335(4): Development of Relativistic NMR in the H Atom

The fundamental Hamiltonian is:

$$H_0 = H - m_e c^2 = \frac{1}{m_e}\left(\frac{\gamma^2}{1+\gamma}\right)p_0^2 + U \quad -(1)$$

where H is the relativistic Hamiltonian:

$$H = \gamma m_e c^2 + U \quad -(2)$$

Here

$$\gamma = \left(1 - \frac{p_0^2}{m_e^2 c^2}\right)^{-1/2} \quad -(3)$$

is the Lorentz factor. In this notation m_e is the mass of an electron, for example the electron of the H atom, and H_0 is the Hamiltonian H covered by removal of the rest energy

$$E_0 = m_e c^2 \quad -(4)$$

Here

$$\underline{p}_0 = m_e \underline{v}_0 \quad -(5)$$

where $\underline{v}_0$ is the electron's velocity. In the H atom the potential energy U is:

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \quad -(6)$$

where ϵ_0 is the S.I. vacuum permittivity and r is the distance between the proton and the electron. In the H atom the nucleus consists of one proton. Finally c is the vacuum speed of light.

). In the limit:

$$v_0 \ll c, \quad -(7)$$

then

$$\gamma \to 1 \quad -(8)$$

so

$$H_0 \to \frac{1}{2m_e} p_0^2 + U \quad -(9)$$

<u>Q.E.D.</u>

The Hamiltonian (1) can be written as:

$$H_0 = \frac{1}{m_e} \underline{p_1} \cdot \underline{p_1} + U \quad -(10)$$

where

$$\underline{p_1} = \left(\frac{\gamma^2}{1+\gamma} \right)^{1/2} \underline{p_0} \quad -(11)$$

The nuclear potential $\underline{A}_N$ due to the proton is:

$$\underline{A}_N = \frac{\mu_0}{4\pi r^3} \underline{m}_N \times \underline{r} \quad -(12)$$

where μ_0 is the vacuum permeability and $\underline{m}_N$, the nuclear magnetic dipole moment. The latter is

$$\underline{m}_N = g_N \frac{e}{2m_p} \underline{I} \quad -(13)$$

where g_N is the proton g factor, m_p the mass of the proton and $\underline{I}$ the spin angular momentum of the proton. We have:

3)

$$g_N = 5.5857 \quad -(14)$$

and

$$I_Z \phi = m_I \hbar \phi \quad -(15)$$

where

$$m_I = -I, \ldots, I \quad -(16)$$
$$= -\frac{1}{2} \text{ and } \frac{1}{2}.$$

A positive sign has been used in eq. (13) to be consistent with the magnetic dipole moment of the electron:

$$\underline{m}_e = g_e \frac{e}{2m_e} \underline{S} \quad -(17)$$

where g_e is the g factor of the electron:

$$g_e = 2 \quad -(18)$$

and

$$S_Z \phi = \hbar m_s \phi \quad -(19)$$

with

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

The electron and proton g factors are different because the proton has an intricate internal structure.

Under the influence of the nuclear or proton potential $\underline{A}_N$ the hamiltonian becomes:

$$H = \frac{1}{m_e}\left(\underline{p}_1 - e\underline{A}_N\right)\cdot\left(\underline{p}_1 - e\underline{A}_N\right) + U \quad -(21)$$

using the minimal prescription:

$$\underline{p}_1 \rightarrow \underline{p}_1 - e\underline{A}_N \quad -(22)$$

4)

Classically:

$$H_0 = \frac{1}{m_e}\left(p_1^2 - 2e\,\underline{p}_1 \cdot \underline{A}_N + e^2 A_N^2\right) \quad -(23)$$

Defining:

$$\underline{p}_N = e\underline{A}_N \quad -(24)$$

the Hamiltonian is:

$$H_0 = \frac{1}{m_e}\left(p_1^2 - 2\,\underline{p}_1 \cdot \underline{p}_N + p_N^2\right) \quad -(25)$$

where

$$\underline{p}_1 \cdot \underline{p}_N = \frac{\mu_0}{4\pi r^3 e m_e}\,\underline{p}_1 \cdot \underline{m}_N \times \underline{r}$$

$$= \frac{\mu_0 e}{4\pi r^3 m_e}\,\underline{m}_N \cdot \underline{r} \times \underline{p}_1$$

$$= \frac{\mu_0 e}{4\pi r^3 m_e}\,\underline{m}_N \cdot \underline{L}_1 \quad -(26)$$

where the orbital angular momentum $\underline{L}_1$ is:

$$\underline{L}_1 = \underline{r} \times \underline{p}_1 \quad -(27)$$

The interaction Hamiltonian between the electron and proton is therefore:

$$H_{int} = -\frac{2}{m_e}\,\underline{p}_1 \cdot \underline{p}_N \quad -(28)$$

i.e.

