OPTICAL NMR FROM THE DIRAC EQUATION - A REPLY TO BUCKINGHAM AND PARLETT.

by

M. W. Evans,
Deaprtment of Physics and Astronomy,
York University, 4700 Keele Street,
North York, Toronto,
Ontario M3J 1P3,
Canada.

ABSTRACT

The Dirac equation of the fermion in a circularly polarized electromagnetic field produces optical NMR shifts of the same order of magnitude as observed in the recent experiments of Warren et al. By decreasing the frequency of the irradiation field the Dirac equation shows that electromagnetically induced NMR lines can be observed in the infrared or visible range in theory. A recent paper by Buckingham and Parlett {9} is criticized in detail.

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1. INTRODUCTION

In his original derivation of the half integral spin of the electron, Dirac assumed {1} that the electromagnetic potential vector $\underline{A}$ was a real quantity, so that the cross product $\underline{A} \times \underline{A}$ is zero identically. This is adequate for a static magnetic field, but more generally $\underline{A}$ is complex, and the conjugate product $\underline{A} \times \underline{A}^*$ is non-zero { 2 }. It has magnetic symmetry and is responsible for inverse Faraday induction {3 - 6}. In this note we use $\underline{A} \times \underline{A}^*$ in Dirac's original derivation { 1 } to adequately reproduce the order of magnitude of optically induced NMR shifts observed recently by Warren et al. {7, 8} using visible frequencies. The agreement of experiment and data is strongly indicative of the usefulness of this technique, especially if the visible frequency laser used by Warren et al. {7,8} is replaced by a radio frequency field. In this case the Dirac equation of one fermion in the field indicates theoretically the possibility of NMR in the infra red or visible.

A recent paper by Buckingham and Parlett { 9 } is criticised using these results from the original Dirac equation { 1 }.

2. NMR OF ONE FERMION IN A CIRCULARLY POLARIZED RADIATION FIELD.

There is no reason to assume that NMR and/or ESR must always be practiced with static magnetic fields, or that a Pauli spinor must always interact with a static magnetic field. The conjugate product $\underline{A} \times \underline{A}^*$ of an electromagnetic wave has magnetic symmetry, and produces magnetic resonance from the Dirac equation of one fermion in the field. The wave equation for a fermion in a static magnetic field ~~is~~ {10}, expected from analogy with the classical hamiltonian is {1}:

~~$(p_0 + eA_0 - \rho_1(\underline{\sigma} \cdot (\underline{p} + e\underline{A})) - \rho_3 mc)\psi = 0$~~

$$((p_0 + eA_0)^2 - (\underline{p} + e\underline{A})^2 - m^2c^2)\psi = 0 \qquad - \textcircled{1} \qquad \cancel{(1)}$$

~~where ψ is the wavefunction, ρ_1 and ρ_3 are 4x4 matrices;~~

where $p_\mu := (p_0, \underline{p})$ is the energy / momentum 4-vector, and the potential 4-vector is $A_\mu := (A_0, \underline{A})$.

The charge and mass of the fermion are e and m respectively and c is the speed of light in vacuo. Eqn. (1) was written by Dirac for a real $\underline{A}$. For a complex $\underline{A}$, it becomes

$$((p_0 + eA_0)(p_0 + eA_0^*) - (\underline{p} + e\underline{A}) \cdot (\underline{p} + e\underline{A}^*) - m^2c^2)\psi = 0, \qquad - (2)$$

where it has been assumed that $\underline{A}$ is also complex. In order to make his theory of the electron resemble eqn. (1) as closely as possible, Dirac ~~uses the equation~~ ~~multiplies eqn. ( ) by the factor~~: carries out a product of factors for real $\underline{A}$ [1]. For complex $\underline{A}$ we obtain [10] an equation which

~~which for a complex potential 4 vector becomes:~~

~~giving the product { }~~

~~This~~ replaces eqn. (31), chapter 11, of ref. (1). The conjugate product $\underline{A}$ x $\underline{A}^*$ originates in the term $e^2(\underline{\sigma} \cdot \underline{A}^*)(\underline{\sigma} \cdot \underline{A})$ using the expansion:

$$(\underset{\sim}{\sigma}\cdot\underline{B})(\underset{\sim}{\sigma}\cdot\underline{C}) = \underline{B}\cdot\underline{C} + i(\underset{\sim}{\sigma}\cdot\underline{B}\times\underline{C}) \qquad -(3)$$

as ~~shown~~ used by Dirac {1}. Straightforward calculation {10} then shows that the eigenvalue of the interaction energy between the field and one fermion is:

$$W := En - mc^2 \sim \frac{e^2c^2(\underset{\sim}{\sigma}\cdot\underline{A})(\underset{\sim}{\sigma}\cdot\underline{A}^*)}{En + mc^2 + ecA_0} - ecA_0 . \qquad -(4)$$

