ECE2 AND RIGOROUS NMR THEORY

by

M. W. Evans and H Eckardt,

CIVIL LIST, AIAS AND UPITEC

(www.webarchive.org.uk, www.aias.us, www.upitec.org, www.atomicprecision.com

www.e3tm.net)

ABSTRACT

The effect on NMR spectra of discarding the Dirac approximation is evaluated, using various starting hamiltonians. It is shown that the rigorous development of NMR theory has an effect on the familiar chemical shift, and spin orbit and spin spin interaction between electrons and nuclei.

Keywords: ECE2, rigorous theory of NMR, chemical shift, spin orbit and spin spin interaction.

UFT335

1. INTRODUCTION

In recent papers of this series {1 - 12} the systematic evaluation has been initiated of the effect of removing the Dirac approximation to the hamiltonian of special relativity. It has been shown that the Dirac approximation makes the classical non relativistic hamiltonian vanish, a drastically unphysical result. Nonetheless, this approximation has been repeated endlessly for nearly ninety years. Once it is removed, new and original spectral effects appear, and moreover, these effects depend on subjective choice of solution of the rigorous hamiltonian in the SU(2) basis introduced by Dirac. This is profoundly unsatisfactory because the basics of relativistic quantum mechanics have been shown to be subjective and not objective as required in natural philosophy. The only way forward is to develop the subject systematically from the beginning in order to try to find the correct method of solution. In this paper, NMR spectra are worked out from the first principles of the new theory. The latter can be described essentially as ECE2 special relativity - equations that look like those of special relativity, but which are written in a space with identically non zero torsion and curvature.

Section 2 is a short summary of detailed calculations found in the background notes posted with UFT335 on www.aias.us. Notes 335(1) and 335(2) consider a rigorous hamiltonian made up of the spin angular momentum of a proton and electron, for example in atomic hydrogen. The Landé method used in the theory of the anomalous Zeeman effect is adopted for this problem, In Notes 335(3) and 335(4) the rigorous theory of the chemical shift is developed, using an analogy of spin orbit interaction theory. Finally, in Note 335(6), rigorous hyperfine interaction theory is developed for electron / nucleus spin orbit and spin spin interaction in NMR. In all cases the effect of discarding the Dirac approximation should be measurable in standard FT NMR spectrometers

Section 3 evaluates and graphs energy levels of the rigorous theory in order to show that the theoretical spectra from the rigorous approach differ form those obtained with the Dirac approximation.

2. DEVELOPMENT OF RIGOROUS HAMILTONIANS

The essence of nuclear magnetic resonance (NMR) is that the nucleus of an atom or molecule contains a magnetic dipole moment:

$$\underline{m}_N = g_N \frac{e}{2m_p} \underline{I} \qquad -(1)$$

Here g_N is the nuclear g factor, m_p the mass of the proton, e the modulus of the charge on the electron and $\underline{I}$ the nuclear spin angular momentum. The interaction hamiltonian between the magnetic dipole moment and a magnetic flux density $\underline{B}$ is:

$$H_{int} = -\underline{m}_N \cdot \underline{B}. \qquad -(2)$$

As shown in immediately preceding papers the interaction between the magnetic field and the spin angular momentum $\underline{S}$ of an electron is given rigorously by:

$$H_{int} = -2\frac{e}{m_e}\left(\frac{\gamma^2}{1+\gamma}\right)\underline{S}\cdot\underline{B} \qquad -(3)$$

where γ is the Lorentz factor:

$$\gamma = \left(1 - \frac{p_0^2}{m^2c^2}\right)^{-1/2}. \qquad -(4)$$

Here m_e is the mass of the electron, and $\underline{p}_0$ is its classical linear momentum. The complete spin hamiltonian in the simplest atom, hydrogen (H) is therefore:

$$H_{int} = -2\frac{e}{m_e}\left(\frac{\gamma^2}{1+\gamma}\right)\underline{S}\cdot\underline{B} - g_N\frac{e}{2m_p}\underline{I}\cdot\underline{B} \qquad -(5)$$

In a yet more rigorous theory the nuclear part of this hamiltonian would also be worked out without approximation. This type of hamiltonian is defined in detail in Note 335(1), together with the nuclear magnetic resonance condition.

