they are currently researched by techniques such as effects of structural variations on antineoplastic activity,[30] nuclear magnetic resonance,[33] circular dichroism,[34] and computational simulations.[8,35] Future work in our laboratory will examine fluorescence decays of other intercalative agents in poly[d(G-C)-d(G-C)],

poly[d(A-T)-d(A-T)], and other DNA types.

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Optical Phase Conjugation in Nuclear Magnetic Resonance: Laser NMR Spectroscopy

M. W. Evans

Theory Center, Cornell University, Ithaca, New York 14853 (Received: June 5, 1990)

The role of optical phase conjugation in nuclear magnetic resonance (NMR) spectroscopy is discussed theoretically in terms of the extra quantized angular momentum $\mathbf{J}_\pi$, produced by the conjugate product π of a powerful pump laser such as a Nd:YAG. Elementary first-order time-dependent perturbation theory is used to derive an expression for a novel molecular property Y_{ij} tensor that mediates the induction by π of an orbital molecular magnetic moment $\mathbf{m}_\pi$, which couples in to the spin magnetic moment of the nucleus. The tensor Y_{ij} is expressed in terms of the product of matrix elements of a transition molecular orbital magnetic moment multiplied by matrix elements of the dynamical molecular electronic orbital polarizability, a quantity that mediates the effect of π on the interaction Hamiltonian. It is shown that the conventional NMR detail splits according to Clebsch, Gordan, and Landé coupling between $\mathbf{J}_\pi$ and $\mathbf{I}$, the nuclear spin quantum number, a potentially useful phenomenon.

(1) Introduction

This paper introduces a potentially useful analytical technique based on the effect of powerful pulses of pump laser radiation in conventional nuclear magnetic resonance spectrometers. It is shown theoretically that the conjugate product (π) of the laser introduces a quantized orbital molecular angular momentum ($\mathbf{J}_\pi$) that couples to the nuclear spin angular momentum (I) through the Clebsch–Gordan theorem governing angular momenta in quantum mechanics. Being a quantized angular momentum, $\mathbf{J}_\pi$ is described by two quantum numbers,[1] J_π and $M_{\pi J}$, both of which are capable of coupling to I and therefore of splitting the conventional NMR spectrum into detail dependent on new atomic or molecular property tensors. This provides experimental information on the tensors and can be used in the analytical laboratory to supplement conventional NMR spectroscopy by directing the pump laser in the same Z axis as the applied magnetic flux density **B** of the spectrometer.

Part 2 of this paper defines the conjugate product of the pump laser and the interaction Hamiltonian with an atomic or molecular ensemble, thus defining the orbital electronic polarizability α_s. Part 3 is a brief demonstration of conservation of Wigner reversality (T) and parity inversion symmetry (P)[2,3] in the experiment consisting of measuring nuclear resonance with π parallel or antiparallel to **B** of the NMR spectrometer. Part 4 introduces the orbital atomic or molecular magnetic dipole moment $\mathbf{m}_\pi$ produced by π through a novel molecular property tensor Y_{ij}, which is defined with elementary first-order perturbation theory from the time-dependent Schrödinger equation. Part 5 is a discussion, still in elementary terms, of the Clebsch–Gordan coupling between the quantized orbital angular momentum defined by $\mathbf{J}_\pi$ and the quantized nuclear spin angular momentum I. This coupling de-

fines new energy levels, transitions between which are picked up by the resonating probe of the NMR spectrometer in the usual way. The Clebsch, Gordan, and Landé coupling greatly enriches the customary NMR spectrum, and a discussion closes the paper with estimates of the frequency splitting for a given pump laser electric field strength in volts per meter.

(2) Definition of the Conjugate Product π of the Pump Laser

A description of the physical meaning of wave and optical conjugation has been given by Zel'Dovich et al.[4] Its effects are usually investigated experimentally[4] by using a pump laser and a device such as a reflective holographic grating or by using four-wave mixing. It is increasingly used for a variety of purposes, including[4] optical phase conjugation interferometry (using a phase conjugate mirror), phase conjugation resonance, light guides, pulse temporal spread, self-targeting, spatial/time modulation, bistable optical devices, tunable filters, nonlinear selection, nonlinear phase conjugate spectroscopy, and other effects. Approximately 150 publications per year are produced[4] on optical phase conjugation, and the technology is readily available for the development of laser NMR spectrometers.

