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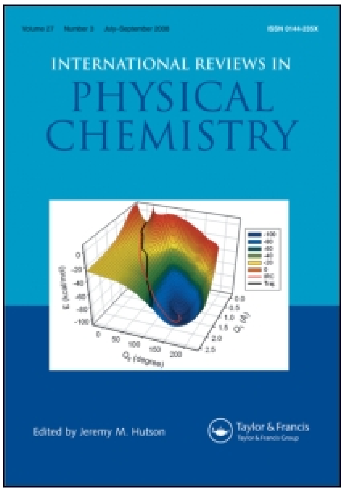

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Through the looking glass: a quantum-electrodynamical view of optical activity

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Circular dichroism and optical activity are well known manifestations of optical activity. In recent years several novel types of optical activity have been observed. An achiral system bathed in an intense beam of circularly polarized light shows chiral behaviour which can be detected as circular dichroism or optical rotation. In another type of induced circular dichroism, a chiral solvent is used to induce chirality. Theories of natural and induced optical activity are reviewed within a unified framework using quantum electrodynamics.

Chiral discrimination refers to the dependence of the interaction energy of two chiral molecules upon the relative handedness of the two species. The intermolecular interaction can be modified by the presence of an intense radiation field. Theories of discriminatory interactions are discussed within a quantum-electrodynamical viewpoint.

1. Introduction

A landmark in twentieth century physical science is Dirac's formulation (1927) of quantum electrodynamics. An essential feature of this theory is the quantization of the electromagnetic field. Dirac successfully applied his theory to derive the Einstein *A*- and *B*-coefficients. His derivation differs from that of Einstein in that it is direct and avoids the use of statistical arguments. Further, he was able to relate these coefficients to atomic quantities such as electric dipole transition moments. Other processes, such as scattering of radiation by atoms, were analysed in a similar manner and the cross-sections were also expressed in terms of electric dipole moments. Theories of optical activity, however, require consideration of absorption and emission of radiation by chiral molecules beyond the electric dipole approximation. It is necessary to include variations of the vector potential over the molecule, and thus take into account higher multipolar interactions. For example, the quantum-electrodynamical calculation of circular dichroism is a direct extension (Power and Thirunamachandran 1974) of Dirac's theory of the *B*-coefficient by including magnetic dipole couplings.

Quantum electrodynamics is the most successful theory known at present. The quantization of the electromagnetic field is a key step in the theory and leads to a corpuscular aspect complementary to the field. The quantized particle is the photon obeying Bose–Einstein statistics. Recent experimental and theoretical studies on antibunching of photons (see, for example, Walls 1979) demonstrated the necessity of going beyond semiclassical analysis. It is the photon concept that is central to quantum electrodynamics: photons are the carriers of the energy and momentum of the electromagnetic field. Further, virtual photons act as mediators for intermolecular interactions. Dispersion interactions, for example, are viewed as arising from exchange of virtual photons associated with fluctuations of the electromagnetic vacuum (Casimir and Polder 1948, Power 1964). These fluctuations are another fundamental feature of the quantized electromagnetic field. Discriminatory interactions between optically active molecules, another aspect of chirality, may be discussed in a similar manner except that higher multipolarity of the sources must be taken into account.

Quantum electrodynamics provides a theoretical framework for the analysis of chiroptical effects. In this paper, we discuss its application to some of these phenomena (see also, Craig and Thirunamachandran 1984). In Section 2, after outlining the basic theory, we obtain the expression for circular dichroism, namely the differential rates for absorption of left- and right-circularly polarized light by a chiral molecule, and the related result for optical rotatory dispersion. In Section 3, the theory is applied to induced circular dichroism, where chirality is induced by either a circularly polarized laser field or a chiral solvent. As a final application, we discuss in Section 4 chiral discriminatory interactions between enantiomers.