In Note 335(2) it is developed with the well known Landé method used in the anomalous Zeeman effect. The result of this method is that Eq. (5) can be expressed as:

$$H_{int} = -e g_{\underline{M}} \underline{I} \cdot \underline{B} \quad -(6)$$

where:

$$g_{\underline{M}} = \frac{1}{2} \left(\frac{1}{m_e} \left(\frac{\gamma^2}{1+\gamma} \right) \left(1 + \frac{S(S+1) - \underline{I}(\underline{I}+1)}{\underline{M}(\underline{M}+1)} \right) + \frac{g_N}{m_p} \left(1 + \frac{\underline{I}(\underline{I}+1) - S(S+1)}{\underline{M}(\underline{M}+1)} \right) \right) \quad -(7)$$

and where the quantum number M is defined as:

$$\underline{M} = \underline{I} + S, \ldots, |\underline{I} - S|. \quad -(8)$$

The total angular momentum is:

$$\underline{M} = \underline{I} + \underline{S}. \quad -(9)$$

Therefore electron spin resonance is described by:

$$H_{ESR} = -e g_{\underline{M}} \underline{S} \cdot \underline{B} + \ldots \quad -(10)$$

and nuclear magnetic resonance by:

$$H_{NMR} = -e g_{m} \underline{I} \cdot \underline{B} + \ldots \quad -(11)$$

The ESR and NMR resonance frequencies are the same:

$$\omega_{res} = e g_{\underline{M}} B_Z \quad -(12)$$

and both are affected by discarding the Dirac approximation

The most important feature of NMR and MRI is the chemical shift due to the magnetic flux density generated by the nuclear magnetic dipole moment:

$$\underline{B}(\underline{m}_N) = -\frac{\mu_0}{4\pi r^3}\left(\underline{m}_N - 3\hat{\underline{r}}\,\hat{\underline{r}}\cdot\underline{m}_N\right) \quad -(13)$$

where μ_0 is the vacuum permeability. This magnetic flux density is equivalent to the nuclear vector potential:

$$\underline{A}_N = \frac{\mu_0}{4\pi r^3}\,\underline{m}_N \times \underline{r}\,. \quad -(14)$$

In the usual theory of NMR the presence of the nuclear vector potential changes the electronic linear momentum $\underline{p}_0$ according to the minimal prescription:

$$\underline{p}_0 \rightarrow \underline{p}_0 - e\underline{A}_N \quad -(15)$$

so the usual hamiltonian:

$$H = \frac{p_0^2}{2m} + U \quad -(16)$$

is changed to:

$$H = \frac{1}{2m}\left(\underline{p}_0 - e\underline{A}_N\right)\cdot\left(\underline{p}_0 - e\underline{A}_N\right) + U \quad -(17)$$

where U is the Coulomb potential between the electron and the nucleus. As shown in detail in Note 335(3), the interaction hamiltonian:

$$H_{int} = -\frac{e}{m_e}\,\underline{p}_0\cdot\underline{A}_N + \cdots \quad -(18)$$

gives the energy of interaction:

$$E = -\int \underline{A}_N \cdot \underline{j}\, d\tau \quad -(19)$$

where the current density is:

$$\underline{j} = \frac{e}{2m_e}\left(\phi^* \underline{p}_0 \phi + \phi\, p_0^* \phi^*\right). \quad -(20)$$

Using Eq. (2) this interaction energy is:

$$E = -\underline{m}_N \cdot \underline{B}_N = -\int \underline{A}_N \cdot \underline{j}\, d\tau \quad -(21)$$

and is responsible for the chemical shift. This is because the magnetic flux density $\underline{B}_N$ is present in addition to the applied magnetic flux density of the NMR spectrometer.

Chemical shifts of all kinds are affected by the removal of the Dirac approximation. In the class one hamiltonian this removal of an unphysical approximation is represented by:

$$\frac{p_0^2}{2m_e} \rightarrow \frac{p_0^2}{2m_e}\left(\frac{\gamma^2}{1+\gamma}\right). \quad -(22)$$

The theory is developed further in Notes 335(4) and 335(5). In the absence of any consideration of the nuclear vector potential, the rigorous class one hamiltonian in the O(3) basis is:

$$H_0 = H - m_e c^2 = \frac{1}{m_e}\left(\frac{\gamma^2}{1+\gamma}\right) p_0^2 + U \quad -(23)$$

where

$$U = -\frac{e^2}{4\pi\epsilon_0 r}. \quad -(24)$$

In the presence of a nuclear vector potential $\underline{A}_N$ The hamiltonian is changed by the minimal prescription and as shown in Note 335(4) the interaction hamiltonian becomes:

$$H_{int} = -\frac{2e}{m_e}\,\underline{p}_1\cdot\underline{p}_N, \quad -(25)$$

where

$$\underline{p}_1 = \left(\gamma^2/(1+\gamma)\right)^{1/2}\underline{p}_0, \quad -(26)$$

$$\underline{p}_N = e\underline{A}_N. \quad -(27)$$

The nuclear magnetic flux density can be defined as:

$$\underline{B}_N = \frac{\mu_0 e}{2\pi m_e r^3}\,\underline{L}_1 \quad -(28)$$

where:

$$\underline{L} = \underline{r}\times\underline{p}_1. \quad -(29)$$

is an orbital angular momentum of the electron. In the presence of the external magnetic field $\underline{B}$ of the NMR spectrometer the complete interaction hamiltonian is:

$$H_{int} = -\underline{m}_N\cdot\left(\underline{B}+\underline{B}_N\right). \quad -(30)$$