In Dirac's approximation [1] $En \sim mc^2$, and assuming that $A_0 = 0$, (Coulomb gauge), then:

$$W \sim \frac{e^2}{2m}\left(\underline{A}\cdot\underline{A}^* + i\underset{\sim}{\sigma}\cdot\underline{A}\times\underline{A}^*\right). \qquad -(5)$$

Therefore the interaction term $i\underline{\sigma}\cdot\underline{A}\times\underline{A}^*$ emerges directly from the Dirac equation, and is responsible for radiation induced fermion (e.g. nuclear) magnetic resonance. The $\underline{B}^{(3)}$ field of Evans and Vigier {11-15} is defined as:

$$\underset{\sim}{B}^{(3)*} := -i\frac{e}{\hbar}\underline{A}\times\underline{A}^* \equiv -i\frac{e}{\hbar}\underset{\sim}{A}^{(1)}\times\underline{A}^{(2)}, \qquad -(6)$$

giving the interaction energy between fermion and magnetic field in the standard form:

$$En_{int} = -\frac{e}{m}\left(\frac{\hbar}{2}\underset{\sim}{\sigma}^{(3)}\right)\cdot\underline{B}^{(3)*} \qquad -(7)$$

i.e. in the same form as that between the spinor and a static magnetic field.

In terms of intensity (I, W m^{-2}), otherwise known as power density, and beam angular frequency (ω, rad s^{-1}), the $\underline{B}^{(3)}$ field from eqn. (6) is {10}:

$$\begin{aligned}\underset{\sim}{B}^{(3)} &= \frac{e\mu_0 c}{\hbar}\frac{I}{\omega^2}\underline{e}^{(3)} \\ &= 5.723\times10^{17}\frac{I}{\omega^2}\underline{e}^{(3)} \qquad -(8)\end{aligned}$$

where μ_0 is the permeability in vacuo and where $\underline{e}^{(3)}$ is a unit vector in the (3) axis of frame ((1), (2), (3)) {11-15}.

3. COMPARISON WITH EXPERIMENTAL DATA.

Fermion resonance occurs at a probe angular frequency ω_{res} defined by transitions from the negative to the positive states of the spinor $\underline{\sigma}^{(3)}$ in eqn (7):

$$\hbar\omega_{res} = \frac{e^2c^2B^{(0)2}}{2m\omega^2}\left(1-(-1)\right). \qquad -(9)$$

The resonance frequency of the probe field is therefore, for one fermion:

$$\omega_{res} = \left(\frac{e^2\mu_0 c}{\hbar m}\right)\frac{I}{\omega^2}; \qquad -(10)$$

and is inversely proportional to the square of the angular frequency. For proton (^{1}H) resonance we adjust this result empirically [10] for the different Landé factors of the proton (5.5857) and the electron (2.002), and multiply (10) by the ratio 5.5857/2.002, giving:

$$\omega_{res}\left({}^1H\right) = 1.532\times10^{25}\,\frac{I}{\omega^2}. \qquad -(11)$$

If the pump frequency ω is about 5,000 cm^{-1} in the visible, and if I is chosen to be a moderate 10 W per square centimetre, the resonance frequency ω_{res} from eqn. (11) is about 1.7 Hz. This is in good qualitative agreement with the data by Warren et al. {7,8}. who observed shifts as large as about 2 Hz for a laser of intensity about 3 watts per square centimetre, shifts which changed direction with the sense of circular polarization of the beam. However, the overall pattern of results {7, 8} was complicated and the shifts were small, because, understandably, a visible frequency was used. Eqn. (11) now shows that much greater shifts are expected agreement with data is all that can be reasonably expected from eqn. (   ), which is for one unshielded fermion.

The Ar^+ laser frequencies used by Warren et al. {7,8} were 528.7 nm, 488 nm, and 476.5 nm, giving resonance frequencies from eqn. (11) of respectively 0.12 Hz, 0.10 Hz, and 0.09(8) Hz for I of 10 watts per square centimetre. These are many orders of magnitude greater than those in the received phenomenology of Buckingham and Parlett {9} but are at the extreme edge of contemporary detection capability. Eqn. (11), (essentially the Dirac equation), shows that for ^{13}C the shifts would be more than an order of magnitude smaller, and therefore undetectable, because of the inverse mass dependence and smaller Landé factor of ^{13}C. This is again in qualitative agreement with the experimental results {7,8}.