Recently, it has been shown[5–11,13–15] that the conjugate product π has the same P and T symmetries[12] as static magnetic flux

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density, **B**, and is capable of generating a variety of novel spectroscopic effects usually attributed to **B**. These include the following: Faraday A, B, and C terms;[5-11] Zeeman splitting;[13] forward–backward birefringence and dichroism;[14] electron and nuclear spin resonance[15] in the absence of a magnet (i.e., with the pump laser alone). It also produces a variety of spectroscopic effects[16] through Clebsch–Gordan coupling of $\mathbf{J}_\pi$ with intrinsic atomic and molecular angular momenta, the usual electronic orbital (**L**), framework (**O**), electron spin (**S**), and nuclear spin (**I**) angular momenta, thereby causing a rich variety of new spectral splittings[16] across the regions of the electromagnetic spectrum. The various new phenomena[5-11,13-15] are mediated by novel atomic and molecular property tensors. Additionally, in chiral (optically active) molecular ensembles and chiral crystal point groups[16] produces direct electric polarization,[17] whose molecular dynamical effects have been computer simulated[18] for (S)-CHBrClF. The conjugate product π induces an electric dipole moment through a novel molecular property tensor that is supported only in chiral media. The bulk polarization due to π[17-19] can be used for a variety of applications, ranging from nonlinear optical dielectric and far-infrared spectroscopy[20] to all optical switching devices.[21]

For laser NMR spectroscopy, the conjugate product is defined through the vector product of the electric field strengths from Maxwell's equations of the classical electromagnetic field:

$$\mathbf{E}_R{}^+ = E_0(\mathbf{i} + i\mathbf{j})e^{i\theta_R} \qquad \mathbf{E}_L{}^+ = E_0(\mathbf{i} - i\mathbf{j})e^{i\theta_L}$$
$$\mathbf{E}_R{}^- = E_0(\mathbf{i} - i\mathbf{j})e^{-i\theta_R} \qquad \mathbf{E}_L{}^- = E_0(\mathbf{i} + i\mathbf{j})e^{-i\theta_L} \tag{1}$$

where

$$\theta_L = \omega t - \kappa_L \cdot \mathbf{r} \qquad \theta_R = \omega t - \kappa_R \cdot \mathbf{r} \tag{2}$$

Here R and L denote, respectively, right and left circular polarization, and + and − denote positive and negative complex conjugates. The conjugate product is

$$\pi = \mathbf{E}_L{}^+ \times \mathbf{E}_L{}^- = -\mathbf{E}_R{}^+ \times \mathbf{E}_R{}^- = 2E_0{}^2 i\mathbf{k} \tag{3}$$

and is a complex quantity that changes sign if the pump laser is switched from right to left circular polarization and vanishes in plane or incoherently polarized lasers. It depends on the square of the electric field strength E_0, which in a small, commercially available Nd:YAG laser can reach 10^9 V m^{-1} by focusing and Q-switching.[22] We have 1 W/cm^2 = 27 V/cm. Note that π has the important property of being time independent. It is negative to T and positive to P and therefore has the same T and P symmetries as static magnetic flux density. It has been discussed by Wagnière[23] in terms of diagrammatic perturbation theory.[24]

The interaction Hamiltonian between π and the molecular ensemble has been shown[13-18] to be

$$\Delta H_1 = -\tfrac{1}{2}\alpha_{ij}\pi_{ij}$$
$$\alpha_{ij} \equiv \alpha_{ij}' - i\alpha_{ij}'' \tag{4}$$

where α_{ij} is the atomic or molecular electronic orbital polarizability. Its imaginary part

$$\alpha_{sk} \equiv \epsilon_{ijk}\alpha_{ij}'' \tag{5}$$

is a complex, rank one, axial vector, which can be related through the Levi–Civita tensor[13-18] to the usual rank two definition of molecular polarizability. To obtain a real Hamiltonian, the imaginary conjugate product π multiplies the imaginary part of α_{ij}, which is defined by