2. General theory and application to circular dichroism and optical rotatory dispersion

2.1. *Theory*

In contrast to elementary quantum mechanics, quantum electrodynamics includes radiation as part of the total dynamical system. The time evolution of such a system is governed by a hamiltonian operator which can be written as the sum of the hamiltonians for the molecules and for the electromagnetic field together with an interaction energy operator:

$$H = H_{\mathrm{mol}} + H_{\mathrm{rad}} + H_{\mathrm{int}} \tag{1}$$

In (1), H_{mol} is the conventional molecular hamiltonian encountered in quantum chemistry and H_{rad} is the hamiltonian for the radiation field. H_{rad} may be written, in terms of the transverse displacement field $\mathbf{d}(\mathbf{r})$ and the magnetic field $\mathbf{b}(\mathbf{r})$, as

$$H_{\mathrm{rad}} = \frac{1}{8\pi}\int \{\mathbf{d}^2(\mathbf{r}) + \mathbf{b}^2(\mathbf{r})\}\, dV \tag{2}$$

The quantization of the electromagnetic field is carried out by expanding $\mathbf{d}(\mathbf{r})$ and $\mathbf{b}(\mathbf{r})$ into modes $(\mathbf{k}, \lambda)$ and expressing the coefficients in terms of creation and annihilation operators for photons. The hamiltonian (2) for the radiation field then becomes a sum of harmonic oscillator hamiltonians

$$H_{\mathrm{rad}} = \sum_{\mathbf{k},\lambda} \{a^{(\lambda)\dagger}(\mathbf{k})a^{(\lambda)}(\mathbf{k}) + \tfrac{1}{2}\}\hbar\omega \tag{3}$$

with $\omega = ck$. The explicit expansions for $\mathbf{d}(\mathbf{r})$ are given by (4) and (5).

$$\mathbf{d}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar ck}{V}\right)^{1/2}\{\mathbf{e}^{(\lambda)}(\mathbf{k})a^{(\lambda)}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}) - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k})a^{(\lambda)\dagger}(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{r})\} \tag{4}$$

$$\mathbf{b}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar ck}{V}\right)^{1/2}\{\mathbf{b}^{(\lambda)}(\mathbf{k})a^{(\lambda)}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}) - \bar{\mathbf{b}}^{(\lambda)}(\mathbf{k})a^{(\lambda)\dagger}(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{r})\} \tag{5}$$

$\mathbf{e}^{(\lambda)}(\mathbf{k})$ is the complex polarization vector for the mode $(\mathbf{k}, \lambda)$ and $\mathbf{b}^{(\lambda)}(\mathbf{k}) = \hat{\mathbf{k}} \times \mathbf{e}^{(\lambda)}(\mathbf{k})$. The interaction term in (1) is often written as a multipolar series, and the first few terms are

$$H_{\mathrm{int}} = -\boldsymbol{\mu}\cdot\mathbf{d}(\mathbf{R}) - \mathbf{m}\cdot\mathbf{b}(\mathbf{R}) - \mathbf{Q} : \nabla\mathbf{d}(\mathbf{R}) \tag{6}$$

For many applications of radiation theory it is sufficient to consider the electric dipole term alone. However for chiroptical processes, it is necessary to go beyond the electric dipole approximation and include the magnetic dipole and electric quadrupole terms.

In the Schrödinger picture, the time evolution of the state vector of the system is governed by

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \tag{7}$$

For most processes of interest it is sufficient to use Fermi's rule for transition rates which follows from (7). For a transition $|f\rangle \leftarrow |i\rangle$, this rate is

$$\Gamma = \frac{2\pi}{\hbar}|M_{fi}|^2\rho \tag{8}$$

where M_{fi} is the matrix element for the process and ρ is the number of levels per unit energy. For detailed accounts of the theory the reader may consult textbooks (see for example, Power 1964, Craig and Thirunamachandran 1984).

2.2. *Circular dichroism*

For circular dichroism we require the rate of absorption of circularly polarized light of both helicities by the chiral molecule. The appropriate matrix element for this process is first order in H_{int} given by (6). For randomly oriented molecules, the electric quadrupole does not contribute and is not considered further. For incident light of mode $(\mathbf{k}, \lambda)$ in the number state $|n(\mathbf{k}, \mathrm{L/R})\rangle$, we have (Power and Thirunamachandran 1974)

$$\begin{aligned}\langle f|H_{\text{int}}|i\rangle &= -i\left(\frac{2\pi n\hbar ck}{V}\right)^{1/2} \exp(i\mathbf{k}\cdot\mathbf{R})\langle f|\boldsymbol{\mu}\cdot\mathbf{e}^{(\mathrm{L/R})}(\mathbf{k}) + \mathbf{m}\cdot\mathbf{b}^{(\mathrm{L/R})}(\mathbf{k})|i\rangle \\ &= -i\left(\frac{2\pi n\hbar ck}{V}\right)^{1/2} \exp(i\mathbf{k}\cdot\mathbf{R})(\boldsymbol{\mu}^{m0} \mp i\mathbf{m}^{m0})\cdot\mathbf{e}^{(\mathrm{L/R})}(\mathbf{k})\end{aligned} \tag{9}$$

