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Chiral discrimination in optical trapping and manipulation

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Abstract

When circularly polarized light interacts with chiral molecules or nanoscale particles powerful symmetry principles determine the possibility of achieving chiral discrimination, and the detailed form of electrodynamic mechanisms dictate the types of interaction that can be involved. The optical trapping of molecules and nanoscale particles can be described in terms of a forward-Rayleigh scattering mechanism, with trapping forces being dependent on the positioning within the commonly non-uniform intensity beam profile. In such a scheme, nanoparticles are commonly attracted to local potential energy minima, ordinarily towards the centre of the beam. For achiral particles the pertinent material response property usually entails an electronic polarizability involving transition electric dipole moments. However, in the case of chiral molecules, additional effects arise through the engagement of magnetic counterpart transition dipoles. It emerges that, when circularly polarized light is used for the trapping, a discriminatory response can be identified between left- and right-handed polarizations. Developing a quantum framework to accurately describe this phenomenon, with a tensor formulation to correctly represent the relevant molecular properties, the theory leads to exact analytical expressions for the associated energy landscape contributions. Specific results are identified for liquids and solutions, both for isotropic media and also where partial alignment arises due to a static electric field. The paper concludes with a pragmatic analysis of the scope for achieving enantiomer separation by such methods.



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1. Introduction

Optical trapping is a generic term for methods to capture, translate or guide particles with one or more laser beams, through directly applied optical forces. With the smallest particles such as atoms or diatomic molecules, the necessity to overcome stochastic, thermally driven effects usually requires cold trapping methods and sustained deceleration forces [1–6]—the latter being most easily achieved through repeated resonant absorption, and requiring the use of laser wavelengths selected to match spectral properties of the sample. On the other hand, for large (often micron-sized) dielectric particles there are a variety of more broadly applicable methods that can be deployed, based on the position-dependent forces produced by spatially varying fields [7, 8]—most commonly the quasi-Gaussian transverse distribution of a TEM₀₀ laser mode [9]. Between these extremes, nanoscale and molecular trapping effects [10] can, in general, be brought about by a forward-Rayleigh scattering mechanism, the necessary forces also being dependent on the positioning within the beam and, therefore, also exploiting a non-uniform intensity beam profile. Further effects arise as a result of optically induced forces between trapped particles: the interplay of such effects has been surveyed in a recent review by Čižmár *et al* [11].

Whilst the material response responsible for any Rayleigh scattering mechanism entails an electronic polarizability that generally involves transition electric dipoles, it is possible for additional contributory effects to arise through the engagement of magnetic transition dipoles (for the same electronic transitions), in the case of chiral molecules. The latter transition moments can provide an extra contribution to the local position-dependent energies and, hence, an associated optical force. Recently there has been a resurgence of interest in these and other forces specifically associated with chirality [12–21]. It emerges that a chiral molecule irradiated with circularly polarized light displays a discriminatory optomechanical response between left- and right-handed input polarizations. Based on the contrast with the behaviour of a racemic mixture (left-handed and right-handed chiral molecules in equal proportion), for which an identical response is produced with circularly polarized light of either left or right polarized input, there have been claims of enantiomer-specific detection [22] and methods of spatial separation [15–18, 23–25] for such molecules. Despite numerous past theoretical studies on optical methods to control or selective engage with molecular chirality—see for example [26–36]—the context for the recently renewed attention to such effects, especially in the physics community, may largely be credited to advances in experimental work on chiral metamaterials [37–40].

The following account begins, in section 2, by emphasizing the difference between the calculation of an optical force—employed when the initial and final states of the system (including the radiation states) are identical—and calculating a rate expression to describe an optical process in which the initial and final states differ. In connection with the present work, it is crucial to understand that chirality effects in optical trapping have a fundamental relationship to *optical rotation* [41, 42] (i.e. a rotation of optical polarization). In contrast, the fundamental differences from circular dichroism [43, 44] will be highlighted. Continuing in section 3, potential energy contributions to optical trapping through electric dipole, electric

quadrupole and magnetic dipole interactions are discussed. Section 4 examines the fundamental symmetry principles that determine the possibility of chiral differential response; this follows the establishment of the molecular and radiation properties that are entailed. Section 5 explores the detailed form of such effects in the case of optical trapping. Isotropic and partially oriented systems are analysed in section 6, and the paper concludes with a discussion on the physical possibility of enantiomer separation due to an optical trapping force arising from chiral light.