$$\alpha_{sk} \equiv \alpha_{ij}'' - \alpha_{ji}'' \tag{6}$$

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where the individual components are obtained from the definition of the imaginary part of the dynamical polarizability[5]

$$\alpha_{ij}'' = -\alpha_{ji}'' = -\frac{2}{\hbar} \sum_{m \neq n} \frac{\omega}{\omega_{mn}{}^2 - \omega^2} \operatorname{Im}(\langle n|\mu_i|m\rangle\langle m|\mu_j|n\rangle) \tag{7}$$

from time-dependent first-order quantum perturbation theory. In eq 7, μ_i and μ_j are electric dipole matrix elements between states n and j, with transition frequency

$$\omega_{mn} = \omega_m - \omega_n \tag{8}$$

in radians per second. Note that α_{ij}'' is antisymmetric in index reversal and vanishes with the measuring frequency ω. At the resonance condition

$$\omega \doteq \omega_{mn} \tag{9}$$

the line-shape functions g and f of semiclassical theory[5] are introduced to describe absorption and dispersion.

(3) Conservation of Wigner T and P Symmetries in the Complete Experiment

Wigner realized[2,3,25] that a complete experiment must conserve reversality, i.e., motion reversal symmetry (T) and parity inversion symmetry (P).[5-7,8-12] With π of the pump laser parallel to **B** of the NMR spectrometer the effect of T is to reverse the directions[8-11] of both π and **B**, so that the product $\pi \cdot \mathbf{B}$ is unchanged. T also has the effect of reversing the NMR observable, which can be described as a macroscopic magnetization, an oscillating angular momentum projection that creates a magnetic flux through an effective gyromagnetic ratio. This remains relatively unchanged with respect to **B** or π. Finally T has no effect on the molecular structure being investigated, so that the variables of the motion-reversed experiment are relatively the same as those of the original. The complete experiment conserves Wigner's principle of reversality. Similarly, P leaves both π and **B** unaffected, so that the product is unchanged. P inverts the positions of each atom, but a structure such as that of water is indistinguishable from the original after application of P and a proper rotation. Finally P has no effect on the magnetization flux of the NMR observable. The P-inverted complete experiment is also indistinguishable from the original and passes the test of the Wigner principle of parity conservation.

(4) Quantized Orbital Magnetic Dipole Moment and Orbital Angular Momentum Due to π

The orbital magnetic dipole moment induced by π is defined through the semiclassical[5] relation

$$m_{\pi i} = Y_{ij}\pi_j + \dots \tag{10}$$

where Y_{ij} is a dynamic atomic or molecular property tensor to be determined from the time-dependent Schrödinger equation. The molecular quantity $m_{\pi i}$ is quantized (because Y_{ij} is quantized) and is proportional, as usual, to a quantized orbital atomic or molecular angular momentum:

$$\mathbf{m}_\pi = \gamma_e \mathbf{J}_\pi \tag{11}$$

where $-\gamma_e \hbar$ is the Bohr magneton. Since $\mathbf{J}_\pi$ is a quantized angular momentum, it must be described by two quantum numbers, which emerge from the fundamental commutators and postulates of quantum mechanics. These are defined as J_π and

$$m_{\pi J} = J_\pi, J_\pi - 1, \dots, -J_\pi \tag{12}$$

which defines the value taken by the Z component of $\mathbf{J}_\pi$. Section 5 describes the way in which J_π and $m_{\pi J}$ couple to the nuclear spin angular momentum (**N**) of an atom or molecule, the quantity responsible for conventional NMR in response to a static applied **B**. The conventional NMR spectrum is therefore greatly enriched by the presence of the pump laser's conjugate product.