In (9), $\boldsymbol{\mu}^{m0}$ and $\mathbf{m}^{m0}$ are the electric and magnetic dipole moments associated with the transition $m \leftarrow 0$. Substituting (9) in (8), expressing ρ in terms of radiant energy density per unit frequency $\mathscr{I}(\omega)$, and carrying out the random orientational average, we obtain

$$\begin{aligned}\langle\Gamma^{(\mathrm{L/R})}\rangle &= \frac{2\pi}{3\hbar^2}|\boldsymbol{\mu}^{m0} \mp i\mathbf{m}^{m0}|^2\mathscr{I}(\omega) \\ &= B^{(\mathrm{L/R})}\mathscr{I}(\omega)\end{aligned} \tag{10}$$

The difference of the absorption rates is

$$\langle\Gamma^{(\mathrm{L})}\rangle - \langle\Gamma^{(\mathrm{R})}\rangle = \frac{8\pi}{3\hbar^2}R^{m0}\mathscr{I}(\omega) \tag{11}$$

where R^{m0}, the optical rotatory strength, is given by

$$R^{m0} = \mathrm{Im}\,(\boldsymbol{\mu}^{m0}\cdot\mathbf{m}^{m0}) \tag{12}$$

This pseudoscalar quantity is directly related to the experimentally measured extinction coefficient $\varepsilon(\omega)$ through the Beer–Lambert law

$$I(\omega, z) = I(\omega, 0)\exp(-\eta\varepsilon(\omega)z) \tag{13}$$

where η is the number of absorbers per unit volume and $I(\omega, z)$ is the irradiance per unit frequency. For attenuation through an optically active medium, $\varepsilon(\omega)$ depends on the helicity of the light, and the difference is given by

$$\int \{\varepsilon^{(\mathrm{L})}(\omega)-\varepsilon^{(\mathrm{R})}(\omega)\}\frac{d\omega}{2\pi}=B^{(\mathrm{L})}-B^{(\mathrm{R})}=\frac{8\pi}{3\hbar^2}R^{m0} \tag{14}$$

We remark that the usual Einstein B-coefficient based on the electric dipole approximation is independent of the handedness of the light and is

$$B=\langle\Gamma\rangle/\mathscr{I}(\omega)=\frac{2\pi}{3\hbar^2}|\boldsymbol{\mu}^{m0}|^2 \tag{15}$$

2.3. *Optical rotation*

Optical rotation is the property of rotation of the plane of polarization when plane-polarized light is transmitted by an assembly of chiral molecules. The process may be treated as elastic forward scattering with change of polarization only. It is sufficient to calculate the amplitude for the change from the incident polarization $\mathbf{e}^{(1)}$ to the orthogonal polarization $\mathbf{e}^{(2)}$, with $\mathbf{e}^{(1)}$, $\mathbf{e}^{(2)}$, and $\hat{\mathbf{k}}$ forming a right-handed triad. It is thus possible to employ a two-state model to calculate the angle of rotation (Power and Thirunamachandran 1971). The state of the forward scattered beam is

$$|\psi(t)\rangle=\{\cos(Mt/\hbar)|1\rangle-\sin(Mt/\hbar)|2\rangle\} \tag{16}$$

where M is the imaginary part of the matrix element M_{fi} for scattering with change of polarization. To second order, M_{fi} is

$$M_{fi}=-\left(\frac{2\pi\hbar ck}{3V}\right)n^{1/2}\sum_m\left\{e_i^{(2)}e_j^{(2)}\left(\frac{\mu_i^{0m}m_i^{m0}}{E_{m0}-\hbar ck}+\frac{m_j^{0m}\mu_i^{m0}}{E_{m0}+\hbar ck}\right)\right.$$
$$\left.-e_i^{(1)}e_j^{(1)}\left(\frac{m_j^{0m}\mu_i^{m0}}{E_{m0}-\hbar ck}+\frac{\mu_i^{0m}m_j^{m0}}{E_{m0}+\hbar ck}\right)\right\} \tag{17}$$

