

# Pump Laser Induced Atomic and Molecular Angular Momentum: Some Spectral Effects

M. W. EVANS

*Theory Center, Cornell University, Ithaca, New York 14853*

Some new spectral effects of the conjugate produce  $\pi$  of the electric field strengths of a pump laser are introduced in atomic and molecular spectroscopy through a mediating molecular property tensor: atomic or molecular spin polarizability  $\alpha_s$ . Both  $\pi$  and  $\alpha_s$  have the parity inversion and motion reversal symmetries of angular momentum, and the quantum theory of angular momentum applies in both cases, with the interaction Hamiltonian  $-\alpha_s \cdot \pi/2$ . Some simple examples are considered of the effect of  $\pi$  in atomic and molecular electronic, vibration-rotation, pure rotation, and resonance spectroscopy. © 1990 Academic Press, Inc.

## INTRODUCTION

Much of the interpretation of atomic and molecular spectra depends on the quantum theory of angular momentum, which is a cornerstone of contemporary spectroscopy. In this paper, a new source of angular momentum is introduced into atomic and molecular electronic spectroscopy and molecular vibration-rotation and rotation spectroscopy. It is generated through the conjugate product,  $\pi$ , of the electric field strengths of the classical electromagnetic field, and interacts with the ensemble through a Hamiltonian involving a new molecular property tensor  $\alpha_s$ , the atomic or molecular electronic spin polarizability.

Both  $\pi$  and  $\alpha_s$  have the positive parity inversion (P) and negative motion reversal (T) symmetries of orbital or spin angular momentum, and in consequence of the magnetic dipole moment  $\mathbf{M}$  and static magnetic flux density  $\mathbf{B}$ . Spectral effects customarily attributed to  $B$  are also caused theoretically by  $\pi$ , effects which clearly pervade a large part of spectroscopy. Theoretical predictions of several of these are given in this paper, with estimates of order of magnitude and suggested experimental configurations.

Section 1 defines the conjugate product and interaction Hamiltonian, and provides an expression for spin polarizability from semiclassical theory (1). Section 2 defines the angular momentum  $\mathbf{J}_\pi$  due to  $\pi$ , and summarizes its quantum mechanical properties in terms of standard angular momentum theory. Section 3 discusses possible coupling schemes between  $\mathbf{J}_\pi$  and the various intrinsic atomic and molecular orbital and spin electronic and nuclear angular momenta, leading to the anticipation of new and observable spectral phenomena. Section 4 is a simple example of Zeeman splitting due to  $\pi$ . Section 5 discusses its effect on electronic spectra, and Section 6 on vibration-rotation and rotation spectra.

## 1. THE CONJUGATE PRODUCT AND INTERACTION HAMILTONIAN

Conjugate products in the classical electromagnetic field were the subject of an early review by Ward (2), and were shown, soon afterwards (3), to be responsible for magnetization in the inverse Faraday effect (4, 5). Define the right (R) and left (L) circularly polarized + and - conjugates in IUPAC convention as follows for the electric field strengths (E) of the classical electromagnetic field:

$$\left. \begin{aligned} \mathbf{E}_R^+ &= E_0(\mathbf{i} + i\mathbf{j})e^{i\theta_R}; & \mathbf{E}_L^+ &= E_0(\mathbf{i} - i\mathbf{j})e^{i\theta_L} \\ \mathbf{E}_R^- &= E_0(\mathbf{i} - i\mathbf{j})e^{-i\theta_R}; & \mathbf{E}_L^- &= E_0(\mathbf{i} + i\mathbf{j})e^{-i\theta_L} \end{aligned} \right\}. \quad (1)$$

