

335(3): Relativistic Correction to the Chemical Shift Theory of N.M.R.

Consider the non-relativistic Hamiltonian of an electron in an atom or molecule:

$$H = \frac{p^2}{2m_e} + U \quad - (1)$$

The electron is affected by the magnetic dipole moment of a nucleus in the atom or molecule:

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

where g_N is the nuclear g factor, m_p the proton mass, and \underline{I} the nuclear spin angular momentum. The magnetic dipole moment of the electron is:

$$\underline{m}_1 = -g_e \frac{e}{2m_e} \underline{S} = -\frac{e}{m_e} \underline{S} \quad - (3)$$

where g_e is the g factor of the electron:

$$g_e = 2 \quad - (4)$$

The energy of interaction between the two dipoles is:

$$E(\text{int}) = \frac{\mu_0}{4\pi r^3} (\underline{m}_1 \cdot \underline{m}_2 - 3 \underline{m}_1 \cdot \underline{\hat{r}} \underline{\hat{r}} \cdot \underline{m}_2) \quad - (5)$$

therefore the magnetic flux density due to the nuclear magnetic dipole is:

$$\underline{B}(\underline{m}_2) = -\frac{\mu_0}{4\pi r^3} \left(\underline{m}_2 = 3 \hat{r} \hat{r} \cdot \underline{m}_2 \right) - (6)$$

It can be shown that this is equivalent to a nuclear potential:

$$\underline{A}_2 = \frac{\mu_0}{4\pi r^3} \underline{m}_2 \times \underline{r} - (7)$$

Therefore in the non-relativistic theory the potential \underline{A}_2 has the effect:

$$\underline{p}_0 \rightarrow \underline{p}_0 - e \underline{A}_2 - (8)$$

is the minimal prescription. The Hamiltonian (1) is therefore changed to:

$$\begin{aligned} H &= \frac{1}{2m_e} (\underline{p}_0 - e \underline{A}_2) \cdot (\underline{p}_0 - e \underline{A}_2) + U \\ &= -\frac{e}{m_e} \underline{p}_0 \cdot \underline{A}_2 + \dots \end{aligned} \quad - (9)$$

The energy of interaction is: - (10)

$$E = \langle H \rangle = -\frac{e}{m_e} \int \psi^* \underline{p}_0 \cdot \underline{A}_2 \psi d\tau$$

This expression \underline{p}_0 is hermitian w.r.t the property:

$$\underline{p}_0 = -\underline{p}_0^* - (11)$$

because:

$$\underline{p}_0 \psi = -i\hbar \underline{\nabla} \psi \quad - (12)$$

$$\underline{p}_0^* \psi = i\hbar \underline{\nabla} \psi \quad - (13)$$

The operator \underline{A}_2 is real valued so:

$$\begin{aligned} \int \psi^* \underline{A}_2 \cdot \underline{p}_0 \psi d\tau &= \int (\underline{p}_0^* \cdot \underline{A}_2 \psi^*) \psi d\tau \quad - (14) \\ &= \frac{1}{2} \left(\int (\underline{p}_0^* \cdot \underline{A}_2) \psi^* \psi d\tau + \int \underline{A}_2 \cdot (\underline{p}_0^* \psi^*) \psi d\tau \right) \\ &= \int \underline{A}_2 \cdot \psi \underline{p}_0^* \psi^* d\tau, \end{aligned}$$

$$\begin{aligned} \text{so } E &= -\frac{e}{2m_e} \int \underline{A}_2 \cdot (\psi^* \underline{p}_0 \psi + \psi \underline{p}_0^* \psi^*) d\tau \\ &= -\int \underline{A}_2 \cdot \underline{j}_1 d\tau \quad - (15) \end{aligned}$$

$$\text{where } \underline{j}_1 = \frac{e}{2m_e} (\psi^* \underline{p}_0 \psi + \psi \underline{p}_0^* \psi^*) \quad - (16)$$

A current density operator.