As in circular dichroism, when the molecules are randomly oriented, the electric quadrupole moment does not contribute to optical rotation. After orientational averaging, we obtain

$$M_{fi}=-\left(\frac{8\pi\hbar^2c^2k^2}{3V}\right)n^{1/2}\sum_m\frac{iR^{m0}}{E_{m0}^2-(\hbar ck)^2} \tag{18}$$

From (16) the angle of rotation θ of the plane of polarization satisfies

$$\theta=n^{-1/2}\frac{Mt}{\hbar} \tag{19}$$

for small θ. In (19), t is the time taken by light to traverse the path-length of the sample; in the dilute gas approximation, $t=l/c$. It is usual to express the angle of rotation as rotation per unit length. Thus the specific rotation ϕ is

$$\phi=\frac{8\pi\hbar ck^2\eta}{3}\sum_m\frac{R^{m0}}{E_{m0}^2-(\hbar ck)^2} \tag{20}$$

where η is the number of scatterers per unit volume.

3. Induced circular dichroism

3.1. *Laser-induced circular dichroism*

Laser-induced circular dichroism is the differential absorption by an achiral molecule in the presence of an intense beam of circularly polarized light. The achiral molecule acquires chirality by admixing levels of different parity by virtual transitions induced by the non-resonant laser beam. In quantum-electrodynamical terms, this phenomenon may be regarded as arising from an interference of first and third-order amplitudes for absorption (Thirunamachandran 1979). The first-order term is the conventional one-photon absorption matrix element in the electric dipole approximation and is given by the $\boldsymbol{\mu}^{m0}$ part of (9). The third-order term is a second-order perturbation by the laser field of the single-photon matrix element for the probe beam. We consider the case where the pump beam is left-circularly polarized and the mode is $(\mathbf{k}', \mathrm{L})$. The third-order matrix element is

$$M_3^{(\mathrm{L/R})} = -i\left(\frac{2\pi \mathrm{n}'\hbar \mathrm{ck}'}{V}\right)\left(\frac{2\pi n\hbar ck}{V}\right)^{1/2} \bar{e}_i^{(\mathrm{L})}(\mathbf{k}')e_j^{(\mathrm{L})}(\mathbf{k}')e_k^{(\mathrm{L/R})}(\mathbf{k})\beta_{ijk}^{m0} \tag{21}$$

where

$$\begin{aligned}\beta_{ijk}^{m0} = \sum_{r,s}\Bigg(&\frac{\mu_i^{ms}\mu_j^{sr}\mu_k^{r0}}{(E_{sm}-\hbar\omega')(E_{r0}-\hbar\omega)}+\frac{\mu_j^{ms}\mu_i^{sr}\mu_k^{r0}}{(E_{sm}+\hbar\omega')(E_{r0}-\hbar\omega)}+\frac{\mu_j^{ms}\mu_k^{sr}\mu_i^{r0}}{(E_{sm}+\hbar\omega')(E_{r0}+\hbar\omega')}\\ &+\frac{\mu_i^{ms}\mu_k^{sr}\mu_j^{r0}}{(E_{sm}-\hbar\omega')(E_{r0}-\hbar\omega')}+\frac{\mu_k^{ms}\mu_i^{sr}\mu_j^{r0}}{E_{s0}(E_{r0}-\hbar\omega')}+\frac{\mu_k^{ms}\mu_j^{sr}\mu_i^{r0}}{E_{s0}(E_{r0}+\hbar\omega')}\Bigg)\end{aligned} \tag{22}$$