Here  $\theta_L$  and  $\theta_R$  are the phases, defined as usual by

$$\theta_L = \omega t - \mathbf{K}_L \cdot \mathbf{r}; \quad \theta_R = \omega t - \mathbf{K}_R \cdot \mathbf{r}, \quad (2)$$

where  $\mathbf{K}$  is the propagation vector and  $\omega$  the angular frequency. The minus to plus conjugate product is then

$$\boldsymbol{\pi} = \mathbf{E}_L^- \times \mathbf{E}_L^+ = -\mathbf{E}_R^- \times \mathbf{E}_R^+ = -2E_0^2 i\mathbf{k}, \quad (3)$$

where  $\mathbf{k}$  is a unit vector in  $Z$  of the laboratory frame ( $X, Y, Z$ ). Note that  $\boldsymbol{\pi}$  is purely imaginary, time independent, and reverses sign between left and right circular polarization. It vanishes for an unpolarized or linearly polarized laser. In a small, commercially available, neodymium doped yttrium aluminium garnet (Nd:YAG laser) it can reach about  $10^{18}$  volts<sup>2</sup> m<sup>-2</sup> (6) by  $Q$ -switching and focusing. It reverses sign with  $T$ , because the laser propagates in the opposite direction, and is therefore  $T$  negative. It is positive to  $P$  because it is the vector product of two  $P$  negative electric field strengths.

The interaction Hamiltonian of  $\boldsymbol{\pi}$  with a molecular ensemble is written as

$$\Delta H = -\frac{1}{2}\alpha_{ij}E_iE_j - \dots, \quad (4)$$

where  $\alpha_{ij}$  is a molecular dynamic polarizability (7). This is a dynamic complex molecular property tensor, whose real part is positive to  $T$  and symmetric in the indices  $i$  and  $j$ , and whose imaginary part is negative to  $T$  and antisymmetric in the indices  $i$  and  $j$ . A real, scalar, interaction Hamiltonian is obtained from the tensor contraction (7-9)

$$\Delta H = -\frac{1}{2}\pi_{ij}\alpha_{sij} + \dots, \quad (5)$$

where the quantity  $\alpha_{sij}$  is defined here as *the electronic spin polarizability*. Using the purely mathematical relation

$$\alpha_{si} = \epsilon_{ijk}\alpha_{sjk}, \quad (6)$$

where  $\epsilon_{ijk}$  is the Levi-Civita tensor, the spin polarizability can be written as the rank one axial vector

$$\alpha_{sk} = \alpha_{ij} - \alpha_{ji} \quad (7)$$

which is positive to  $P$  and negative to  $T$ . The interaction Hamiltonian can therefore be written as

$$\Delta H = -\frac{1}{2}\pi_k\alpha_{sk}, \quad (8)$$

a product of two axial vectors, each of which is T negative and P positive. Therefore  $\Delta H$  is analogous to the interaction Hamiltonian

$$\Delta H_1 = -B_k M_k \quad (9)$$

between static magnetic flux density  $\mathbf{B}$  and the molecular or atomic magnetic dipole moment  $\mathbf{M}$ , both of which are P positive, T negative axial vectors. The magnetic dipole moment  $\mathbf{M}$  is proportional to the sum of orbital and spin angular momenta in an atom or molecule, and therefore angular momentum has the same positive P and negative T symmetries.

The order of magnitude of  $\alpha_s$  is about  $10^{-38} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$  and for  $E_0$  of about  $10^8$  volts  $\text{m}^{-1}$ ,  $\pi_k \alpha_{sk}$  is of the order of  $kT$ . The equivalent  $\mathbf{B}$  for  $\mathbf{M}$  of the order of the Bohr magneton is about one tesla.

The conjugate property  $\pi$  therefore provides an atom or molecule with angular momentum  $\mathbf{J}_k$  which is in general quantized (Section 2) and which couples with the various intrinsic angular momenta of the atom or molecule according to general Clebsch–Gordan rules outlined in Section 3. The overall effect of  $\pi$  on probe broadband radiation is therefore to cause splitting of spectral features, accompanied by several other fundamental effects such as circular birefringence and dichroism (10) analogous to the Faraday  $A$ ,  $B$ , and  $C$  terms due to  $\mathbf{B}$ .

