Chemical shift, fine and hyperfine structure in RFR spectroscopy

M.W. Evans[1]

Alpha Institute for Advanced Studies (www.aias.us)

The theory of radiatively induced fermion resonance (RFR) is developed from the Einstein–Cartan–Evans (ECE) wave equation to include considerations of the chemical shift, which is site specific and gives rise to the main features of the RFR spectrum. Experimental conditions are defined under which the RFR chemical shift is observable. Superimposed on the main chemical shift spectrum is fine and hyperfine detail due to spin spin interaction between nuclei. The great advantage of RFR over ESR or NMR is its greatly increased resolution, achieved without the use of expensive magnets. Thus fine and hyperfine detail is much better resolved.

1. Introduction

Radiatively induced fermion resonance (RFR) is the detection of the inverse Faraday effect (IFE) by resonance [1–12]. The IFE is magnetization by circularly polarized electromagnetic radiation. Thus RFR bears the same relation to IFE as ESR or NMR do to magnetization by a permanent magnet. The existence of RFR was first inferred from the inverse Faraday effect, and later from the Einstein Cartan Evans (ECE) wave equation [1–12] in a well defined semi-classical limit. In this paper the theory of RFR is developed to show the existence of the RFR chemical shift, due to a nuclear potential added to the external electromagnetic field potential. The RFR chemical shift is site specific and different for each fermion in an atom or molecule, and so gives rise to a novel kind of resonance spectrum in all materials, a spectrum that can built up without the use of expensive permanent magnets. The resolution of the RFR spectrum is increased by tuning $1/\omega^2$ of the pump beam that replaces the permanent magnet. The pump beam is a circularly polarized radio frequency field of power density I (watts per square meter) and angular frequency ω. In theory, the resolution of the RFR spectrum is much higher than that of ESR or NMR, allowing the resolution of

[1]e-mail: emyrone@aol.com

fine and hyperfine structure which may be obscured in ESR or NMR due to lack of resolution.

   In Section 1.2 the semi-classical hamiltonian term responsible for RFR is obtained from the ECE wave equation in a well defined semi-classical limit using the SU(2) basis in which the Pauli matrices comprise the basis set. Resonance occurs between the states of the Pauli matrix when a photon is absorbed from a probe beam, which may be the beam of a Fourier transform infra red interferometer for example. Having set up the hamiltonian for RFR in an unshielded fermion such as that in an electron beam, the chemical shift theory is developed in Section 1.3. Firstly in Section 1.3 a brief overview is given of chemical shift theory in ESR and NMR, which is a quantum theory, then the chemical shift theory is developed for RFR and the RFR shielding constant calculated in terms of externally applied and nuclear potential amplitudes. Finally in Section 1.4 an overview of fine and hyperfine structure in RFR is given following standard ESR and NMR theory.

1.2   The RFR Hamiltonian

The interaction between an electromagnetic and fermionic field is understood most generally by first considering the fermionic ECE wave equation [1–12]:

$$\left(\Box + kT\right)q_\mu^a = 0 \tag{1}$$

where q^a is the fermionic wave-function and where:

$$T = -\frac{R}{k} \tag{2}$$

is the scalar canonical energy-momentum density defined by:

$$R = q_a^\lambda \partial^\mu \left(\Gamma_{\mu\lambda}^\nu q_\nu^a - \omega_{\mu b}^a q_\lambda^b\right) \tag{3}$$

where R is the scalar curvature and where k is Einstein's constant. For a free fermion, Eq. (1) becomes the Dirac equation:

$$\left(\Box + \left(\frac{mc}{\hbar}\right)^2\right)\psi = 0 \tag{4}$$

where m is its mass, $\hbar$ is the reduced Planck constant and c the speed of light in a vacuum. On the semi-classical level the interaction of the fermion with an

electromagnetic four potential may be considered using the minimal prescription:

$$p^{\mu} \rightarrow p^{\mu} + eA^{\mu} \tag{5}$$

where e is the magnitude of the fermion charge, for example an electron. Using the quantum classical operator equivalence relations [13]:

$$p^{\mu} = i\hbar\partial^{\mu}, \ E = i\hbar\frac{\partial}{\partial t}, \ \boldsymbol{p} = -i\hbar\boldsymbol{\nabla} \tag{6}$$

the Dirac equation with minimal prescription becomes the Einstein equation:

$$\left(p^{\mu} + eA^{\mu}\right)\left(p_{\mu} + eA_{\mu}^{*}\right) = m^{2}c^{2} \tag{7}$$

whose non-relativistic limit gives the hamiltonian:

$$H = \frac{1}{2m}\left(\boldsymbol{p} + e\boldsymbol{A}\right)\cdot\left(\boldsymbol{p} + e\boldsymbol{A}^{*}\right). \tag{8}$$

