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Nuclear electromagnetic resonance spectroscopy

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An argument is made for the existence of nuclear electromagnetic resonance (NER) between the interaction Hamiltonian due to the conjugate product $\boldsymbol{\pi}$ of electric fields of a powerful pump laser and a new concept of nuclear spin polarizability, and a resonating electromagnetic probe field in the appropriate frequency range. NER is mediated theoretically by the interaction of $\boldsymbol{\pi}$ with an axial vector quantity identified as nuclear spin polarizability, $\boldsymbol{\alpha}_s''$. The latter is defined through off-diagonal matrix elements of nuclear transition electric dipole moments, between states of different parity, and the perturbation Hamiltonian, $-\boldsymbol{\pi} \cdot \boldsymbol{\alpha}_s''$, provides the nucleus with net spin, analogously with the interaction of nuclear spin, $\boldsymbol{I}$, external static magnetic flux density $\boldsymbol{B}$, the basis of NMR spectroscopy. This analogy is based on the identical parity and motion reversal symmetries of $\boldsymbol{\pi}$ and $\boldsymbol{B}$; and $\boldsymbol{I}$ and $\boldsymbol{\alpha}_s''$.

1. Introduction

The well known and widely used technique of nuclear magnetic resonance (NMR) spectroscopy has a long and distinguished history. The experiments of Gerlach and Stern [1], and of Rabi *et al.* [2], provided unequivocal first evidence for the existence of particle (electronic and nuclear) spin inside an atom, a challenge met theoretically by Dirac. NMR depends on the concept of nuclear spin quantum number, which has been found to vary from 0 to about 6 for different elementary nuclei. The angular momentum of the nucleus [3] is denoted $\boldsymbol{I}\hbar$, where $\hbar$ is the reduced Planck constant $\hbar/2\pi$, and the nuclear magnetic moment is $\boldsymbol{m} = \gamma\hbar\boldsymbol{I}$, where γ is the gyromagnetic ratio. Both $\boldsymbol{I}$ and $\boldsymbol{m}$ have negative motion reversal (T) symmetry, and positive parity inversion (P) symmetry [4–6]. The interaction of $\boldsymbol{m}$ with externally applied static magnetic flux density ($\boldsymbol{B}$) results in the torque

$$\boldsymbol{T}_{ql} = \boldsymbol{m} \times \boldsymbol{B}, \tag{1}$$

which gives the nucleus net angular acceleration. The interaction energy equivalent to this torque is

$$\Delta H_l = -\gamma\hbar\boldsymbol{B} \cdot \boldsymbol{I}, \tag{2}$$

which in contemporary NMR resonates with a radiofrequency probe electromagnetic field, whose frequency is about

$$\begin{aligned} \omega_l &\doteqdot 60{\cdot}0\,\text{MHz} \\ &\doteqdot |\boldsymbol{B}|\mu_N/\hbar. \end{aligned} \tag{3}$$

For $\boldsymbol{B}$ of 1·0 Tesla, multiplying an order of magnitude given by the nuclear magnetron, μ_N, which is about $5 \times 10^{-27}\,\text{J T}^{-1}$, the frequency ω_l is in the MHz range, 60 MHz in older instruments which were designed for proton resonance, and now up to the GHz range, depending on the nucleus being investigated.

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In this paper we use symmetry and analytical theory to argue for the existence of nuclear electromagnetic resonance (NER), in which the magnetic field of NMR instruments is replaced by electromagnetic radiation, a pump laser, for example a Nd:YAG (neodymium doped yttrium/aluminium garnet); or a Nd:YLF (neodymium doped yttrium/lithium fluoride) laser. A Nd:YAG which can deliver, when simultaneously focused and Q-switched, in pulse trains, an electric field strength of up to 10^9 V m^{-1} [7], is commercially available and relatively inexpensive.