## 2. DEFINITION OF ANGULAR MOMENTUM DUE TO $\pi$

Define the magnetic dipole moment due to  $\pi$  through the equation

$$M_{\pi i} = \beta_{ij} \pi_j + \dots, \quad (10)$$

where the tensor  $\beta_{ij}$  is given from semiclassical perturbation theory {1} as

$$\beta_{ij} = -\frac{2}{\hbar} \sum_{m \neq n} \frac{\langle n | M_i | m \rangle \langle m | \alpha_{sj} | n \rangle}{\omega_{mn}} \quad (11)$$

for the quantum transition between state  $n$  and  $m$ . Here  $M_i$  is the transition magnetic dipole moment and  $\alpha_{sj}$  is the transition spin polarizability for a transition frequency

$$\omega_{mn} = \omega_m - \omega_n \quad (12)$$

in radians  $\text{sec}^{-1}$ . The spin polarizability is defined through

$$\alpha_{sk} \equiv \alpha'_{sk} - i\alpha''_{sk} = (\alpha'_{ij} - \alpha'_{ji}) - i(\alpha''_{ij} - \alpha''_{ji}) \quad (13)$$

with

$$\alpha'_{ij} = \frac{2}{\hbar} \sum_{m \neq n} \frac{\omega_{mn} \text{Re}(\langle n | \mu_i | m \rangle \langle m | \mu_j | n \rangle)}{\omega_{mn}^2 - \omega^2} = \alpha'_{ji} \quad (14)$$

and

$$\alpha''_{ij} = -\frac{2}{\hbar} \sum_{m \neq n} \frac{\omega \text{Im}(\langle n | \mu_i | m \rangle \langle m | \mu_j | n \rangle)}{\omega_{mn}^2 - \omega^2} = -\alpha''_{ji} \quad (15)$$

from standard semiclassical theory ( $I$ ). The tensor  $\beta_{ij}$  is therefore made up of a transition magnetic dipole moment  $M_i$  multiplied into orthogonal transition electric dipole moments. The induced magnetic dipole moment  $M_{\pi i}$  in Eq. (10) must be purely imaginary, and because  $\pi_j$  is purely imaginary, the dynamic molecular property tensor  $\beta_{ij}$  must be purely real. This tensor is constructed from a purely imaginary transition magnetic dipole moment which multiplies a complex transition spin polarizability, and in order for the tensor to be overall real, as required, only the complex part of the spin polarizability can contribute. This is defined through

$$\alpha''_{sk} = \alpha''_{ij} - \alpha''_{ji} = 2\alpha''_{ij} \quad (16)$$

using the semiclassical definition (15) for the right hand side components.

The induced magnetic dipole moment on the left hand side of Eq. (10) is equated as follows to a purely complex (i.e. quantized) angular momentum induced by the conjugate product

$$\begin{aligned} M_{\pi i} &\propto \gamma_e J_\pi; & M_{\pi z} &\propto M_{J_\pi} \gamma_e \hbar \\ M_{J_\pi} &= J_\pi, J_\pi - 1, \dots, -J_\pi, \end{aligned} \quad (17)$$

where  $-\gamma_e \hbar$  is the Bohr magneton.

The order of magnitude of the tensor  $\beta_{ij}$  can be estimated by taking a transition frequency  $\omega_{mn}$  of about  $10^{15}$  radians  $\text{sec}^{-1}$ , just below the visible; a spin polarizability ( $I$ ) of about  $10^{-38}$   $\text{J}^{-1} \text{C}^2 \text{m}^2$ ; and  $\hbar$  about  $10^{-34}$   $\text{J sec}$ . For the transition magnetic moment we take the order of magnitude of the Bohr magneton, which is about  $10^{-23}$   $\text{J T}^{-1}$ . This produces  $10^{-42}$   $\text{C}^2 \text{m}^2 \text{T}^{-1} \text{J}^{-1}$  for the new molecular property tensor  $\beta_{ij}$ . This can be increased considerably at the resonance condition

$$\omega_{mn} \doteq \omega \quad (18)$$

when the denominators in Eqs. (14) and (15) become very small. The resonance condition is accompanied by spectral absorption in the usual way. The condition (18) may be achieved by tuning a probe laser, parallel to the pump, to the transition frequency  $\omega_{mn}$ . This pump/probe configuration is similar to the standard experimental configuration used, for example, in the optical Kerr effect.