In the SU(2) basis this hamiltonian is:

$$H = \frac{1}{2m}\boldsymbol{\sigma}\cdot\left(p + e\boldsymbol{A}\right)\boldsymbol{\sigma}\cdot\left(p + e\boldsymbol{A}^{*}\right). \tag{9}$$

For a complex valued, circularly polarized, electromagnetic potential:

$$\boldsymbol{A} = \boldsymbol{A}^{(1)} = \frac{A^{(0)}}{\sqrt{2}}\left(\boldsymbol{i} - i\boldsymbol{j}\right)e^{i\phi}, \tag{10}$$

$$\boldsymbol{A}^{*} = \boldsymbol{A}^{(2)} = \frac{A^{(0)}}{\sqrt{2}}\left(\boldsymbol{i} + i\boldsymbol{j}\right)e^{-i\phi}, \tag{11}$$

there exists an interaction term:

$$H = -i\frac{e^{2}}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{A}^{(1)} \times \boldsymbol{A}^{(2)}. \tag{12}$$

The conjugate product is:

$$A^{(0)2}\boldsymbol{k} = -i\boldsymbol{A}^{(1)} \times \boldsymbol{A}^{(2)} \tag{13}$$

so there are two energy levels in the interaction term (12):

$$H_+ = \frac{e^2}{2m} A^{(0)2} \tag{14}$$

and

$$H_- = -\frac{e^2}{2m} A^{(0)2}. \tag{15}$$

Radiatively induced fermion resonance (RFR) occurs when a probe beam photon is absorbed as follows:

$$\hbar\omega_{\text{res}} = H_+ - H_- \tag{16}$$

where ω_{res} is the resonance angular frequency. Using the fundamental optical relations [14]:

$$A^{(0)2} = \mu_0 c^2 \frac{I}{\omega^2} \tag{17}$$

where I is power density in watts per square meters and where μ_0 is the vacuum permeability the RFR resonance frequency for an electron is found to be:

$$\omega_{\text{res}} = \left(\frac{e^2 \mu_0 c^2}{\hbar m} \right) \frac{I}{\omega^2}. \tag{18}$$

It is proportional to I, the pump beam power density, and inversely proportional to the pump beam angular frequency ω.

1.3 Chemical shift theory

The above theory has been developed for a free electron (in an electron beam), in which there is no chemical shift present. In the presence of a nuclear potential A_N this resonance frequency is shifted from that given in Eq. (18). In this section an overview is first given of chemical shift theory in ESR and NMR, and the theory is extended to RFR chemical shifts. In ESR and NMR chemical shift theory the basic method is to use the minimal prescription:

$$\boldsymbol{p} \rightarrow \boldsymbol{p} + e\boldsymbol{A} \tag{19}$$

where the vector potential is:

$$\boldsymbol{A} = \boldsymbol{A}_{\text{ext}} + \boldsymbol{A}_N. \tag{20}$$

Here $\boldsymbol{A}_{\text{ext}}$ is the vector potential of the applied external magnetic field, and $\boldsymbol{A}_N$ the vector potential due to a nucleus:

$$\boldsymbol{A}_N = \frac{\mu_0}{4\pi r^3} \boldsymbol{m}_N \times \boldsymbol{r} \tag{21}$$

where $\boldsymbol{m}_N$ is the nuclear dipole moment and $\boldsymbol{r}$ the distance between the nucleus and the resonating fermion. The chemical shift is site specific and builds up the ESR or NMR spectrum as is well known. The ESR or NMR chemical shift can be calculated from the Schrödinger–Pauli equation [1–12] using the hamiltonian operator:

$$\hat{H} = \frac{1}{2m} \boldsymbol{\sigma} \cdot (\boldsymbol{p} + e\boldsymbol{A}) \boldsymbol{\sigma} \cdot (\boldsymbol{p} + e\boldsymbol{A}). \tag{22}$$

The relevant part of the hamiltonian for ESR or NMR is:

$$\hat{H}_{\text{int}} = i \frac{e}{2m} \boldsymbol{\sigma} \cdot (\boldsymbol{A} \times \boldsymbol{p} + \boldsymbol{p} \times \boldsymbol{A}). \tag{23}$$

It is seen that on the classical level:

$$\hat{H}_{\text{int}} (\text{classical}) = 0 \tag{24}$$

so ESR and NMR can be understood only in quantum mechanics using:

$$\hat{H}_{\text{int}} \psi = E\psi. \tag{25}$$

The hamiltonian operator (23) operates on the wave function V through:

$$\hat{H}_{\text{int}} = \frac{e\hbar}{2m} \boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} \times \boldsymbol{A} + \boldsymbol{A} \times \boldsymbol{\nabla}). \tag{26}$$