In section 2, symmetry arguments are made for the use in NER of a pump laser quantity $\boldsymbol{\pi}$, generated by the conjugate product of its electric field strength, which has the same P and T symmetries as $\boldsymbol{B}$. Section 3 describes the theoretical basis for the interaction of $\boldsymbol{\pi}$ with a nculear quantity which is named "nuclear spin polarizability", an axial vector denoted by $\boldsymbol{\alpha}_s''$ which has the same P and T symmetries as $\boldsymbol{I}$. The interaction Hamiltonian is

$$\Delta H_2 = -\tfrac{1}{2}\boldsymbol{\pi}\cdot\boldsymbol{\alpha}_s'', \tag{4}$$

which torques the nucleus through

$$\boldsymbol{T}_{q2} = \tfrac{1}{2}\boldsymbol{\alpha}_s'' \times \boldsymbol{\pi}, \tag{5}$$

both quantities bearing a clear analogy to the interaction of $\boldsymbol{I}$ and $\boldsymbol{B}$. This gives the nucleus a net angular acceleration through $\boldsymbol{\pi}$ of the pump laser. Section 4 makes an order of magnitude estimate of where the resonance frequencies are to be found for a given order of magnitude of the quantity $\boldsymbol{\alpha}_s''$, which is defined through off-diagonal matrix elements of nuclear transition electric dipole moments of different parity, as discussed, for example, in chapter 6 of Abragam [3]. Nuclei appear to have no *permanent* electric dipole moments in the absence of parity violating electroweak forces [8–10], which would allow non-vanishing expectation values of transition electric dipole moments between nuclear eigenstates of the *same* parity. NER is therefore potentially useful for the study of P violation in nuclear properties.

Finally, section 5 is a discussion of the consequences of NER, its likely applications, similarities to and differences from NMR, and provides some analysis of optical phenomena expected from the Hamiltonian (4) by application of semiclassical Rayleigh refringent scattering theory [11].

2. Definition of the laser conjugate product $\boldsymbol{\pi}$

The conjugate product $\boldsymbol{\pi}$ of the pump laser is generated from the fact that an electromagnetic field can be left (L) or right (R) circularly polarized. Each of these components can be written as a plus (+) or minus (−) complex conjugate, and the vector product of the conjugate causes the phenomenon of optical rectification [12–15]. The four possible electric field strengths are therefore

$$\begin{aligned} \boldsymbol{E}_-^{(L)} &= E_0(\boldsymbol{i} + i\boldsymbol{j})e^{-i\theta_L}; \quad \boldsymbol{E}_-^{(R)} = E_0(\boldsymbol{i} - i\boldsymbol{j})e^{-i\theta_R}; \\ \boldsymbol{E}_+^{(L)} &= E_0(\boldsymbol{i} - i\boldsymbol{j})e^{i\theta_L}; \quad \boldsymbol{E}_+^{(R)} = E_0(\boldsymbol{i} + i\boldsymbol{j})e^{i\theta_R}; \end{aligned} \tag{6}$$

where $\boldsymbol{i}$ and $\boldsymbol{j}$ are unit vectors in X and Y, respectively, of the laboratory frame (X, Y, Z); where i is the root of minus one; and where the phases are defined by

$$\theta_L = \omega t - \boldsymbol{K}_L\cdot\boldsymbol{r}; \quad \theta_R = \omega t - \boldsymbol{K}_R\cdot\boldsymbol{r}. \tag{7}$$

where ω is the angular frequency of the pump laser, and $\boldsymbol{K}$ its propagation vector, directed along Z. This is a photon momentum, and is therefore negative to both P and

T. The conjugate product

$$\boldsymbol{\pi} = \boldsymbol{E}_{-}^{(L)} \times \boldsymbol{E}_{+}^{(L)} = -\boldsymbol{E}_{-}^{(R)} \times \boldsymbol{E}_{+}^{(R)} = -2E_0^2 i\boldsymbol{k} \tag{8}$$

is therefore positive to P and negative to T, i.e. has the same symmetry characteristics as static magnetic flux density, $\boldsymbol{B}$. Physically, $\boldsymbol{\pi}$ comes form the helical pattern drawn out by the tip of the electric field strength vector of the pump laser, a helix drawn around the axis Z of the forward motion of the photon momentum, or propagation, vector $\boldsymbol{K}$. The latter reverses in direction with T, and the product $\boldsymbol{\pi}$, an axial vector in Z, also reverses with T. Its P symmetry is positive, because it originates from the product of the two electric field strengths, each of negative P.