2. Comparison of an optical force with a process

To accurately describe the optical trapping of a chiral molecule, a quantum theoretical outlook [45, 46] is deployed. Before proceeding to our main analysis, it is helpful to make clear a distinction between forms of quantum amplitude derivation with similar methodology, but entirely different spheres of application—namely processes and forces. We begin by generalizing a few of the key points drawn out in a recent detailed analysis [47]. In a complete quantum analysis, the Hamiltonian energy is promoted to an operator status and may be decomposed into three terms, corresponding to molecular, radiation and interaction Hamiltonians. The latter acts as a perturbation to the system that is initially in a stationary state, hence, perturbation theory is employed. Using the resolvent operator formalism of time-dependent perturbation theory [48], which involves the matrix operator M , the following infinite series is determined

$$M_{\text{FI}} \equiv \langle F | M | I \rangle = \langle F | \sum_{p=0}^{\infty} H_{\text{int}} (T_0 H_{\text{int}})^p | I \rangle, \quad (1)$$

where $| I \rangle$ and $| F \rangle$ respectively denote the initial and final states of a complete system (in the sense that the representation accommodates both matter and radiation states), H_{int} is the interaction Hamiltonian, and $T_0 \approx (E_I - H_0)^{-1}$ in which E_I is the energy of the initial state and H_0 is the unperturbed Hamiltonian.

For cases where the initial and final states are identical, which can be understood as phenomena rather than processes, only diagonal elements of the matrix element, M_{FI} , are significant; the result of equation (1) thus represents an expectation value with respect to the operator M . Here, it should be emphasized that there is no net transfer of energy, linear or angular momentum from the radiation field to the molecule (or molecules) in such circumstances. This signifies that, for example, the occupancy of each radiation mode is unchanged, as also is the population of each molecular state. For such a system, with $\langle M_{\text{II}}(\mathbf{r}) \rangle \equiv \langle M(\mathbf{r}) \rangle$ for conciseness with \mathbf{r} as the position of the molecule, equation (1) becomes

$$M_{\text{II}}(\mathbf{r}) \equiv \langle I | M | I \rangle(\mathbf{r}) = \prod_{\mathbf{k}, \eta} \langle \varphi | \langle n_{\mathbf{k}, \eta} | M | n_{\mathbf{k}, \eta} \rangle | \varphi \rangle(\mathbf{r}), \quad (2)$$

where the system states are explicitly decomposed into molecular and radiation basis states: $|\varphi\rangle$ is the state of the molecule with wavefunction φ , and $|n_{\mathbf{k}, \eta}\rangle$ denotes the radiation state for a mode with wavevector \mathbf{k} and polarization η . In this situation the calculations are essentially those of time-independent perturbation theory, since both the molecular and radiation states are identical in the initial and final states, and the physically observable energy shift (or potential

energy), ΔE , is identified with the real part of $M_{\text{II}}(\mathbf{r})$. The optical force acting on the molecule is given by the following

$$\mathbf{F}(\mathbf{r}) = -\text{Re} \nabla M_{\text{II}}(\mathbf{r}). \quad (3)$$

This is the expression used to determine the optical trapping force.

In contrast, when the initial and final states differ, off-diagonal elements arise. Consequently, the physical observable is no longer represented by an energy shift but by a time-dependent rate, $\Gamma(t)$, normally derived directly from equation (1) via the Fermi rule [49], i.e. $\Gamma(t) \propto |M_{\text{FI}}|^2$. Physically, the time evolution from the initial to the final state must be considered in such a situation. An example of such processes is the differential absorption of left- and right-circularly polarized light known as circular dichroism. Indeed, in the latter type of event, which involves circularly polarized photon absorption, the initial and final states cannot be identical because of the exchange that occurs between the matter and radiation of both energy and linear momentum. In passing we note that, in the absorption process involved in circular dichroism, spin angular momentum of $\pm\hbar$ is transferred to the molecule, the sign determined by the input radiation circularity but irrespective of the enantiomer employed. As has been established [50], there is no connection between circular dichroism and orbital angular momentum transfer.