Therefore:

$$\mathbf{p} \to -i\hbar\nabla \tag{27}$$

and Eq. (25) becomes:

$$\frac{e\hbar}{2m}\left(\boldsymbol{\sigma}\cdot\nabla\times\left(A\psi\right)+\boldsymbol{\sigma}\cdot\left(A\times\nabla\right)\psi\right)=E\psi. \tag{28}$$

Note that the vector curl operates on both A and ψ as follows:

$$\nabla\times\left(A\psi\right)=\left(\nabla\times A\right)\psi+\nabla\psi\times A \tag{29}$$

from vector analysis, which also gives:

$$\left(A\times\nabla\right)\psi=A\times\nabla\psi. \tag{30}$$

Defining the magnetic field as:

$$\mathbf{B}=\nabla\times A \tag{31}$$

the energy is found to be:

$$E=\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}. \tag{32}$$

There are two energy levels:

$$E_{+}=\frac{e\hbar}{2m}B \tag{33}$$

$$E_{-}=-\frac{e\hbar}{2m}B \tag{34}$$

and resonance occurs when a probe beam photon is absorbed as follows:

$$\hbar\omega_{\text{res}}=E_{+}-E_{-}. \tag{35}$$

The resonance frequency of ESR and NMR is therefore:

$$\omega_{\text{res}}=\frac{eB}{m} \tag{36}$$

a quantum mechanical result.

In Eq. (36) the magnetic field is:

$$\boldsymbol{B} = \boldsymbol{B}_{\text{ext}} + \boldsymbol{B}_N \tag{37}$$

and this is usually expressed [14] as:

$$\boldsymbol{B} = (1 - \sigma) \boldsymbol{B}_{\text{ext}} \tag{38}$$

where:

$$\sigma = -\frac{B_N}{B_{\text{ext}}} \tag{39}$$

is the shielding constant. For each nucleus the shielding constant is different, so there is an ESR or NMR spectrum. In ethanol for example it consists of three lines in the ratio 3:2:1.Thesamefundamental principles apply to MRI, in which an inhomogeneous magnetic field is used.

The RFR chemical shift is developed from the hamiltonian (12) and is understood classically in the SU(2) basis. In the presence of A_N, the conjugate product is changed as follows:

$$\left(\boldsymbol{A}^{(1)} + \boldsymbol{A}_N \right) \times \left(\boldsymbol{A}^{(2)} + \boldsymbol{A}_N \right) = -i \left(\left(\frac{A^{(0)}}{\sqrt{2}} e^{i\phi} + A_X \right) \left(i \frac{A^{(0)}}{\sqrt{2}} e^{-i\phi} + A_Y \right) \right. $$
$$\left. - \left(-i \frac{A^{(0)}}{\sqrt{2}} e^{i\phi} + A_Y \right) \left(\frac{A^{(0)}}{\sqrt{2}} e^{-i\phi} + A_X \right) \right) \boldsymbol{k}. \tag{40}$$

The calculation is simplified if we assume:

$$\boldsymbol{A}_N = A_X \boldsymbol{i} + A_Y \boldsymbol{j} \tag{41}$$

otherwise there are more terms in Eq. (40). Working out the algebra in Eq. (40) gives the result:

$$H = \frac{e^2}{2m} \left(A^{(0)2} + \sqrt{2} A^{(0)} \left(A_X - i A_Y \right) \cos \phi \right) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{42}$$

and it is seen that the RFR resonance frequency is shifted by the presence of

the nuclear potential. This shift is site specific as in ESR and NMR, and so there is an RFR chemical shift spectrum of great potential utility.

It is more convenient experimentally to use the root mean square hamil-tonian:

$$\left\langle H^2 \right\rangle^{\frac{1}{2}}$$
$$= \frac{e^2}{2m} \left\langle A^{(0)4} + 2A^{(0)2} \left(A_X^2 + A_Y^2 \right) \cos^2 \phi + 2\sqrt{2} A^{(0)3} \cos\phi \right\rangle^{\frac{1}{2}} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{43}$$

Now use:

$$\left\langle \cos\phi \right\rangle = 0 \tag{44}$$

$$\left\langle \cos^2 \phi \right\rangle = \frac{1}{2} \tag{45}$$

to find that:

$$\left\langle H^2 \right\rangle^{\frac{1}{2}} = \frac{e^2}{2m} A^{(0)} \left(A^{(0)2} + A_X^2 + A_Y^2 \right)^{\frac{1}{2}} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{46}$$

Therefore the root mean square power density of the beam is needed:

$$I = \left\langle I^2 \right\rangle^{\frac{1}{2}}. \tag{47}$$

The power density itself is proportional to:

$$I \propto \boldsymbol{A}^{(1)} \cdot \boldsymbol{A}^{(2)} = A^{(0)2}. \tag{48}$$