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The time-dependent Schrödinger equation

$$\left(i\hbar \frac{\partial}{\partial t} - H\right)\psi = V\psi \tag{13}$$

is solved for Y_{ij} as follows: As in standard semiclassical theory,[5] the perturbed wave function ψ_n' is expanded as

$$\psi_n' = [\psi_n^{(0)} + \sum_{j \neq n} a_{jn\beta}\pi_\beta\psi_j^{(0)}]e^{-i\omega_n t} \tag{14}$$

with the perturbation energy

$$V = -\alpha_{s\beta}(E_0^2)_\beta \tag{15}$$

and the unperturbed Hamiltonian

$$H = \hbar\omega_j \tag{16}$$

In the absence of V, eq 13 reduces to

$$\left(i\hbar \frac{\partial}{\partial\hbar} - H\right)\psi = 0 \tag{17}$$

with the steady-state nondegenerate wave function

$$\psi = \psi_n^{(0)}e^{-i\omega_n t} \tag{18}$$

providing the relation

$$\hbar(\omega_n - \omega_j)\psi_n^{(0)}e^{-i\omega_n t} = 0 \tag{19}$$

to be used later.

These definitions in eq 13 provide the result

$$\hbar(\omega_n - \omega_j)\sum_{j \neq n} a_{jn\beta}\pi_\beta\psi_j^{(0)}e^{-i\omega_n t} = -\alpha_{s\beta}E_{0\beta}^2\psi_n^{(0)}e^{-i\omega_n t} + $$
$$\hbar(\omega_j - \omega_n)\psi_n^{(0)}e^{-i\omega_n t} - \alpha_{s\beta}E_{0\beta}^2\sum_{j \neq n} a_{jn\beta}\pi_\beta\psi_j^{(0)}e^{-i\omega_n t} \tag{20}$$

which reduces to

$$\hbar\sum_{j \neq n}(\omega_j - \omega_n)a_{jn\beta}\pi_\beta\psi_j^{(0)}e^{-i\omega_n t} = -\alpha_{s\beta}E_{0\beta}^2\psi_n^{(0)}e^{-i\omega_n t} \tag{21}$$

by using (19) and neglecting[5] the term on the right-hand side of (20), which is second order in the perturbation, a standard approximation in first-order perturbation theory.[5] This approximation gives

$$a_{jn\beta} = \frac{\langle j|\alpha_{s\beta}|n\rangle}{\hbar(\omega_j - \omega_n)} \tag{22}$$

by multiplying both sides of eq 21 by ψ_j^* and integrating over all configuration space. The wave function (14) is therefore

$$\psi_n' = \left[\psi_n^{(0)} + \sum_{j \neq n}\frac{\langle j|\alpha_{s\beta}|n\rangle}{\hbar(\omega_j - \omega_n)}E_{0\beta}^2\psi_j^{(0)}\right]e^{-i\omega_n t} \tag{23}$$

The magnetic dipole moment of eq 11 is now found from
$$m_\alpha = \langle n'|m_\alpha|n'\rangle =$$
$$\int \left(\psi_n^{(0)} + \sum_{j \neq n}\frac{\langle j|\alpha_{s\beta}|n\rangle}{\hbar(\omega_j - \omega_n)}E_0^2\psi_j^{(0)}e^{i\omega_n t}\right)^* m_\alpha \times$$
$$\left(\psi_n^{(0)} + \sum_{j \neq n}\frac{\langle j|\alpha_{s\beta}|n\rangle}{\hbar(\omega_j - \omega_n)}E_{0\beta}^2\psi_j^{(0)}e^{i\omega_n t}\right) d\tau \tag{24}$$

and comparing terms in π_β with eq 10, giving the result

$$Y_{\alpha\beta} = \sum_{j \neq n}\frac{\langle j|\alpha_{s\beta}|n\rangle\langle j|m_\alpha|n\rangle}{\hbar(\omega_j - \omega_n)} + \sum_{j \neq n}\frac{\langle j|\alpha_{s\beta}|n\rangle\langle n|m_\alpha|j\rangle}{\hbar(\omega_j - \omega_n)} \tag{25}$$

for the new molecular property tensor $Y_{\alpha\beta}$, neglecting the term in (24) that is second order in π_β, again a standard approximation.[5]

(5) Effect on the NMR Spectrum; Clebsch-Gordan Coupling of Quantized Angular Momenta J_π and N