The differential rate of absorption of a photon from the probe beam is

$$\begin{aligned}\Gamma^{(\mathrm{L})}-\Gamma^{(\mathrm{R})} &= \frac{2\pi}{\hbar}\{|M_1^{(\mathrm{L})}+M_3^{(\mathrm{L})}|^2-|M_1^{(\mathrm{R})}+M_3^{(\mathrm{R})}|^2\}\rho\\ &= \frac{2\pi}{\hbar}\{M_1^{(\mathrm{L})}\bar{M}_3^{(\mathrm{L})}+\bar{M}_1^{(\mathrm{L})}M_3^{(\mathrm{L})}-M_1^{(\mathrm{R})}\bar{M}_3^{(\mathrm{R})}-\bar{M}_1^{(\mathrm{R})}M_3^{(\mathrm{R})}\}\rho\end{aligned} \tag{23}$$

Inserting (9) and (21) into (23) and performing a rotational average, we obtain

$$\langle\Gamma^{(\mathrm{L})}\rangle-\langle\Gamma^{(\mathrm{R})}\rangle = \frac{4\pi^2}{3\hbar^2 c}I'\mathscr{I}(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')\mu_\lambda^{m0}(\beta_{\mu\lambda\mu}^{m0}-\beta_{\lambda\mu\mu}^{m0}) \tag{24}$$

where I' is the irradiance of the pump beam and $\mathscr{I}$ is the energy density per unit frequency of the probe beam. It is useful to introduce the parameter Δ to express induced circular dichroism through (25).

$$\Delta = \frac{\langle\Gamma^{(\mathrm{L})}\rangle-\langle\Gamma^{(\mathrm{R})}\rangle}{\langle\Gamma^{(\mathrm{L})}\rangle+\langle\Gamma^{(\mathrm{R})}\rangle} \tag{25}$$

Noting that the sum of the absorption rates is to a good approximation $2\mathscr{I}$ times the Einstein B-coefficient, we have

$$\Delta = \frac{\pi I'(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')}{c}\frac{\mu_\lambda^{m0}(\beta_{\mu\lambda\mu}^{m0}-\beta_{\lambda\mu\mu}^{m0})}{|\boldsymbol{\mu}^{m0}|^2} \tag{26}$$

In addition to the factor dependent on the transition moments, Δ is linear in the irradiance of the pump beam and in the cosine of the angle between the two beams.

In natural circular dichroism, the differential absorption rate depends on the pseudoscalar rotatory strength, with opposite sign for the two enantiomers. In laser-induced dichroism, the enantiomeric equivalents are the two possible circular polarizations of the pump beam. A change of helicity of the pump beam is equivalent to a change in the sign of $\hat{\mathbf{k}}$ in (26), giving a change of sign in the differential ratio.

3.2. *Molecule-induced circular dichroism*

We have seen in Section 3.1 how an achiral molecule can acquire chirality by its interaction with intense electromagnetic fields. Another possible way in which chirality may be induced in an achiral molecule is through interaction with a chiral solvent (Bosnich 1967, Hayward and Totty 1971). In this section we outline a theoretical framework within the Heisenberg picture for this phenomenon. An analysis within the Schrödinger picture may be found in a paper by Craig *et al.* (1976). In the Heisenberg formalism, the electromagnetic field of both the incident radiation and that of the chiral molecule C are coupled to the achiral molecule A, resulting in absorption (Power and Thirunamachandran 1984). These time-dependent fields interact with the time-dependent transition moments of A. It is sufficient to take into account the electric dipole moment operator of A alone since the chirality is contained in the electromagnetic field. The matrix element for i.c.d. is

$$M_{fi}=\langle f|-\boldsymbol{\mu}(\mathrm{A},t)\cdot\mathbf{d}(\mathbf{R}_{\mathrm{A}},t)|i\rangle \tag{27}$$

where $\mathbf{d}(\mathbf{R}_{\mathrm{A}},t)$ is the displacement vector operator at time t at the position $\mathbf{R}_{\mathrm{A}}$. The initial state corresponds to both molecules in their ground states and the radiation field in a number state for a circularly polarized beam:

$$|i\rangle=|E_0^{\mathrm{A}},E_0^{\mathrm{C}};n(\mathbf{k},\mathrm{L/R})\rangle \tag{28}$$

The final state is

$$|f\rangle=|E_m^{\mathrm{A}},\ E_0^{\mathrm{C}};\ (n-1)(\mathbf{k},\mathrm{L/R})\rangle \tag{29}$$