### 3. COUPLING OF $\mathbf{J}_\pi$ TO INTRINSIC MOLECULAR AND ATOMIC ANGULAR MOMENTA

The coupling rules of angular momenta are fundamentally responsible for spectral splitting in electronic, vibration-rotation, rotation, and hyperfine spectroscopies of many different kinds. In this section we take the customary definitions of intrinsic angular momenta and use the Clebsch-Gordan theorem to illustrate the general effect of  $\mathbf{J}_\pi$ . In general  $\mathbf{J}_\pi$  couples to the total molecular angular momentum  $\mathbf{J}$  which is composed of electronic ( $\mathbf{S}$ ) and nuclear ( $\mathbf{N}$ ) spin angular momenta, electronic orbital angular momentum ( $\mathbf{L}$ ), and overall angular momentum of the nuclear framework ( $\mathbf{O}$ ). The overall effect of  $\mathbf{J}_\pi$  coupled to  $\mathbf{J}$  is given by the Clebsch-Gordan Theorem as

$$J_\pi + J, \quad J_\pi + J - 1, \quad \dots, \quad |J_\pi - J|;$$

i.e., the maximum allowed angular momenta eigenvalue components range from  $J + J_\pi$  to  $|J - J_\pi|$ , allowing many more transitions between different quantum states than in the absence of  $\mathbf{J}_\pi$ . If the total angular momentum is made up of a combination of  $\mathbf{O}$  and  $\mathbf{L}$ , neglecting spin, then each  $J$  term is itself made up of subterms  $O + L$ ,  $O + L - 1, \dots, |O - L|$ . Therefore  $\mathbf{J}_\pi$  couples in to all of these sublevels of angular momentum in general, according to the rule

$$J_\pi + L, J_\pi + L - 1, \dots, |J_\pi - L| \text{ for each } O; \quad M = M_\pi + M_L;$$

$$J_\pi + O, J_\pi + O - 1, \dots, |J_\pi - O| \text{ for each } L; \quad M_L = L, L - 1, \dots, -L;$$

$$\text{i.e.,} \quad J_\pi + L + O, \dots, |J_\pi - |L - O||.$$

Furthermore, spin orbit coupling is present between  $\mathbf{S}$  and  $\mathbf{L}$ , leading to the sublevels  $S + L, \dots, |S - L|$ , all of which couple to  $\mathbf{O}$ ,  $\mathbf{J}$ , and  $\mathbf{J}_\pi$ . Finally, hyperfine detail is present through coupling to the nuclear spin  $\mathbf{N}$ , and this detail also couples to  $\mathbf{S}$ ,  $\mathbf{L}$ ,  $\mathbf{O}$ ,  $\mathbf{J}$ , and  $\mathbf{J}_\pi$  in different parts of the electromagnetic spectrum.

The frequency separation of the splitting depends roughly on  $\alpha_{si}\pi_i/2\hbar$ , and this can be easily observable with powerful pulses of Nd:YAG radiation.

#### 4. ZEEMAN TYPE SPLITTING DUE TO $\mathbf{J}_\pi$

A simple example of the splitting is that of the singlet term  $^1P$  of an atom, which corresponds to  $S = 0, L = 1$ . In the presence of  $\mathbf{J}_\pi$  we expect the angular momentum states

$$J_\pi + 1, J_\pi, \dots, |J_\pi - 1|; \quad M_\pi = J_\pi, J_\pi - 1, \dots, -J_\pi;$$

with  $\mathbf{J}_\pi$  defined as in Eq. (17) of Section 2. The singlet transition between the  $^1S$  and  $^1P$  states is split into sublevels, governed by the coupling between the intrinsic angular momenta and the induced angular momentum (magnetic moment) defined in Eq. (17). The energy separation of the highest and lowest sublevel is  $\Delta H_s = \alpha_{si}\pi_i/2$ , i.e., gives information on the spin polarizability. The theory of the normal Zeeman effect (due to  $\mathbf{B}$ ) uses the interaction Hamiltonian between  $\mathbf{B}$  and the molecular magnetic moment ( $\mathbf{M}$ ) to lift degeneracies. The theory of spectral splitting due to  $\pi$  used here differs fundamentally, in that it uses a coupling scheme between the angular momentum  $\mathbf{J}_\pi$  induced by  $\pi$  and the total intrinsic molecular angular momentum. For a  $^1P$  term in an atom, the coupling with the  $L$  quantum number, for example, is