4. CRITICISM OF REMARKS BY BUCKINGHAM AND PARLETT {   }.

Buckingham and Parlett {   } have given a simple phenomenological theory of the optical NMR phenomenon which leads to results that are several orders of magnitude smaller than the data observed by Warren et al. {   }. These authors apparently believe that the results by Warren et al. {   } are artifact, because their phenomenology produces shifts many orders of magnitude too low. In so doing they do not consider the Dirac equation, which is a precise equation of the relativistic quantum field theory. They assert that the correct mechanism must be one based on the antisymmetric electronic polarizability: essentially a perturbation calculation for the chemical shift. These authors have not met the challenge posed by the data of Warren et al. {   }, and have preferred to state well known phenomenology which does not explain anything new. It is erroneously asserted {   } that B defined by eqn. (   ) violates C symmetry, whereas it has been shown already {   } that the B cyclics trivially conserve C symmetry. A variation of the conjugate product is used {

for the same intensity (I) at radio frequencies { 10 }. Qualitative agreement with data is all that can be reasonably expected from eqn. (11), which is for one unshielded fermion.

4. CRITICISM OF REMARKS BY BUCKINGHAM AND PARLETT { 9 }.

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remarks ~~thereafter~~ of mass spectra [illegible] as D.P.P. out

The Ar^+ laser frequencies used by Warren et al. [7,8] were 528.7 nm, 488 nm, and 476.5 nm, ~~under~~ giving shifts from eqn. (11) of 0.12 Hz, 0.10 Hz and 0.09(8) Hz respectively. These are at the extreme edge of contemporary detection capability, in agreement again with the experimental results [7,8]. and eqn. (11) (essentially the Dirac eqn.) shows ~~that~~ for ^{13}C and ^{1}H, the shifts would be about ~~[illegible]~~ 15 times smaller than in and therefore undetectable. This is because of the inverse mass dependence in eqn. (10).

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REFERENCES

{1} P. A. M. Dirac, "Quantum Mechanics", 4th. edn., (Oxford University Press, Oxford, 1974).

{2} G. Wagnière, Phys. Rev., A, 40, 2437 (1989); G. H. Wagnière, "Linear and Nonlinear Optical Properties of Molecules." (VCH, Basel, 1993).

{3} R. Zawodny, in M. W. Evans and S. Kielich (eds.), "Modern Nonlinear Optics.", a special topical issue of I. Prigogine and S. A. Rice (series eds.), "Advances in Chemical Physics." (Wiley Interscience, New York, 1993), vol. 85(1).

{4} J. P. van der Ziel, P. S. Pershan and L. D. Malmstrom, Phys. Rev. Lett., 15, 190 (1965); Phys. Rev., 143, 574 (1966).

{5} J. Deschamps, M. Fitaire and M. Lagoutte, Phys. Rev. Lett., 25, 1330 (1970).

{6} T. W. Barrett, H. Wohltjen and A. Snow, Nature, 301, 694 (1983).

{7} W. S. Warren, S. Mayr, D. Goswami and A. P. West Jr., Science, 255, 1683 (1992); 259, 836 (1993).

{8} D. Goswami, Ph. D. Thesis (Princeton University, 1994).

{9} A. D. Buckingham and L. C. Parlett, Science, 264, 1748 (1994).

{10} M. W. Evans, J.-P. Vigier, S. Roy and S. Jeffers, "The Enigmatic Photon, Vol. 3, Theory and Practice of $\mathbf{B}^{(3)}$." (Kluwer, Dordrecht, 1996).

{11} M. W. Evans and J.-P. Vigier, "The Enigmatic Photon, Vol. One, The Field $\mathbf{B}^{(3)}$", (Kluwer, Dordrecht, 1994).

{12} M. W. Evans and J.-P. Vigier, "The Enigmatic Photon, Vol. Two, Non-Abelian Electrodynamics." (Kluwer, Dordrecht, 1995).

{13} M. W. Evans, Physica B, 190, 310 (1993); L. D. Barron, Physica B, 190, 307 (1993).

{14} M. W. Evans, Physica B, 182, 227, 237 (1992); 183, 103 (1993).

{15} M. W. Evans, Found. Phys., 24, 892, 1519, 1671 (1994); 25, 175, 383 (1995); M. W. Evans, Found. Phys. Lett., 7, 67, 209, 379, 437, 577, 591 (1994); 8, 83, 187, 253, 279 (1995).

{16} S. Woźniak, M. W. Evans and G. Wagnière, Mol. Phys., 75, 81, 99 (1992).

{17} M. W. Evans, J. Phys. Chem., 95, 2256 (1991).

{18} M. W. Evans, Int. J. Mod. Phys., B, 5, 1963 (1991).

{19} M. W. Evans, Opt. Phot. News, 2(12), 42 (1991); Physica B, 179, 157 (1992); Physica B, 179, 157 (1992); J. Mol. Spect., 154, 1 (1992); Mod. Phys. Lett., 6, 1237 (1992).

{20} M. W. Evans and C. Pelkie, J. Opt. Soc. Am., B, 9(7), 1020 (1992).