In spin orbit format (Note 335(4)):

$$H_{int} = -\frac{\gamma_N\mu_0 e^2}{4\pi m_e m_p r^3}\left(\frac{\gamma^2}{1+\gamma}\right)^{1/2}\underline{I}\cdot\underline{L} \quad -(31)$$

where $\underline{I}$ is the spin angular momentum of the nucleus and $\underline{L}$ is the orbital angular momentum of the electron. In the H atom there is only one electron and one proton.

In direct analogy with the usual spin orbit theory of electrons, the energy levels are given by expectation values as follows:

$$E_{int} = -\frac{\gamma_N\mu_0 e^2}{4\pi m_e m_p}\left\langle\left(\frac{\gamma^2}{1+\gamma}\right)^{1/2}\frac{\underline{I}\cdot\underline{L}}{r^3}\right\rangle \quad -(32)$$

Now assume that this can be written as:

$$E_{int} = -\frac{g_N \mu_0 e^2}{4\pi m_e m_p} \left(\frac{\gamma^2}{1+\gamma}\right)^{1/2} \left\langle \frac{\underline{I} \cdot \underline{L}}{r^3} \right\rangle \quad -(33)$$

using expectation values to give:

$$A = \frac{\gamma^2}{1+\gamma} = \left(1 - \left(\frac{\alpha}{n}\right)^2 + \left(1 - \left(\frac{\alpha}{n}\right)^2\right)^{1/2}\right)^{-1} \quad -(34)$$

as in immediately preceding papers. Here α is the fine structure constant and n the principal quantum number of the H atom. Hydrogenic wavefunctions have been used in a first approximation as in previous work. In analogy with spin orbit theory of electrons:

$$\left\langle \frac{\underline{I} \cdot \underline{L}}{r^3} \right\rangle = \hbar^2 \left(\frac{J(J+1) - L(L+1) - I(I+1)}{2 a_0^3 n^3 L\left(L+\frac{1}{2}\right)(L+1)} \right) \quad -(35)$$

where a_0 is the Bohr radius and where the quantum numbers are defined by the Clebsch Gordan series:

$$J = L + I, \ldots, |L - I|. \quad -(36)$$

For the proton of the nucleus of the H atom:

$$I = \frac{1}{2} \text{ or } -\frac{1}{2}. \quad -(37)$$

In the presence of an external magnetic field the complete hamiltonian is:

$$\begin{aligned} H &= -\underline{m}_N \cdot \underline{B} + E_{int} \quad -(38) \\ &= -g_N e \hbar m_I B_Z / (2 m_p) + E_{int} \end{aligned}$$

where the interaction energy is:

$$E_{int} = -\frac{g_N \mu_0 e^2 A^{1/2} \hbar^2}{4\pi m_e m_p} \cdot \left(\frac{J(J+1) - L(L+1) - \underline{I}(\underline{I}+1)}{2a_0^3 n^3 L(L+1/2)(L+1)} \right) \quad -(39)$$

The NMR resonance condition is:

$$\hbar\omega = E(m_{\underline{I}} - 1) - E(m_{\underline{I}}) \quad -(40)$$

so it is clear that the entire spectrum is affected by the factor:

$$A = \frac{\gamma^2}{1+\gamma}. \quad -(41)$$

This effect is within range of an ordinary FT NMR spectrometer.

Finally in this section it is shown that the well known theory of hyperfine interaction in NMR is changed at a foundational level by removing the Dirac approximation.

Hyperfine structure in NMR is generated by the interaction of the magnetic spin dipole moment of an electron with the nuclear magnetic field due to the spin angular momentum $\underline{I}$ of the nucleus. In the Dirac approximation the magnetic spin dipole moment of an electron is:

$$\underline{m}_S = \frac{e}{m_e} \underline{S} \quad -(42)$$

but the rigorous definition (see preceding papers and notes) is:

$$\underline{m}_S = 2\left(\frac{\gamma^2}{1+\gamma}\right) \frac{e}{m_e} \underline{S}. \quad -(43)$$

The nuclear magnetic spin dipole moment is:

$$\underline{m}_N = g_N \frac{e}{2m_p} \underline{I} \quad -(44)$$

where g_N is the nuclear g factor and m_p the proton mass in atomic H, where the nucleus consists of one proton. In a fully rigorous theory $\underline{m}_N$ must also be corrected for the removal of the Dirac approximation, but to a first approximation the definition (44) is used.