The displacement vector used in (27) is found to second order in the moments of the chiral molecule. We have

$$\mathbf{d}(\mathbf{R}_{\mathrm{A}},\ t)=\mathbf{d}^{(0)}(\mathbf{R}_{\mathrm{A}},\ t)+\mathbf{d}^{(1)}(\mathbf{R}_{\mathrm{A}},\ t)+\mathbf{d}^{(2)}(\mathbf{R}_{\mathrm{A}},\ t)+\dots \tag{30}$$

where $\mathbf{d}^{(0)}$ is the familiar free-field operator; $\mathbf{d}^{(1)}$ does not change photon numbers and therefore does not contribute to (27). The $\mathbf{d}^{(2)}$ term depends linearly on the creation and annihilation operators. It is given by

$$\begin{aligned}d_i^{(2)}(\mathbf{R}_{\mathrm{A}},t)=i\sum_{\mathbf{k},\mathrm{L/R}}\left(\frac{2\pi\hbar ck}{V}\right)^{1/2}&\exp(i\mathbf{k}\cdot\mathbf{R}_{\mathrm{A}})a^{(\mathrm{L/R})}(\mathbf{k})\\ &\{[e_k^{(\mathrm{L/R})}(\mathbf{k})\alpha_{jk}(k)+b_k^{(\mathrm{L/R})}(\mathbf{k})G_{jk}(k)](-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\\ &+[e_k^{(\mathrm{L/R})}(\mathbf{k})G_{kj}(k)](ik\varepsilon_{ijl}\nabla_l)\}\frac{\exp\{ik(|\mathbf{R}_{\mathrm{A}}-\mathbf{R}_{\mathrm{C}}|-ct)\}}{|\mathbf{R}_{\mathrm{A}}-\mathbf{R}_{\mathrm{C}}|}+\mathrm{h.c.}\end{aligned} \tag{31}$$

where $\alpha_{jk}(k)$ is the frequency-dependent polarizability of C and $G_{jk}(k)$ is the mixed electric-magnetic analogue,

$$G_{jk}(k)=\sum_r\left(\frac{\mu_j^{0r}m_k^{r0}}{E_{r0}-\hbar ck}+\frac{m_k^{0r}\mu_j^{r0}}{E_{r0}+\hbar ck}\right) \tag{32}$$

A measure of induced circular dichroism is the difference in the rates of absorption between left- and right-circulary polarized light by A in the presence of C. The difference of absorption rates depends on the orientation of the molecules with respect to the incident beam and their relative geometrical position. However, to relate this difference to experimental measurements made in a fluid phase it is necessary to average the calculated difference. This is usually done in two stages: first, a tumble average with respect to the direction of the beam, and secondly a random orientational average of the molecules with respect to each other. For the cases where the measurements show a marked temperature dependence, it is necessary to perform a Boltzmann-weighted average. We consider only the high-temperature limit for which the fully averaged result is found to be

$$\langle\Gamma^{(\mathrm{L})}\rangle-\langle\Gamma^{(\mathrm{R})}\rangle=\frac{4\pi\mathscr{I}}{9\hbar^2}|5\mathrm{k}^{m0}(\mathrm{A})|^2\,\mathrm{Im}\,G_{vv}(k)$$

$$\times\frac{1}{R^3}\left(-\frac{4\sin 2kR}{kR}-\frac{6\cos 2kR}{k^2R^2}+\frac{3\sin 2kR}{k^3R^3}\right) \qquad (33)$$

where $\mathbf{R}=\mathbf{R}_{\mathrm{A}}-\mathbf{R}_{\mathrm{C}}$. In the near zone where the intermolecular separation R is much less than the reduced wavelength of the radiation $kR \ll 1$, the averaged differential rate (33) reduces to

$$\Delta\Gamma=\frac{128\pi k^2\mathscr{I}}{135\hbar^2 R}|^{km0}(\mathrm{A})|^2\,\mathrm{Im}\,G_{vv}(k) \qquad (34)$$

We note that (34) depends on R^{-1} rather than R^{-3}, the expected dependence of the 'true' static limit. This is because of the fact that in this limit there is no coupling between the electric dipole transition moment of A and the magnetic transition moment of C.