In the absence of A_x and A_y, the hamiltonian and root mean square hamil-tonian are the same:

$$H = \left\langle H^2 \right\rangle^{\frac{1}{2}} = \frac{e^2 A^{(0)2}}{2m} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{49}$$

There are two root mean square energy levels in Eq. (46):

$$\left\langle H^2 \right\rangle_+^{\frac{1}{2}} = \frac{e^2}{2m} A^{(0)} \left(A^{(0)2} + A_X^2 + A_Y^2 \right)^{\frac{1}{2}} \tag{50}$$

and

$$\left\langle H^2 \right\rangle_-^{\frac{1}{2}} = \frac{e^2}{2m} A^{(0)} \left(A^{(0)2} + A_X^2 + A_Y^2 \right)^{\frac{1}{2}} \tag{51}$$

and the chemically shifted RFR resonance occurs when a probe beam photon is absorbed as follows:

$$\hbar\omega_{\text{res}} = \left\langle H^2 \right\rangle_+^{\frac{1}{2}} - \left\langle H^2 \right\rangle_-^{\frac{1}{2}}. \tag{52}$$

Thus:

$$\omega_{\text{res}} = \frac{e^2 A^{(0)2}}{\hbar m} \left(1 + \frac{A_X^2 + A_Y^2}{A^{(0)2}} \right)^{\frac{1}{2}}. \tag{53}$$

This result may be expressed in terms of I and ω as follows:

$$\omega_{\text{res}} = \left(\frac{e^2 \mu_0 c^2}{\hbar m} \right) \frac{I}{\omega^2} \left(1 + \frac{\left(A_X^2 + A_Y^2 \right)}{\mu_0 c^2} \frac{\omega^2}{I} \right). \tag{54}$$

and the RFR shielding constant may be defined as:

$$\sigma_{RFR} = \frac{A_X^2 + A_Y^2}{A^{(0)2}} \tag{55}$$

so the chemically shifted RFR frequency is:

$$\omega_{\text{res}} = \left(\frac{e^2 \mu_0 c^2}{\hbar m} \right) \frac{I}{\omega^2} \left(1 + \sigma_{REF} \right)^{\frac{1}{2}}. \tag{56}$$

1.4   Fine and hyperfine RFR structure

As in standard ESR and NMR theory [14] various types of spin spin interaction also contribute to the RFR spectrum.

1) The fine structure is due to electron electron spin spin interaction.

2) The hyperfine structure is due to electron - nuclear spin spin interaction.

3) The fine NMR structure is due to nuclear nuclear spin spin interaction.

The theory of this spectral structure in RFR follows the theory in ESR and NMR. In the latter theory, following the standard notation [14], perturbation theory is used as is well known. The same perturbation theory can be used in RFR. If the unperturbed eigenstates of $H^{(\circ)}$ are $|n\rangle$, the ground state is $|0\rangle$. The first order correction in NMR or ESR is:

$$E^{(1)} = -g_e r_e \hbar B m_s \tag{57}$$

and the energy correction to second order is:

$$E^{(2)} = \sum_n {}^1 \left(\frac{\langle 0|H^{(1)}|n\rangle \langle n|H^{(1)}|0\rangle}{E_0 - E_n} \right) \tag{58}$$

where

$$H^{(1)} = -g_e r_e \mathbf{s} \cdot \mathbf{B} + \lambda \mathbf{I} \times \mathbf{s} - r_e \mathbf{I} \cdot \mathbf{B}. \tag{59}$$

In the numerator, the terms proportional to the magnetic field are:

$$\langle 0|-g_e r_e s \cdot \mathbf{B}|n\rangle \langle n|\lambda \mathbf{I} \cdot s|0\rangle + \langle 0|\lambda \mathbf{I} \cdot s|n\rangle \langle n|-g_e r_e s \cdot B|0\rangle. \tag{60}$$

The spin hamiltonian is defined as [14]:

$$H^{\text{spin}} = -g_{ZZ} \gamma_e B S_Z. \tag{61}$$

For spin orbit coupling for example:

$$H^{\text{spin}} = g \frac{\mu_B}{\hbar} B S_Z + A(\theta) I_Z S_Z + C I_Z S_Z \tag{62}$$

and:

$$M_I = I, I-1, \cdots, -I \tag{63}$$

so there are $2I + 1$ resonance lines spaced by $C+A(0)$. In a liquid:

$$\langle A(0)\rangle = 0.$$

<div align="right">(64)</div>

It is seen that the spacing does not depend on the magnetic field strength, but if the main chemically shifted lines are not well separated, the fine and hyperfine structure will overlap and not be completely resolved. This is often the case in ESR and NMR. In RFR the spacing of the chemically shifted lines may be increased greatly by tuning , and the fine and hyperfine structures will be completely resolved, a major analytical advantage.

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M.W. Evans