Note that $\boldsymbol{\pi}$ changes sign if the circular polarity of the pump laser is changed from right to left (this is analogous to reversing the direction of $\boldsymbol{B}$ in NMR). Second, $\boldsymbol{\pi}$ does not depend on the phase, is a finite quanity which does not average to zero over a finite macroscopic time interval. It is proportional to the square of the electric field strength of the pump laser, which in a Nd:YAG can reach $10^{18}\,V^2\,m^{-2}$ [7].

The other possible conjugate products to second order are

$$\boldsymbol{E}_{+}^{(L)} \times \boldsymbol{B}_{-}^{(L)} = \boldsymbol{E}_{+}^{(R)} \times \boldsymbol{B}_{-}^{(R)} = 2E_0 B_0 \boldsymbol{k}, \tag{9}$$

and

$$\boldsymbol{B}_{-}^{(L)} \times \boldsymbol{B}_{+}^{(L)} = -\boldsymbol{B}_{-}^{(R)} \times \boldsymbol{B}_{+}^{(R)} = 2B_0^2 i\boldsymbol{k}, \tag{10}$$

where $\boldsymbol{B}_{\pm}^{L,R}$ is the time dependent magnetic flux density of the pump laser. These are respectively proportional to $E_0 B_0$ and to B_0^2, and are therefore about c and c^2 times smaller than (8), where c is the magnitude of the velocity of light. Each conjugate product can, theoretically, torque the nucleus with an equivalent perturbation Hamiltonian. In this paper no further consideration is given to (9) and (10).

3. The interaction Hamiltonian, nuclear spin polarizability

The interaction Hamiltonian between $\boldsymbol{\pi}$ and the nucleus is assumed to be a product with a complex, dynamic, electric, *nuclear*, polarizability tensor. It is useful to write the axial vector (rank 1 tensor) $\boldsymbol{p}$ as the matrix quantity

$$\pi_{ij} = \begin{bmatrix} 0 & 2E_0^2 i & 0 \\ -2E_0^2 i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{11}$$

using the purely mathematical relation

$$\pi_i = \varepsilon_{ijk}\pi_{jk}, \tag{12}$$

where ε_{ijk} is the Levi Civita symbol. The interaction Hamiltonian becomes [11]:

$$\Delta H_2 = -\tfrac{1}{2}\pi_{ij}\alpha_{ij}. \tag{13}$$

This product is a tensor contraction [11], i.e., a scalar, whose equivalent perturbation frequency is

$$\omega_2 \doteqdot \pi_{ij}\alpha_{ij}/\hbar. \tag{14}$$

if an electromagnetic probe is tuned to this frequency, resonance will occur, causing absorption of the probe radiation in direct analogy with NMR. In general, the nuclear polarizability is defined in analogy with the electronic dynamical polarizability [11] as

being made up, in the laboratory frame (X, Y, Z), of real and imaginary components

$$\alpha'_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\left[\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle)\right] \tag{15}$$

and

$$\alpha''_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\left[\frac{\omega}{\omega_{jn}^2 - \omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle)\right] \tag{16}$$

where

$$\omega_{jn} = \omega_j - \omega_n. \tag{17}$$

The real part of the nuclear polarizability is + to P and + to T, the imaginary part is + to P and − to T. The complete nuclear polarizability is

$$\alpha_{\alpha\beta} = \alpha'_{\alpha\beta} - i\alpha''_{\alpha\beta} \tag{18}$$

This definition assumes that the nuclear eigenstates are discrete [11] and is written in terms of the nuclear electric dipole transition elements associated with the transition frequency ω_{jn} between the nuclear eigenstates j and n. In the absence of parity violation the states j and n must be of opposite parity for a nonvanishing nuclear transition electric dipole moment, as discussed by Abragam [3].