3. The source of energy contributions to optical trapping

As identified in the previous section, the physical observable of optical trapping is an energy shift (or potential energy), ΔE : the molecular mechanism does not involve either electronic population transfer or any exchange of momentum with the molecule, and consequently the initial and final states are identical in such a case. (Note: we are not concerned here with the principles that govern the trapping of Mie-scale or larger particles, where internal refraction does lead to momentum transfer.) The corresponding expressions for optical trapping are generated from time-dependent perturbation theory, i.e. from equation (2), to give in the second-order

$$\Delta E = \text{Re} M_{\text{II}} \simeq \text{Re} \left\{ \sum_R \frac{\langle I | H_{\text{int}} | R \rangle \langle R | H_{\text{int}} | I \rangle}{E_I - E_R} \right\}, \quad (4)$$

where I denotes an identical initial and final system state, R is an intermediate state, E is the energy of the state denoted by the subscript and H_{int} is the interaction Hamiltonian that, in the multipolar formulation, is given by [51–53]

$$H_{\text{int}} = -\varepsilon_0^{-1} \mu_i d_i^\perp(\mathbf{r}) - \varepsilon_0^{-1} Q_{ij} \nabla_j d_i^\perp(\mathbf{r}) - m_i b_i(\mathbf{r}) + \dots \text{h.o.t.} \quad (5)$$

Here, μ_i and Q_{ij} are the electric dipole and quadrupole moment operators, and m_i is the magnetic dipole operator; h.o.t. denotes higher order terms. In this equation and throughout the following, there is implied summation over repeated Cartesian indices i, j etc. The second and third contributions to equation (5) signify the response to spatial variation of the local fields (as given by the leading correction terms to the minimal coupling formula) after transforming to the multipolar form of interaction Hamiltonian. The electric dipole ($E1$) interaction is directly associated with the dominant contribution to the Taylor series expansion of the vector potential;

the electric quadrupole ($E2$) and magnetic dipole ($M1$) follow, each delivering a contribution that is typically two–three orders of magnitude lower.

To continue, the operator components $d_i^\perp(\mathbf{r})$ and $b_i(\mathbf{r})$ in equation (5)—which, in a full quantum description, are promoted from the field vector status they would have in a semi-classical approach—generally involve a plane wave summation over all wave-vectors, \mathbf{k} , and polarizations, η , and are written as follows

$$\mathbf{d}^\perp(\mathbf{r}) = i \sum_{\mathbf{k}, \eta} \left(\frac{\hbar c k \epsilon_0}{2V} \right)^{1/2} \left\{ \mathbf{e}_{\mathbf{k}}^{(\eta)} a_{\mathbf{k}}^{(\eta)} e^{i(\mathbf{k} \cdot \mathbf{r})} - \bar{\mathbf{e}}_{\mathbf{k}}^{(\eta)} a_{\mathbf{k}}^{\dagger(\eta)} e^{-i(\mathbf{k} \cdot \mathbf{r})} \right\}, \quad (6)$$

$$\mathbf{b}(\mathbf{r}) = i \sum_{\mathbf{k}, \eta} \left(\frac{\hbar k}{2\epsilon_0 c V} \right)^{1/2} \left\{ \mathbf{b}_{\mathbf{k}}^{(\eta)} a_{\mathbf{k}}^{(\eta)} e^{i(\mathbf{k} \cdot \mathbf{r})} - \bar{\mathbf{b}}_{\mathbf{k}}^{(\eta)} a_{\mathbf{k}}^{\dagger(\eta)} e^{-i(\mathbf{k} \cdot \mathbf{r})} \right\}, \quad (7)$$

where $\mathbf{e}_{\mathbf{k}}^{(\eta)}$ and $\mathbf{b}_{\mathbf{k}}^{(\eta)}$ are the generalized electric and magnetic polarization unit vectors ($\bar{\mathbf{e}}_{\mathbf{k}}^{(\eta)}$ and $\bar{\mathbf{b}}_{\mathbf{k}}^{(\eta)}$ being their complex conjugate), respectively, V is an arbitrary quantization volume containing n photons, and $a_{\mathbf{k}}^{(\eta)}$, $a_{\mathbf{k}}^{\dagger(\eta)}$ are the photon annihilation and creation operators for a mode (\mathbf{k}, η) ; $\mathbf{e}_{\mathbf{k}}^{(\eta)}$, $\mathbf{b}_{\mathbf{k}}^{(\eta)}$ and \mathbf{k} are chosen to be a right-handed triad. The ladder operators act on the radiation states through the following: $a_{\mathbf{k}}^{(\eta)} |n_{\mathbf{k}, \eta}\rangle = n^{\frac{1}{2}} |(n-1)_{\mathbf{k}, \eta}\rangle$ and $a_{\mathbf{k}}^{\dagger(\eta)} |n_{\mathbf{k}, \eta}\rangle = (n+1)^{\frac{1}{2}} |(n+1)_{\mathbf{k}, \eta}\rangle$. Notwithstanding the use of a plane wave expansion in (6) and (7), any suitably complete basis set will suffice and deliver the same result.