It is well-known that conventional, **B**-induced nuclear magnetic resonance is due to the nuclear spin quantum number **I**. Con-

temporary nuclear theory can now predict **I** with accuracy and the *g* factor of NMR with fair amount of certainty; the latter is, for example, 5.585 for $_1^1$H, 2.256 for $_9^{19}$F, and so on. *I* ranges from $^1/_2$ for the proton to about 6 in different nuclei. Because **I** is a quantized angular momentum, it must be described from the basic postulates of quantum mechanics by two quantum numbers, usually labeled *I* and *M*, which is in the same *Z* axis as **B** and takes the values

$$M_I = I, I - 1, ..., -I \tag{26}$$

Therefore if *I* is $^1/_2$, as in a proton, M_I can be $^1/_2$ and $-^1/_2$, and two energy levels are possible. The transition frequency between energy levels is proportional to the applied B_Z:

$$\hbar\omega = -g_N\gamma_N B_Z\hbar M_I \tag{27}$$

The well-known chemical shift means that **B** at the nucleus is less than the applied **B**, producing the well-known analytical information of NMR. Similarly, there is a chemical shift in the optical effect of this paper and also spin–spin (scalar) coupling, a good account of which is given by Atkins[26] (pp 407ff). In both cases the magnetic moment of the conventional effect is replaced by the spin part of the polarizability vector for each spin, and the magnetic flux density **B** is of course replaced by the conjugate product. The gyromagnetic ratio is replaced by eq 41 of this paper, which links the angular and spin polarizabilities to the angular and spin angular momenta through γ_π, the "gyroptic" ratio.

In the presence of π of a Nd:YAG pump laser in the same *Z* direction as B_Z, the induced orbital angular momentum J_π couples to **I**. The effect on the NMR spectrum being observed by **B** of the spectrometer can be defined through the well-known Clebsch-Gordan theorem, which allows the following quantum numbers:

$$J_\pi + I, J_\pi + I - 1, ..., |J_\pi - I| \tag{28}$$

with

$$M = M_{\pi J} + M_I \tag{29}$$

Each of the main quantum numbers J_π and *I* can take integral or half-integral values in general. The orbital component J_π is usually restricted to integral values by the need to impose appropriate boundary conditions on its wave functions. For *I* there is no such restriction, because it is a spin angular momentum. The effect of Clebsch-Gordan coupling between J_π and **I** is therefore analogous and in addition to those of the well-known nuclear spin–spin coupling between different *N*'s of different nuclei. In HD, for example, there is coupling between spin quantum numbers $I = 1$ of D and $I = ^1/_2$ of H. The total spin angular momentum *I* in the coupled representation takes the values $^3/_2$ and $^1/_2$. NMR resonance occurs when

$$\omega_R = -g_N\gamma_N B_Z\Delta M \tag{30}$$

with the selection rule $\Delta M = 1$. This provides at least two transitions, the Larmor frequencies of the proton and deuteron. These are split further by considerations of spin–spin coupling, giving a possible total of three different proton resonances (β to α with deuterium = 1, 0, -1) and four deuterium resonances (-1 to 0 and 0 to 1, with α or β possible for either transition).

This example shows in detail what would happen if an orbital angular momentum of quantum number $J_\pi = 1$ due to π were to couple with $I = ^1/_2$ of an NMR proton resonance observed with **B** parallel with π in the *Z* axis. In an exactly analogous manner, the original proton NMR line would be split into two fundamental Larmor frequencies (in the above description, for "deuterium" read "orbital electronic angular momentum due to the pump laser"). The split spectrum depends on the magnitude of the angular momentum $(J_\pi(J_\pi + 1))^{1/2}\hbar$ and on the interaction Hamiltonian

$$\Delta H^{(2)} = -\gamma_e J_\pi\cdot\mathbf{B} - \gamma_N\mathbf{I}\cdot\mathbf{B} \tag{31}$$

(26) Atkins, P. W. *Molecular Quantum Mechanics*, 2nd ed.; Oxford University Press: Oxford, 1983.