Using the definition of the tensor contraction on to the scalar of two second rank tensors

$$\begin{aligned}\pi_{ij}\,\alpha''_{ij} = {} & \pi_{xx}\alpha''_{xx} + \pi_{xy}\alpha''_{xy} + \pi_{xz}\alpha''_{xz} \\ & + \pi_{yx}\alpha''_{yx} + \pi_{yy}\alpha''_{yy} + \pi_{yz}\alpha''_{yz} \\ & + \pi_{zx}\alpha''_{zx} + \pi_{zy}\alpha''_{zy} + \pi_{zz}\alpha''_{zz}\end{aligned} \tag{19}$$

the interaction Hamiltonian reduces to

$$\Delta H_2 = -E_0^2(\alpha''_{xy} - \alpha''_{yx}). \tag{20}$$

With the tensor relations

$$\alpha''_{si} = \varepsilon_{ijk}\alpha''_{jk} \tag{21}$$

and

$$\pi_i = \varepsilon_{ijk}\pi_{jk} \tag{22}$$

the Hamiltonian (20) reduces to a product of the Z components of two axial vectors $\boldsymbol{\alpha}''_s$ and $\boldsymbol{\pi}$. These are denoted by 'nuclear spin polarizability vector' and '$\boldsymbol{\pi}$ vector', respectively. The vector $\boldsymbol{\alpha}''_s$ is the antisymmetric part of the imaginary nuclear polarizability tensor α''_{ij}, obtained through the purely tensorial relation

$$\alpha''_{sz} \equiv \begin{bmatrix} 0 & \alpha''_{xy} & 0 \\ -\alpha''_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{23}$$

and is + to P and − to T. The axial vector $\boldsymbol{\pi}$ has the same P and T symmetries as we have seen. The nucleus is torqued by

$$\boldsymbol{T}_{q2} = \tfrac{1}{2}\boldsymbol{\alpha}''_s \times \boldsymbol{\pi}, \tag{24}$$

i.e., is given a net angular acceleration by the laser conjugate product $\boldsymbol{\pi}$. This is analogous to the way the nucleus is torqued by static magnetic flux density $\boldsymbol{B}$ through the nucler magnetic dipole moment.

The nuclear spin polarizability depends on off-diagonal parts of the imaginary nuclear polarizability tensor, i.e., products of orthogonal nuclear transition electric dipole moments between nucler eigenstates n and j of different parity.

The nuclear spin polarizability can be increased greatly in magnitude by tuning, if practically feasible, the pump frequency ω to the transition frequency ω_{jn}

$$\omega \doteqdot \omega_{jn}. \tag{25}$$

If n is the ground eigenstate of the nucleus, then, in condition (25)

$$\omega_{jn} \rightarrow \omega_{jn} - \tfrac{1}{2} i\Gamma_j, \tag{26}$$

where $1/\Gamma_j$ is the lifetime of the excited nuclear eigenstate j. As in semiclassical theories [11] of electronic polarizability, this results in

$$(\omega_{jn}^2 - \omega^2)^{-1} \rightarrow \frac{(\omega_{jn}^2 - \omega^2) + i\omega\Gamma_j}{(\omega_{jn}^2 - \omega^2)^2 + \omega^2\Gamma_j^2} \equiv f + ig, \tag{27}$$

where f and g are the dispersion and absorption lineshape functions, respectively. The nuclear dynamic polarizability in this near resonance condition becomes

$$\alpha'_{\alpha\beta} \rightarrow \alpha'_{\alpha\beta}(f) + i\alpha'_{\alpha\beta}(g), \tag{28}$$

$$\alpha''_{\alpha\beta} \rightarrow \alpha''_{\alpha\beta}(f) + i\alpha''_{\alpha\beta}(g). \tag{29}$$