$$|L + J_\pi|, \dots, |L - J_\pi|,$$

which clearly depends on the quantization of  $\mathbf{J}_\pi$  as given by the quantized molecular property tensor  $\beta_{ij}$  of Eqs. (11) and (15), which in turn depends on transition magnetic and electric dipole moments and their selection rules. The spin polarizability enters through this tensor, and also determines the interaction Hamiltonian between  $\pi$  and the molecular ensemble.

The splitting due to  $\pi$  of the pump laser is therefore proportional to  $E_0^2$ , and to the electronic spin polarizability of the atom for the quantum transition under consideration. This effect due to  $\pi$  is accompanied in atoms and molecules by circular birefringence and dichroism (10), as in the Faraday effect due to  $\mathbf{B}$ .

In molecules, the spectrum is further enriched by coupling of  $\mathbf{L}$  to  $\mathbf{O}$ , the intrinsic angular momentum of the nuclear framework, and  $\mathbf{J}_\pi$  of the pump laser couples to each quantized angular momentum  $L + O$  to  $|L - O|$ .

### 5. EFFECT ON ELECTRONIC ATOMIC AND MOLECULAR SPECTRA

The orbital angular momenta discussed in Section 4 also couple in atoms and molecules to spin angular momenta of both the electrons and nuclei (Russell–Saunders and hyperfine coupling respectively). In this case the quantized angular momenta  $\mathbf{J}$  are given by  $L + S, \dots, |L - S|$  or  $L + N, \dots, |L - N|$ . In light atoms (weak  $L, S$  coupling)  $\mathbf{L}$  and  $\mathbf{S}$  precess slowly around  $\mathbf{J}$ , and in heavy atoms (strong  $L, S$  coupling),  $\mathbf{L}$  and  $\mathbf{S}$  are not clearly specified. In multielectron atoms, the orbital angular momenta of individual electrons are strongly or weakly coupled electrostatically. To all of these angular momenta we can add the induced angular momentum  $\mathbf{J}_\pi$ , which has the effect of creating more quantized angular momentum combinations through the Clebsch–Gordan theorem.

In the hydrogen atom, for example, the transition electric dipole is described in the presence of  $\pi$  by four quantum numbers

$$\langle J_{\pi 2} n_2 l_2 m_{l2} | \mu | J_{\pi 1} n_1 l_1 m_{l1} \rangle.$$

The quantum number  $J_\pi$  due to  $\pi$  supplements the customary  $n, l$ , and  $m$  of the hydrogen atom, so that the usual Laporte selection rule is modified by the need for the products

$$(-1)^{J_{\pi 2} + l_2} (-1)^{l_2} (-1)^{J_{\pi 1} + l_1}$$

and so on for  $J_\pi + l, \dots, |J_\pi - l|$  to be negative for a transition from  $|J_{\pi 1} l_1\rangle$  to  $|J_{\pi 2} l_2\rangle$ . The complete configuration–term–level–state hierarchy of the hydrogen atom is affected by the input of angular momentum  $\mathbf{J}_\pi$  by  $\pi$  of the pump laser, thus leading to a radically new type of electronic spectroscopy.

Where there is more than one electron, as in the helium atom, the Pauli exclusion principle applies; i.e., no two electrons can have the same set of quantum numbers. Note that the presence of  $\mathbf{J}_\pi$  implies, however, that each electron is given a new quantum number, describing  $\mathbf{J}_\pi$ , leading to states previously disallowed by the Pauli exclusion rule. For example, electrons with identical intrinsic quantum numbers become allowed, provided that the quantum numbers  $J_{\pi 1}$  and  $J_{\pi 2}$  of each electron are different. In a many electron atom in the absence of  $\pi$  the Pauli principle allows only  $^1D, ^3P$ , and  $^1S$  from the  $2p^2$  configuration, because there are only three quantum states,  $n, l$ , and  $m$ . The Clebsch–Gordan coupling with  $\mathbf{J}_\pi$  allows many more transitions, because different electrons may have identical  $n, l$ , and  $m$ , but different  $J_\pi$  quantum numbers.