If it is assumed that

$$\Delta H^{(2)} = -(\text{const})\mathbf{J}\cdot\mathbf{B} \tag{32}$$

the Hamiltonian (31) can be written in the Landé form[25] as follows:

$$\Delta H^{(2)} = -(\gamma_e \mathbf{J}_\pi\cdot\mathbf{J} + \gamma_N \mathbf{N}\cdot\mathbf{J})\mathbf{J}\cdot\mathbf{B}/|\mathbf{J}|^2 \tag{33}$$

where

$$\mathbf{J} = \mathbf{J}_\pi + \mathbf{I} \tag{34}$$

is the sum of $\mathbf{J}_\pi$ and $\mathbf{I}$. This can be rewritten as

$$\Delta H^{(2)} = -\frac{1}{2}(\gamma_e + \gamma_N)g_J M_J \hbar B_Z \tag{35}$$

where g_J is the Landé factor for the coupling of $\mathbf{J}_\pi$ and I:

$$g_J = 1 + \frac{J_\pi(J_\pi + 1) - I(I + 1)}{J(J + 1)} \tag{36}$$

where we have used the fact that

$$\frac{\gamma_e - \gamma_N}{\gamma_e + \gamma_N} = \frac{\mu_B - g_N\mu_N}{\mu_B + g_N\mu_N} \div 1 \tag{37}$$

The Z component of $\mathbf{J}$ is M_J, and the resonance condition is given by the selection rule

$$\Delta M_J = \pm 1 \tag{38}$$

This gives the *resonance frequency*

$$\omega_R = (1/2\hbar)(\mu_\beta + g_N\mu_N)g_J B_Z \tag{39}$$

This clearly depends on the Landé mixing of J_π and I, and since the Bohr magneton is about $1000\mu_N$ (μ_N is the nuclear Bohr magneton), the resonance frequency is approximately

$$\omega_R = (1/2\hbar)\mu_B g_J B_Z \tag{40}$$

showing clearly that it is in the "ESR" range for magnetic flux densities B_Z in the customary 1-T region.

(6) Discussion

Equation 40 shows that the resonance frequency depends on the allowed values of J_π and I, the laser-induced electronic orbital angular momentum principal quantum number and the principal nuclear spin angular momentum quantum number, respectively. This is analogous to the anomalous Zeeman effect, where L takes the part of J_π and S takes the part of I. Here L is the orbital electronic quantum number, and S the electron spin quantum number. Therefore, different resonance frequencies will be observed for different quantum states labeled by the two quantum numbers J_π and I, allowing a rich variety of investigative possibilities. The magnitude of $(J_\pi(J_\pi + 1))^{1/2}\hbar$ depends on the square of the electric field strength E_0 of the pump laser, which imparts an interaction energy (4) to the atom or molecule. For an order of magnitude[15] of 10^9 V m^{-1} for α_s this is about kT for $T = 300$ K for E_0 of about 10^9 V m^{-1}. The order of magnitude of the property tensor Y_{ij} that mediates the effect of π is about 10^{-42} C^2 m^2 T^{-1} J^{-1}, and for E_0 of about 10 V m^{-1}, a magnetic moment of the order of the nuclear Bohr magneton is induced by the interaction (10). For E_0 of about 10^7 V m^{-1}, the induced magnetic moment from (10) is of the order of the Bohr magneton. Therefore it is anticipated that pulses of this electric field strength from the Nd:YAG pump laser will produce $J_\pi(J_\pi + 1)$ of the order of $I(I + 1)$ in the Landé factor g_J. The specific optical rectification effect of the pump laser can be isolated experimentally by using contemporary technology, such as a reflective holographic grating.[5] The Nd:YAG is used in the form of trains of powerful pulses to avoid heating of the sample and to give a wide range of electric field strengths with which to tune the instrument for optimization of resonance patterns. From eq 40 these will depend on the field strength E_0 and on the quantum numbers J_π induced by π through the mediating tensor Y_{ij}. The latter depends in turn on the transition condition of the spin polarizability. Double resonance

can be obtained by tuning the pump laser's frequency to ω_{mn}, thus greatly amplifying the spin polarizability, and by tuning the probe (gigahertz) field according to eq 40. In this double-resonance condition, the laser NMR resonance pattern should be greatly amplified.