A rough comparison of order of magnitudes of nuclear and conventional (electronic) polarizabilities may be made in the first approximation by considering the standard Coulomb model of the hydrogen atom, whose Hamiltonian is usually written in terms of the reduced mass of proton and electron. Instead of this, we split the Hamiltonian into its original

$$H = -\frac{\hbar^2\nabla_p^2}{2m_p} - \frac{\hbar^2\nabla_e^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r}, \tag{30}$$

where m_p and m_e are the masses of proton and electron respectively, and where ε_0 is the permittivity *in vacuo*. Here r is the distance between proton and electron. In order to evaluate the eigenfunctions and eigenvalues of the quantized states of the proton (i.e. the hydrogen nucleus in this model), we write *the proton Hamiltonian* as

$$H_p = -\frac{\hbar^2\nabla_p^2}{2m_p} - \frac{e^2}{4\pi\varepsilon_0 r} \tag{31}$$

and comparing this with the standard texbook reduced mass Hamiltonian

$$H_\mu = -\frac{\hbar^2\nabla_\mu^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0 r}, \tag{32}$$

we see that it is identical in all respects, except the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \doteqdot m_e \tag{33}$$

(which is almost precisely the electron mass m_e) has been replaced by the mass of the proton m_p, about 18,000 times heavier. Therefore the nuclear radial wavefunctions of the Coulomb hydrogen atom are identical with the equivalent electronic states with μ replaced everywhere by m_p. Therefore the nucleus (in this case the proton) has n and l quantum numbers, s, p, d orbitals and so on, whose energy levels are

$$E_n = \frac{-m_p e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}; \quad n = 1, 2, \ldots, \tag{34}$$

where n is the principal nuclear quantum number. These are about 18,000 times greater in magnitude than the equivalent electronic energy levels, and are therefore in the far ultraviolet, gamma, or cosmic ray ranges rather than the visible. The difference between the ground state, $n = 1$, and the continuum state ($n = \infty$) for the nucleus is

$$\Delta = \frac{m_p e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \doteq 10^{-14}\ \mathrm{J}, \tag{35}$$

which is about 10^{-14} J per atom, equivalent to about 3,000 million kelvin. The nuclear quantity Δ is the equivalent of the electronic ionization energy, upon which the nuclear distortion polarizability depends through the relation

$$\alpha'_{ij} \propto \frac{e^2 \langle R^2 \rangle}{\Delta}, \tag{36}$$

where $\langle R^2 \rangle$ is the mean square orbital radius of the proton. For the nuclear $1s$ state of the proton of the Coulomb model of the hydrogen atom, the mean orbital radius R is

$$R_{\mathrm{av}} = \frac{8\pi\varepsilon_0 \hbar^2}{m_p e^2}, \tag{37}$$

which is of the order 10^{-40} m. The order of magnitude of the nuclear polarizability from equation (36) is therefore $10^{-52}\ \mathrm{J^{-1}\ C^2\ m^2}$. Using the same model for the usual textbook electronic polarizability, we arrive at an order of magnitude of $10^{-40}\ \mathrm{J^{-1}\ C^2\ m^2}$.