New interaction Hamiltonians are generated between the induced angular momentum  $\mathbf{J}_\pi$  and the various intrinsic angular momenta. For example, it is possible to define the interaction Hamiltonian

$$\Delta H_3 \propto -\gamma_e \mathbf{J} \cdot \mathbf{J}_\pi \quad (19)$$

between  $\mathbf{J}$  and  $\mathbf{J}_\pi$ . If  $\mathbf{J}$  is composed of  $\mathbf{L}$  and  $\mathbf{S}$ , there are three precessional motions present,  $\mathbf{S}$  about  $\mathbf{J}$ ,  $\mathbf{L}$  about  $\mathbf{J}$ , and  $\mathbf{J}$  about the  $\pi$ -induced angular momentum  $\mathbf{J}_\pi$ .

The applied  $\pi$  may, furthermore, be strong enough to break the coupling between  $\mathbf{S}$  and  $\mathbf{L}$  and to couple each component to  $\mathbf{J}_\pi$ .

In molecular electronic spectra there is further enrichment due to the presence of more than one nucleus, so that there is framework angular momentum  $\mathbf{O}$  and coupling between nuclear spins (spin-spin coupling), which may also couple individually or collectively to  $\mathbf{J}_\pi$  from  $\pi$ .

## 6. ROTATION AND VIBRATION ROTATION SPECTRA

In pure rotational motion of a dipolar molecule such as a symmetric top, there are three intrinsic angular momentum quantum numbers,  $J$ ,  $K$ , and  $M$ , which couple to the induced angular momentum  $\mathbf{J}_\pi$ . The selection rules for rotational motion, such as  $\Delta J = \pm 1$ , are modified, because the product of irreducible representations

$$\Gamma(|J_{\pi 1} J_1\rangle) \Gamma(\mu) \Gamma(|J_{\pi 2} J_2\rangle)$$

must include the totally symmetric irreducible representation of the group of rotations. The rotational quantum state  $J$  is split by the Clebsch-Gordan theorem into

$$J + J_\pi, J + J_\pi - 1, \dots, |J - J_\pi|$$

and transitions between these levels can occur with selection rules

$$\Gamma(|J_{\pi 1} J_1\rangle) \Gamma(\mu) \Gamma(|J_{\pi 2} J_2\rangle) \quad \text{contains the totally symmetric representation.}$$

Similar modifications must be made to the  $(2J + 1)$  values of  $K$  and  $M$  of a symmetric top, and the far-infrared spectrum is modified considerably in the presence of  $\mathbf{J}_\pi$  induced by  $\pi$ . The extent of the spectral changes depends on  $E_0^2$  and the property tensor  $\beta_{ij}$ , and on the overall Hamiltonian  $\Delta H$ .

Finally in vibration-rotation spectra, the same considerations allow the prediction of the splitting of rotational fine structure in the  $P$  and  $Q$  branches, with the selection rule  $\Delta J = 1$  again modified as discussed for pure rotational spectra. Similarly, in Raman spectroscopy, the selection rule  $\Delta J = 2$  is modified, and the Rayleigh/Raman scattering develops optical activity ( $I0$ ,  $I1$ ) in analogy with the optical activity in scattered radiation ( $I$ ) due to  $\mathbf{B}$ .