A simple initial experiment for detecting Zeeman splitting due to pump lase optical rectification is suggested as follows in sodium vapor. A simple appreciation of the principles of this experiment may be gained by writing

$$i\alpha_{Sl} = \gamma_\pi(L_l + 2.002S_l) \tag{41}$$

where γ_π is a constant akin to the gyromagnetic ratio, the "gyroptic" ratio, and L and $2S$ are the orbital electronic and spin quantum numbers. Equation 41 can be compared with the well-known relation between the magnetic electronic dipole moment and these same quantum numbers:

$$m_l = \gamma_\epsilon(L_l + 2.002S_l) \tag{42}$$

where γ_ϵ is the gyromagnetic ratio. The constants γ_π and γ_ϵ are related by

$$\gamma_\pi \propto \gamma_\epsilon/(E_0 c) \tag{43}$$

The factors $\gamma_\pi L_l$ and $2\gamma_\pi S_l$ denote respectively the orbital and spin electronic polarizability. The same quantum numbers L and S are used in both cases, and this establishes a close formal analogy between the theory of the normal and anomalous Zeeman effects due to static magnetic flux density, B, and the conjugate product π.

Specifically, the experiment mimics the original demonstration by Zeeman in 1896[27] of the broadening of the two lines of the principal doublet of sodium vapor between the poles of a powerful electromagnet, leading to the well-known theoretical accommodation by Lorentz using his electron theory of radiation and matter. When viewed perpendicular to B, the sodium lines are split into three linearly polarized components, with the central line linearly polarized parallel to B and the other two perpendicular. When B points toward the observer, Zeeman observed two lines on either side of the original with the high- and low-wavelength lines showing right and left circular polarization, respectively.

Instead of B we generate π using state-of-the-art nonlinear optics and apply it in the same relative configurations as used for B by Zeeman. It may be appropriate, for example, to use a commercially available pulsed Nd:YAG system at $\lambda = 532$ nm; with a pulse width of, say, 10 ns, a spectra width of about 0.85 cm^{-1}, an angular width of about a milliradian; and a pulse repetition rate of 1–5 Hz. This delivers a laser intensity with the use of neutral density filters of up to about 10^9 W/cm^2; equivalent to an electric field strength of 10^6 V m^{-1}. To circularly polarize the laser a number of off-the-shelf optical accessories are available, including a simple, photographic type, circularly polarizing camera filter. Essentially, it is necessary to isolate the third Stokes parameter of the laser by circular polarization. Another possibility is a piezooptic modulator or the well-known quarter-wave plate and Nicol prism.

The magnetization due to a type of circularly polarized giant ruby laser was detected as early as the mid-1960s by Malmstrom and co-workers,[28,29] as described, for example, in the textbook by Shen.[30] This is known as the "inverse Faraday effect". In this respect it is notable that the A term[5] of the quantum theory of the forward Faraday effect due to B is precisely the description of Zeeman splitting. It is clear, therefore, that the experimental verification[28,29] of the inverse Faraday effect implies an "inverse", i.e., optically produced, Zeeman effect of the type proposed here.

This should be observable as the broadening and splitting of the sodium D line by the circularly polarizaed pump laser and

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detected by using a contemporary high-resolution interferometric spectrometer or tunable probe laser. The contemporary theory of the normal and anomalous Zeeman effect is adequately described, for example, on pp 243ff of Atkins.[26] In that theory we formally replace **m** by α_s and the gyromagnetic ratio by γ_π. A magnetic field of the order of 1.0 T splits lines in the Zeeman effect by about 0.5 cm^{-1}. The same splitting would require a pump laser electric field strength in the range of 10^6 Volt m^{-1}, as discussed already. This can be achieved easily by Q switching and focusing. Synchronous detection techniques (lock-in amplifiers) may be employed to integrate the time-accumulated effect of the pulsed pump laser by interfacing with the lockin amplifier of the interferometric spectrometer.