4. Order of magnitude estimate of the resonance frequencies

Taking the estimate to $10^{-52}\ \mathrm{J^{-1}\ C^2\ m^2}$ as being roughly correct for the nuclear spin polarizability, and a pump laser E_0^2 of $10^{18}\ \mathrm{V^2\ m^{-2}}$, the perturbation frequency equivalent to the perturbation hamiltonian (20) is $\Delta H_2/\hbar$, which is about 1 radian $\mathrm{s^{-1}}$, or 2π Hz. A probe electromagnetic field directed along the same, Z axis as the pump laser, and tuned to this frequency, would show nuclear electromagnetic resonance absorption. The frequency 2π Hz is lower bound, because it has been calculated for the smallest $1s$ proton orbital of the smallest (hydrogen) atom. It is increased as (1) the number of protons in the nucleus increases; (2) as the energy difference between ground and continuum nuclear states decreases; (3) as the electric field strength of the pump laser increases. Taking all the factors (1) to (3) in combination, we can expect a resonance frequency in about the kHz range or higher, possibly into the MHz range of conventional NMR spectrometers.

5. Discussion

We have discussed one way in which NER can occur in theory, and given an order of magnitude estimate of the expected resonance frequency range based on the textbook model of the quantized hydrogen atom, the proton and electron being bound by a Coulomb force. There are other mechanisms which can be envisaged for the effect of π of the pump laser directly on the magnetic dipole moment of the nucleus, for example

$$M_i = C_{ij} B_j + D_{ijk} \nabla_j E_k + \ldots, \tag{38}$$

where C_{ij} is the nuclear magnetizability and D_{ijk} is the nuclear magnetic dipole/electric quadrupole tensor, which locks in to the gradient $\nabla_j E_k$ of the pump laser's electric field strength. The tensors C_{ij} and D_{ijk} are treated with a Voigt–Born type perturbation in π, e.g.

$$D_{ijk}(\pi_2) = D_{ijk} - iD_{ijkz}\pi_2 + \ldots \tag{39}$$

which has the necessary symmetry characteristics [11, 16–18], i.e. satisfies the Wigner principles of reversality and parity inversion. The perturbation Hamiltonian to be used in the Boltzmann averaging for these mechanisms is again ΔH_2, and again involves the nuclear spin polarizability multiplied into the square of the pump electric field strength. Applying standard semiclassical [11] Rayleigh refringent scattering theory to (39) it follows that this interaction Hamiltonian generates tiny optical activity due to the nuclear characteristics of an atom or molecule, rather than the usual electronic mechanism discussed customarily. A tiny nuclear optical activity of this kind is also generated by a static magnetic flux density, and accompanies the well known Faraday and Zeeman effects.

We have seen that the nuclear energy levels in (34) are roughly 18 000 times greater than the electronic equivalents, so that resonance with these levels would need pump electromagnetic radiation in the far ultraviolet, γ or cosmic ray frequency range rather than a Nd:YAG laser, unless the latter could be tuned to a possible difference mode of the nuclear transition frequencies. If such a source can be tuned to the nuclear transition frequency responsible for the dynamic nuclear spin polarizability, then the latter can be amplified by near resonance of the pump and natural nuclear transition frequencies. The π of this γ-ray source would then cause NER with a probe in the Hz to MHz depending on conditions.

Clearly, there are fundamental differences between NER and NMR. For example, NER is expected to occur in all polarizable nuclei, NMR occurs only in nuclei with non-zero nuclear spin quantum number. The resonance frequency of NER is expected to increase with the size of the nucleus, and is inversely proportional to the energy Δ of equation (35) of the nucleus. It therefore gives fundamental information on this quantity, which contributes to the nuclear spin polarizability. There is nothing akin to this in NMR. There are some similarities expected between NER and NMR: for example, the chemical shift should occur in NER, because the quantity π is shielded from the nucleus by the electrons in analogy to their shielding of $\boldsymbol{B}$ from the nuclear spin. This would allow, if confirmed, a valuable new analytical technique for all molecules and atoms with sufficiently polarizable nuclei.

Finally, there are interesting analogies with the pioneering experiments of Gerlach and Stern [1] and of Rabi *et al.* [2], because a laser field may be expected to deflect the path of an atomic or molecule beam because of the perturbation $\nabla_i E^{(L)}_{-j} \times \boldsymbol{E}^{(L)}_{+k}$, the cross-product of the gradient of one conjugate electric field strength. This produces a beam deflecting force when multiplied into the nuclear spin polarizability.