### Discussion

Since  $\mathbf{J}_\pi$  is an angular momentum it has its quantum mechanical properties; for example, the commutation relations derived from the fundamental postulates

$$\left. \begin{aligned} [J_{\pi i}, J_{\pi j}] &= i\hbar J_{\pi k} \\ [J_{\pi j}, J_{\pi k}] &= i\hbar J_{\pi i} \\ [J_{\pi k}, J_{\pi i}] &= i\hbar J_{\pi j} \end{aligned} \right\} \quad (20)$$

and

$$[J_\pi^2, J_{\pi k}] = 0 \quad (21)$$

with the magnitude

$$J_\pi^2 = J_{\pi i}^2 + J_{\pi j}^2 + J_{\pi k}^2. \quad (22)$$

It has the eigenvalues and eigenfunctions of angular momentum, and obeys the equation

$$J_{\pi}^2 |J_{\pi}, M_{J_{\pi}}\rangle = \hbar^2 J_{\pi}(J_{\pi} - 1) |J_{\pi}, M_{J_{\pi}}\rangle, \quad (23)$$

where

$$M_{J_{\pi}} = J_{\pi}, \dots, -J_{\pi}. \quad (24)$$

Therefore the magnitude and  $k$  component of  $\mathbf{J}_{\pi}$  are quantized; the former is given by

$$(J_{\pi}(J_{\pi} + 1))^{1/2} \hbar,$$

with  $J_{\pi}$  an integer or half integer, and the  $k$  component is  $M_{J_{\pi}} \hbar$ , where  $M_{J_{\pi}}$  ranges over  $J_{\pi}, J_{\pi} - 1, \dots, -J_{\pi}$ . The induced angular momentum  $\mathbf{J}_{\pi}$  due to  $\pi$  is therefore described by two quantum numbers,  $J_{\pi}$  and  $M_{J_{\pi}}$ . The basic commutation relations for  $\mathbf{J}_{\pi}$  allow half-integral values of  $J_{\pi}$ , which disappear only if cyclical boundary conditions are imposed on the wavefunctions of this induced angular momentum. Whether or not such conditions are valid for  $\mathbf{J}_{\pi}$  will be revealed by experimental observation.

In considering the coupling of  $\mathbf{J}_{\pi}$  to the resultant intrinsic molecular or atomic angular momentum  $\mathbf{J}$ , fundamental theory of quantized angular momentum coupling must be used as discussed in the preceding sections. This implies that the magnitude of the total resultant angular momentum is

$$(J_{\text{tot}}(J_{\text{tot}} + 1))^{1/2} \hbar,$$

where  $J_{\text{tot}}$  takes integer and half-integer values in general, and that the  $k$  component of  $\mathbf{J}_{\text{tot}}$  is  $M_{\text{tot}} \hbar$ , with  $M_{\text{tot}}$  ranging over  $J_{\text{tot}}, J_{\text{tot}} - 1$  to  $-J_{\text{tot}}$ . The permitted quantized states of the total resultant angular momentum  $\mathbf{J}_{\text{tot}}$  are given by the Clebsch-Gordan series

$$J_{\pi} + J, J_{\pi} + J - 1, \dots, |J_{\pi} - J|$$

with

$$M_{\text{tot}} = M_J + M_{J_{\pi}}. \quad (25)$$

Transitions between these states, with appropriate selection rules, lead to the variety of spectral effects discussed already.

The quantum numbers  $J_{\pi}$  and  $M_{J_{\pi}}$  of the induced angular momentum  $\mathbf{J}_{\pi}$  depend on the atomic or molecular states  $n$  and  $m$  in the dynamic molecular property tensor  $\beta_{ij}$ , and therefore the pattern of spectral splitting due to  $\pi$  gives information on  $\beta_{ij}$ . By tuning the observation frequency  $\omega$  to the transition frequency  $\omega_{mn}$  different patterns of splitting may be emphasized for different transition frequencies  $\omega_{mn}$  between states  $n$  and  $m$ . This may be achieved experimentally with a pump probe system, the pump providing the quantity  $\pi$ , and the probe's frequency  $\omega$  being tuned to  $\omega_{mn}$ , i.e., adjusted so that

$$\omega_{mn} \doteq \omega. \quad (26)$$



In conclusion, a large number of new effects appears to be possible theoretically from a consideration of fundamental quantum theory of angular momentum coupling between  $\mathbf{J}_r$  and the various intrinsic angular momenta of atoms and molecules.

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