r^3} (\underline{S} \cdot \underline{I} - 3 \underline{S} \cdot \underline{\hat{r}} \underline{\hat{r}} \cdot \underline{I}) \quad (7)$$

and the well known spin orbit hyperfine structure of NMR is changed by  $(\gamma^2 / (1+\gamma))$ .

If the magnetic dipole moments are strongly aligned in an external magnetic field:

$$H_{\text{int}} = \left( \frac{\gamma^2}{1+\gamma} \right) \frac{\mu_0 e^2 g_N \hbar^2}{4\pi m_e m_p} \left( \frac{1-3\cos^2\theta}{r^3} \right) m_I m_S \quad (8)$$

$$m_I = -I, \dots, I \quad (9)$$

$$m_S = -S, \dots, S \quad (10)$$

Now assume that:

$$\left( \frac{\gamma^2}{1+\gamma} \right) = \left( 1 - \left( \frac{d}{n} \right)^2 + \left( 1 - \left( \frac{d}{n} \right)^2 \right)^{1/2} \right)^{-1} \quad - (11)$$

where  $d$  is the fine structure constant and  $n$  the principal quantum number of the H atom. It follows that:

$$E_{\text{int}} = \langle H_{\text{int}} \rangle = \left( 1 - \left( \frac{d}{n} \right)^2 + \left( 1 - \left( \frac{d}{n} \right)^2 \right)^{1/2} \right)^{-1} \frac{\mu_0 e^2 g_N \hbar^2}{4\pi m_e m_p} \int \psi^* \left( \frac{1-3\cos^2\theta}{r^3} \right) \psi d\tau m_I m_S \quad - (12)$$

In the hydrogen atom:

$$m_I = \frac{1}{2}, -\frac{1}{2} \quad - (13)$$

$$m_S = \frac{1}{2}, -\frac{1}{2} \quad - (14)$$

and

$$- (15)$$

The NMR resonance frequency is:

$$h \omega_{\text{NMR}} = E(m_I) - E(m_I, -1) \quad - (16)$$

So:

$$\omega_{\text{NMR}} = \left( 1 - \left( \frac{d}{n} \right)^2 + \left( 1 - \left( \frac{d}{n} \right)^2 \right)^{1/2} \right)^{-1} \frac{\mu_0 e^2 g_N \hbar^2}{4\pi m_e m_p} \int \psi^* \left( \frac{1-3\cos^2\theta}{r^3} \right) \psi d\tau m_S \quad - (17)$$

Unit check

In eq. (12):

$$E = \frac{J^2 C^{-2} n^{-1} C^2 J^2 S^2}{\text{kg m}^2 \text{s}^{-4}} = \frac{J^3}{J^2} = J \quad \checkmark$$

4) where we have used:

$$\int \psi^* \psi d\tau = 1 \quad (18)$$

The selection rules in eq. (16) are:

$$\Delta n = \text{any}, \Delta m_s = 1, 0, -1 \quad (19)$$

However, eq. (16) refers to nuclear resonance as defined in Eq. (15), so the only possible choice of  $m_s$  is

$$m_s = \frac{1}{2} \quad (20)$$

otherwise the resonance frequency  $\omega_{\text{NMR}}$  would be negative and unphysical. Therefore:

$$\omega_{\text{NMR}} = \left( 1 - \left( \frac{d}{n} \right)^2 + \left( 1 - \left( \frac{d}{n} \right)^2 \right)^{1/2} \right)^{-1} \frac{\mu_0 e^2 g_N h}{8\pi m_e m_p} \int \psi^* \left( \frac{1-3\cos^2\theta}{r^3} \right) \psi d\tau \quad (21)$$

The key difference between this result and the usual result using the Dirac approximation is that here is a new type of dependence on the principal quantum number. So:

$$\omega_{\text{NMR}}(\text{corrected}) = \left( 1 - \left( \frac{d}{n} \right)^2 + \left( 1 - \left( \frac{d}{n} \right)^2 \right)^{1/2} \right)^{-1} \omega_{\text{NMR}}$$

and the entire hyperfine splitting spectrum is shifted.