5.1. *Comparison with the optical Stark effect*

A real scaler interaction Hamiltonian can be obtained from the tensor product on the right hand side of (13) only if we use the imaginary part (16) of the dynamic polarizability. Furthermore, we have concentrated in this paper on the contribution to α''_{si} of the *nuclear* polarizability. These two factors distinguish the effect introduced in this paper from the well known optical Autler Townes effect, also known as the dynamic, A.C., or quadratic Stark effect (19–25). The optical Stark effect depends on

the *real* part of the *electronic* polarizability, as, for example, in equation (2.59) of [20]. The real part of they dynamic, electronic, polarizability is defined in equation (15) of this paper, and is a symmetric polar tensor, which has positive motion reversal symmetry (T). It has no rank one axial vector equivalent as in equation (22).

The optical Stark effect is mediated therefore by $\alpha'_{\alpha\beta}$ from equation (15), which has a zero frequency component. Nuclear electromagnetic resonance is a nuclear effect which vanishes at zero frequency from equation (16). The optical Stark effect can, furthermore, be observed [20–24] with lasers which are not necessarily circularly polarized, using counterpropagating dye lasers orthogonal to an atomic beam [20–24]. Nuclear electromagnetic resonance *vanishes* if the laser is not circularly polarized. Its electronic equivalent is the optical Zeeman effect [15, 17] whose selection rules and symmetry characteristics are as different from those of the optical Stark effect as the conventional Zeeman effect is different from the conventional Stark effect. (The conventional Zeeman effect is of course due to static magnetic flux density, and the conventional Stark effect is due to static electric field strength.)

To emphasise the difference between the optical Stark effect and the *electronic* equivalent, the optical Zeeman effect, of the nuclear effect introduced here, consider the electronic interaction Hamiltonian

$$\Delta H_I = -\gamma_\pi(\boldsymbol{L}_z + 2{\cdot}002\,S_z)\,E_0^2 \tag{40}$$

written in terms of the electronic angular momentum $\boldsymbol{L}$ and spin angular momentum $2{\cdot}002\boldsymbol{S}$. Here γ_π is a proportionality constant which we call the gyroptic ratio, whose equivalent in the conventional Zeeman effect is the well known gyromagnetic ratio. If the total electronic angular momentum is J, the selection rules of the optical Zeeman effect are identical with those of the conventional Zeeman effect:

$$\Delta J = 0; \quad \Delta M = 0, \pm 1. \tag{41}$$

As in the conventional effect [25], a probe microwave field can be utilized to record the spectrum. When the pump and probe fields are parallel, $\Delta M = 0$, giving the π components of the optical Zeeman effect; and when perpendicular, $\Delta M = \pm 1$ giving the σ components. In the optical Zeeman effect the static magnetic flux density of the conventional Zeeman effect is replaced by $\boldsymbol{\pi}$, with the same T and P symmetries, and the magnetic dipole moment is replaced by α''_{si} again with the same negative T and positive P symmetries.

The formal analogy between the two effects can therefore be developed straightforwardly, following for example chapter eleven of Townes and Schawlow [25], replacing $\boldsymbol{B}$ everywhere by $\boldsymbol{\pi}$ and the magnetic dipole moment everywhere by α''_{si}.

The optical Stark effect, sometimes known as Stark modulation by a laser, can be observed [20–24] with unpolarized pump lasers, because it does not depend on the T negative P positive conjugate product $\boldsymbol{\pi}$. The optical Zeeman effect *vanishes if the laser is not circularly polarized*, and its quantization properties are the same as those of angular momentum. Like its nuclear counterpart, introduced in this paper, it appears not to have been observed experimentally. However, modifications in the apparatus, for example, of Stroud and co-workers, primarily to ensure circular polarization of the pump laser, appears to be the best route towards observation.

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