The derivation in eqs. (14) to (16) follows from the
 Hermitian property:

$$\int \psi^* \Omega \psi d\tau = \int (\Omega \psi)^* \psi d\tau \quad - (17)$$

where

$$\Omega = \underline{A_2} \cdot \underline{p_0} \quad - (18)$$

so: $\int \psi^* \underline{A_2} \cdot \underline{p_0} \psi d\tau = \int (\underline{A_2} \cdot \underline{p_0} \psi)^* \psi d\tau$

$$= \int (\underline{p_0}^* \cdot \underline{A_2} \psi^*) \psi d\tau \quad - (19)$$

To summarize, the energy of interaction is:

$$E = -\frac{e}{m_e} \int \psi^* \underline{p_0} \cdot \underline{A_2} \psi d\tau$$

$$= -\frac{e}{2m_e} \left(\int \psi^* \underline{p_0} \cdot \underline{A_2} \psi d\tau + \int \psi^* \underline{p_0} \cdot \underline{A_2} \psi d\tau \right)$$

$$= -\frac{e}{2m_e} \left(\int \underline{A_2} \cdot \psi^* \underline{p_0} \psi d\tau + \int (\underline{p_0}^* \cdot \underline{A_2} \psi^*) \psi d\tau \right) \quad - (20)$$

The second term on the right hand side of eq. (20) is developed as follows, noting that \underline{p}^* is an operator, so the Leibniz rule applies:

$$\underline{p}^* \cdot (\underline{A_2} \psi^*) = (\underline{p}^* \cdot \underline{A_2}) \psi^* + \underline{A_2} \cdot (\underline{p}^* \psi^*) \quad - (21)$$

and for divergenceless $\underline{A_2}$:

$$\underline{p}^* \cdot \underline{A_2} = 0 \quad - (22)$$

Therefore:

$$E = -\frac{e}{2m_e} \int \underline{A}_2 \cdot (\psi^\dagger \underline{p}_0 \psi + \psi \underline{p}_0^\dagger \psi^\dagger) d\tau - (23)$$

which is eq. (15), QED.

This interaction energy can be written as:

$$E = -\underline{m}_2 \cdot \underline{B}_2 - (24)$$

and is the interaction of the electron's dipole moment \underline{m}_2 with the nuclear magnetic field \underline{B}_2 . Therefore:

$$E = -\underline{m}_2 \cdot \underline{B}_2 = -\int \underline{A}_2 \cdot \underline{j}_1 d\tau - (25)$$

where

$$\underline{A}_2 = g_N \left(\frac{e}{2m_p} \right) \left(\frac{\mu_0}{4\pi r^3} \right) \underline{I} \times \underline{r} - (26)$$

In the presence of an external magnetic field \underline{B} :

$$E = -\underline{m}_2 \cdot (\underline{B} + \underline{B}_2) - (28)$$

Therefore the frequency is shifted by the presence of \underline{B}_2 . The \underline{B}_2 field depends on the current density \underline{j}_1 in the environment of the particular nucleus being considered, and is the chemical shift.

6) From eqs. (25) and (7) :

$$E = - \int \frac{\mu_0}{4\pi r^3} \underline{j}_1 \cdot \underline{m}_2 \times \underline{r} d\tau \quad (27)$$

$$= - g_N \left(\frac{e}{2m_p} \right) \int \frac{\mu_0}{4\pi r^3} \underline{I} \times \underline{r} \cdot \underline{j}_1 d\tau$$

$$= - g_N \left(\frac{e}{2m_p} \right) \int \frac{\mu_0}{4\pi r^3} \underline{I} \cdot \underline{r} \times \underline{j}_1 d\tau$$

$$= - \gamma_N \underline{I} \cdot \underline{B}_2 \quad (28)$$

where

$$\underline{B}_2 = \int \frac{\mu_0}{4\pi r^3} \underline{r} \times \underline{j}_1 d\tau$$

with:

$$\underline{j}_1 = \frac{e}{2m_e} \left(\psi^\dagger \underline{p}_0 \psi + \psi \underline{p}_0^\dagger \psi^\dagger \right) \quad (29)$$

Correia in the Class One Hamiltonian

The Correia is :

$$\frac{p_0^2}{2m_e} \rightarrow \frac{p_0^2}{m_e} \left(\frac{\gamma^2}{1+\gamma} \right) \quad (30)$$

and will be evaluated in the next note