The nuclear magnetic flux density is:

$$\underline{B}(\underline{I}) = -\frac{\mu_0}{4\pi r^3}\left(\underline{m}_N - 3\,\hat{\underline{r}}\,\hat{\underline{r}}\cdot\underline{m}_N\right) \quad -(45)$$

therefore the interaction hamiltonian is:

$$H_{int} = \left(\frac{\gamma^2}{1+\gamma}\right)\frac{\mu_0 e^2 g_N}{4\pi m_e m_p r^3}\left(\underline{S}\cdot\underline{I} - 3\,\underline{S}\cdot\hat{\underline{r}}\,\hat{\underline{r}}\cdot\underline{I}\right) \quad -(46)$$

and the well known hyperfine structure of NMR is changed by the factor (41). Usually the theory is simplified by aligning the two spin dipoles with the strong external magnetic flux density of an NMR spectrometer, so it reduces to:

$$H_{int}\psi = \frac{A\mu_0 e^2 g_N \hbar^2}{4\pi m_e m_p}\left(\frac{1-3\cos^2\theta}{r^3}\right)m_I m_s \psi \quad -(47)$$

The energy levels are therefore given as in Note 335(6):

$$E_{int} = \frac{A\mu_0 e^2 g_N \hbar^2}{4\pi m_e m_p}\, m_I m_s \int \psi^*\left(\frac{1-3\cos^2\theta}{r^3}\right)\psi\, d\tau \quad -(48)$$

and the NMR resonance frequency is:

$$\omega_{NMR} = \frac{A\mu_0 e^2 g_N \hbar}{8\pi m_e m_p}\int \psi^*\left(\frac{1-3\cos^2\theta}{r^3}\right)\psi\, d\tau \quad -(49)$$

as worked out in Note 335(6).

The removal of the Dirac approximation produces the shift:

$$\omega_{NMR} \rightarrow A\,\omega_{NMR} \qquad -(50)$$

in the hyperfine spectrum, and this is observable in an FT NMR spectrometer.

3. COMPUTATION AND GRAPHICAL ANALYSIS

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ECE2 and rigorous NMR theory

M. W. Evans[*], H. Eckardt[†]
Civil List, A.I.A.S. and UPITEC

(www.webarchive.org.uk, www.aias.us,
www.atomicprecision.com, www.upitec.org)

3 Computation and graphical analysis

In Eq.(34) the factor A correcting the expectation value of the NMR interaction energy (30) is given by

$$A = \frac{\gamma^2}{1+\gamma} = \frac{1}{1-\left(\frac{\alpha}{n}\right)^2+\sqrt{1-\left(\frac{\alpha}{n}\right)^2}} \tag{51}$$

with fine structure constant α and principal quantum number n. The function $A(n)$ has been graphed in Fig. 1 for a continuously extended n. The function drops to 1/2 in a hyperbolic way. The same does $\sqrt{A(n)}$ (not shown). The correction for $n = 1$ is about 0.2 % for A and 0.14 % for $\sqrt{A}$, respectively. The same correction is obtained for the difference energy (40) which is the NMR resonance frequency. Therefore all NMR spectra of Hydrogen are expected to have to be corrected by this amount.

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[*] email: emyrone@aol.com

[†] email: mail@horst-eckardt.de

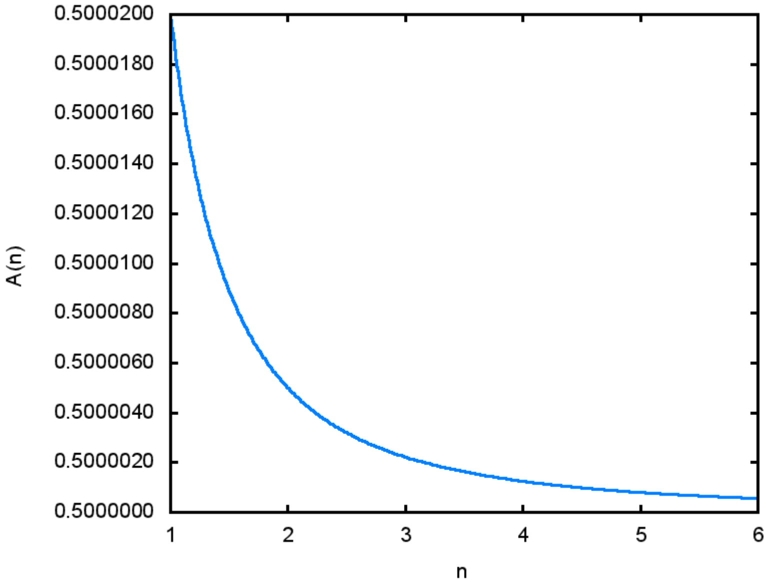

Figure 1: Correction factor $A(n)$ for atomic Hydrogen.

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