4. Chiral discriminatory interactions

The interaction between two chiral molecules, though dominated by electric dipole forces, are subject in addition to smaller forces which are not the same for left-hand–left-hand as for left-hand–right-hand interactions (see for example Craig and Mellor 1976). These forces are also modified by the influence of external radiation (Taylor and Thirunamachandran 1983). The discriminatory potentials discussed in this section are those appearing in resonance interactions and dispersion interactions. There is experimental evidence of discrimination in a wide range of phenomena involving small molecules as well as in biological systems.

The resonance coupling of two chemically identical molecules A and B, one of which is in an excited state, is one of the simplest problems in molecular quantum electrodynamics. The coupling in the electric dipole approximation which is non-specific to handedness is the familiar (McClone and Power 1964)

$$\mu_i^{0m}(\mathrm{A})\mu_j^{m0}(\mathrm{B})V_{ij}(k_{m0},\mathbf{R}) \qquad (35)$$

where

$$V_{ij}(k,\mathbf{R})=\frac{1}{R^3}[(\delta_{ij}-3\hat{R}_i\hat{R}_j)(\cos kR+kR\sin kR)-(\delta_{ij}-\hat{R}_i\hat{R}_j)k^2R^2\cos kR] \qquad (36)$$

The analogous coupling involving the electric and magnetic dipoles is discriminatory and is found from second-order perturbation theory (Craig *et al.* 1971) to be

$$\mathrm{Im}\,\{\mu_i^{0m}(\mathrm{A})m_j^{m0}(\mathrm{B})+m_j^{0m}(\mathrm{A})\mu_i^{mo}(\mathrm{B})\}\,U_{ij}(k_{m0},\mathbf{R}) \tag{37}$$

where

$$U_{ij}(k,\,\mathbf{R})=\frac{\varepsilon_{ijk}\hat{R}_k}{R^3}[kR\cos kR+k^2R^2\sin kR] \tag{38}$$

The values of (37) are small at all distances compared with the pure electric counterpart (35). An estimate of the discriminatory term is about 10^{-5} times the total resonance interaction.

The dispersion interaction between a pair of molecules arises from two-photon exchange and the fully retarded result can be calculated using fourth-order pertubation theory (Casimir and Polder 1948). In the near zone it reduces to the London expression with its R^{-6} dependence. However, in the far zone the retardation modifies the energy leading to an R^{-7} dependence. These results are based on the electric dipole approximation for both molecules and the interactions are non-discriminatory. However, the inclusion of the magnetic dipole couplings leads to forces that are dependent on the relative handedness of the molecules. The resulting energy can be expressed in terms of the optical rotatory strengths of the two molecules (Mavroyannis and Stephen 1962, Craig *et al.* 1971). In the far zone

$$\Delta E=\frac{16\hbar^3c^3}{3\pi R^9}\sum_m\frac{R^{m0}(\mathrm{A})}{E_{m0}^2(\mathrm{A})}\sum_n\frac{R^{n0}(\mathrm{B})}{E_{n0}^2(\mathrm{B})} \tag{39}$$

whereas in the near zone,

$$\Delta E=\frac{4}{3R^6}\sum_{m,\,n}\frac{R^{m0}(\mathrm{A})R^{n0}(\mathrm{B})}{E_{m0}(\mathrm{A})+E_{n0}(\mathrm{B})} \tag{40}$$

Because of the pseudoscalar nature of the optical rotatory strength, ΔE changes sign when one of the molecules is replaced by its enantiomer. It is evident that for chemically identical molecules in their ground states, the specific forces corresponding to (39) and (40) are repulsive when the handedness of A and B are the same, and attractive for opposite handedness.

5. Conclusion

In this survey we have shown how a wide range of chiroptical phenomena involving interactions between molecules and radiation, or between molecules themselves may be understood from a quantum electrodynamical viewpoint. Observables such as circular dichroism, optical rotation, and chiral discrimination are calculated as straightforward extensions of elementary quantum electrodynamics in atoms. We emphasize that the present methods, though they reproduce the results obtainable from semi-classical considerations, are both more fundamental and capable of dealing with phenomena which are beyond the scope of theories using non-quantized electromagnetic fields.

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