Note that there is also broadening and splitting due to the well-known optical (or ac) Stark effect.[31-35] However, the latter depends on the real part of the dynamic polarizability, which is T positive and does not have an axial vector equivalent. In consequence the ac Stark effect can be observed with a pump laser that is not circularly polarized,[31-35] in contrast to the optical Zeeman effect, which can be observed *only with a circularly polarized laser*. The differences between the optical Stark and Zeeman effects are as fundamental as those between the conventional Stark and Zeeman effects, induced respectively with a static electric and magnetic field. In the optical Zeeman effect there should also be the equivalent of the Paschen–Back effect, an anomalous optical Zeeman effect as the optical conjugate product is increased. In diatomics and polyatomics in which there is net electronic angular momentum, the Hund coupling models can be used to describe the various patterns as in Townes and Schawlow, chapter 11.[36]

This is a relatively straightforward "first experiment", which would reveal the degree of pump laser stability needed for a the second type of experiment, in which the pump laser is used with the highly homogeneous magnet of a state-of-the-art NMR or ESR spectrometer. A simple Hamiltonian for this second type would be, for example

$$\Delta H = -\gamma_n \mathbf{I} \cdot \mathbf{B} - \tfrac{1}{2}\gamma_\pi \, \mathbf{J} \cdot \boldsymbol{\pi} \qquad (44)$$

where

$$\mathbf{J} = \mathbf{L} + 2.002\mathbf{S} \qquad (45)$$

and I is the nuclear spin quantum number. In Landé form this is

$$\Delta H \doteq -\gamma_N \left[1 + \frac{I(I+1) - J(J+1)}{2J_{tot}(J_{tot}+1)} \right] \mathbf{J}_{tot} \cdot \mathbf{B} - \frac{\gamma_\pi}{2}\left[1 - \frac{I(I+1) - J(J+1)}{2J_{tot}(J_{tot}+1)} \right] \mathbf{J}_{tot} \cdot \boldsymbol{\pi} \quad (46)$$

where

$$J_{tot} = J + I \qquad (47)$$

is the total angular momentum quantum number. For $I \neq 0$, we have the selection rule, and the NMR pattern in the absence of π is split according to

$$\Delta M_{J_{tot}} = 0, \pm 1 \qquad (48)$$

The splitting depends on the individual values of I and J, in analogy with the extra Landé splittings observed in the theory of the anomalous Zeeman effect.[26]

The question of the homogeneity of the factor E_0^2 from the circularly polarized pump laser may turn out to be critical from experiment one. If so, synchronous detection techniques from infrared radio frequency double resonance may be able to filter out the background noise in E_-^2, leaving the signal, using highly sophisticated state-of-the-art lockin amplifiers interfaced with controlling microcomputers as described for example in Figure 1 of ref 37 in the context of sub-Doppler resolution infrared radio frequency double resonance. Detailed experimental conditions are given in ref 37 and references therein.

Note Added in Proof. Since this manuscript was submitted the verification experiment of laser NMR has been initiated at Princeton University by Prof. W. S. Warren and co-workers.

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Mechanical Properties and Force Field Parameters for Polyethylene Crystal

Naoki Karasawa, Siddharth Dasgupta, and William A. Goddard III*

Materials and Molecular Simulation Center, Beckman Institute (139.74),† California Institute of Technology, Pasadena, California 91125 (Received: December 7, 1989; In Final Form: September 7, 1990)

Crystal structures, phonon dispersion relations, and elastic constants of polyethylene crystal are calculated by using a new force field where the van der Waals parameters are selected on the basis of comparing these properties with experiment. The cell parameters and atomic coordinates are optimized simultaneously, and elastic constants and phonon bands are calculated by using analytic second derivatives at the optimized structure. Yield stresses and surface energies are obtained from calculations of the stress–strain relations in directions perpendicular to polymer chains.

I. Introduction

Given a force field (the analytical description of forces on all atoms in terms of the distances and angles in a structure), one can calculate a number of important properties of crystalline

† Contribution No. 7903.

polymers—structure, elastic constants, yield stresses, vibrational (phonon) states, specific heat, free energy, etc. However, suitable force fields do not exist for most polymers of interest. Herein we report a new force field suitable for polyethylene (PE) and other hydrocarbons using a systematic approach to developing force fields that should be applicable to other polymers of interest.