$$H_{int} = -\frac{\mu_0 e}{2\pi r^3 m_e} \underline{m}_N \cdot \underline{L}_1 = -\underline{m}_N \cdot \underline{B}_{internal} \quad -(29)$$

where the internal magnetic field is:

$$\underline{B}_{internal} = \frac{\mu_0 e}{2\pi r^3 m_e} \underline{L}_1 \quad -(30)$$

Therefore:

$$H_{int} = -2e\,\underline{p}_1 \cdot \underline{A}_N = -\underline{m}_N \cdot \underline{B}_{internal} \quad -(31)$$

is a type of spin orbit interaction, in which the internal magnetic field is affected by the relativistic correction:

$$\boxed{\underline{B}_{internal} = \frac{\mu_0 e}{2\pi r^3 m_e} \underline{r} \times \left(\frac{\gamma^2}{1+\gamma}\right)^{1/2} \underline{p}_0} \quad -(32)$$

The resultant magnetic field experienced by the proton's magnetic dipole moment results in the interaction energy:

$$H_{int} =$$

$$= -\underline{m}_N \cdot \left(\underline{B} + \underline{B}_{int}\right) \quad -(33)$$

Therefore the NMR chemical shift is affected by the correction factor $\left(\gamma^2/(1+\gamma)\right)^{1/2}$; and this should be observable.

The energy levels from eq. (31) are given by the expectation value:

$$E_{int} = \langle H_{int} \rangle = 2ie\hbar \int \psi^* \underline{\nabla} \cdot \left(\left(\frac{\gamma^2}{1+\gamma} \right)^{1/2} \underline{A}_N \psi \right) d\tau \quad -(34)$$

where, from eqs. (12) and (13):

$$\underline{A}_N = g_N \frac{e}{2m_p} \frac{\mu_0}{4\pi r^3} \underline{I} \times \underline{r}. \quad -(35)$$

This is a complicated expression, and it proves more convenient to use the spin orbit format:

$$H_{int} = - \underline{m}_N \cdot \underline{B}_{internal}$$

$$= - \frac{\mu_0 e}{2\pi r^3 m_e} \underline{m}_N \cdot \underline{L}_1$$

$$= - \frac{g_N \mu_0 e^2}{4\pi m_p r^3 m_e} \underline{I} \cdot \underline{L}_1, \quad -(36)$$

$$\boxed{H_{int} = - \frac{g_N \mu_0 e^2}{4\pi m_p r^3 m_e} \left(\frac{\gamma^2}{1+\gamma} \right)^{1/2} \underline{I} \cdot \underline{L}} \quad -(37)$$

$$= - \frac{g_N \mu_0 e^2}{4\pi m_p m_e r^3} \left(\frac{\gamma^2}{1+\gamma} \right)^{1/2} \underline{I} \cdot \underline{L}$$

7) This is the spin - orbit interaction between the electron's orbital angular momentum and the proton's spin angular momentum.

In direct comparison, the spin orbit interaction energy between the electron's spin and orbital angular momentum takes a similar format. Methods used for the electronic spin orbit interaction can be used to work out:

$$\boxed{E_{int} = \langle H_{int} \rangle = -\frac{g_N \mu_0 e^2}{4\pi m_p m_e} \left\langle \left(\frac{\gamma^2}{1+\gamma}\right)^{1/2} \frac{\underline{I} \cdot \underline{L}}{r^3} \right\rangle} \quad -(38)$$

This will be the subject of the next note.

Units Check

1) $\mu_0 = J s^2 C^{-2} m^{-1}$; $\underline{I} \cdot \underline{L} = kg^2 m^4 s^{-2}$, so the units in eq. (38) are correct.

2) $\underline{B}$ = tesla = $J s^{-1} C^{-1} m^{-2}$, $\underline{m} = C m^2 s^{-1}$, so $\underline{m} \cdot \underline{B}$ has the units of joules.

3) $\underline{A}_N = \frac{\mu_0}{4\pi r^3} \underline{m}_N \times \underline{r} = J C^{-1} m^{-1} s^2 = p/e$ ✓✓