The optical trapping potential energy will comprise an electric dipole–electric dipole ($E1$ – $E1$) term, which is the leading term, an electric dipole–electric quadrupole ($E1$ – $E2$) term and an electric dipole–magnetic dipole ($E1$ – $M1$) term, namely

$$\Delta E = \Delta E_{E1-E1} + \Delta E_{E1-E2} + \Delta E_{E1-M1} + \dots \text{h.o.t.}, \quad (8)$$

the explicit result for a chiral molecule is determined in section 5. Each term will have a position-dependence associated with the positional variation in optical field across a trapping beam. Ordinarily, only the $E1$ – $E1$ contribution is considered in calculation. However, small adjustments in the optical force may arise due to the $E1$ – $E2$ and $E1$ – $M1$ contributions. In fact, when quantifying the extent of chiral differentiation, the $E1$ – $E1$ contribution is null and the $E1$ – $E2$ and $E1$ – $M1$ contributions should provide the leading terms; this will be discussed using symmetry arguments in the next two sections.

4. Symmetry origins of chiral differentiation

In considerations of optical phenomena with the potential capacity to distinguish between chiral systems of opposite handedness, the key principles are readily elicited by fundamental symmetry arguments associated with the global operations of time reversal, T [44, 54]. Appeals to the latter have often been deployed in arguments over physical issues, for example, Kramers theorem [55] states that ‘the energy levels of an atom with an odd number of electrons, in the absence of an external magnetic field, are at least double degenerate as a consequence of time reversal invariance’. However, if the systems of interest are neutral molecules without any unpaired electrons (i.e. non-Kramer systems), and no static magnetic fields are present, then precisely the same time reversal arguments are drawn from considerations of spatial inversion, P . This rests on the fact that the quantum electrodynamical Hamiltonian, cast in multipolar

form, involves the radiation field only through its electric displacement field, \mathbf{d}^\perp , and magnetic induction field, \mathbf{b} . Accordingly, one can exploit to equal effect the opposite behaviours of these two fields under space inversion or time reversal: \mathbf{d}^\perp is time-even and space-odd, \mathbf{b} the converse.

As has been shown, the matrix element M_{FI} connecting any system (combined molecule and radiation) states directly furnishes a coupling energy contribution, if those two states are identical, or else, through quadratic deployment in the Fermi rule, a rate. In either capacity, M_{FI} has the physical dimensions and symmetry character of a scalar energy, necessarily of even parity under the operations of either P or T ; the former, spatial symmetry, case is the focus of the following. Since the basis states for perturbative calculations are the eigenstates of H_0 , i.e. the products of unperturbed molecular and radiation states, the matrix element to order n entails a series of terms (each signifying a different combination of electric and magnetic multipoles) that couple radiation and molecular tensors, \mathbf{S} and \mathbf{T} respectively, of equal rank $\geq n$ [56]

$$M_{\text{FI}} = \sum_{e=0}^n \sum_{m=n-e}^n \mathbf{S}_{e; m; n-e-m}^{(r)} \otimes \mathbf{T}_{e; m; n-e-m}^{(r)} \quad (9)$$

Here, each tensor is distinguished by the labels (e, m, q) corresponding to the number of $E1$, $M1$ and $E2$ interactions, respectively; the sum of which equals the number of interactions, n , while the rank is given by $r = e + m + 2q$. The radiation tensors are constructed as outer products of polarization-determined field vector components for each of the optical modes involved in the fundamental interaction, both ‘input’ and ‘output’ modes—and also any wave-vector components, once the dipole approximation is removed.

Let us denote $\{c_{\text{R}}\}$ as the helicity of all the relevant optical modes, essentially signifying a specified sense of circularity for each mode that is circularly or elliptically polarized. Correspondingly, $\{c_{\text{M}}\}$ can designate the stereoisomeric form of the chiral molecules involved—though the fundamental interactions in the present application involve only individual molecules. The result of performing space inversion on either component is denoted by an overbar. For each of the M_{FI} constituents cast in equation (9), the effects of space inversion as they apply either to the radiation and the matter together, or individually, are considered.

First, and trivially, it is verified that all observables remain unchanged under P , signifying for instance that the rates and energies associated with $\{c_{\text{R}}\}$ and $\{c_{\text{M}}\}$ are identical to those for $\{\bar{c}_{\text{R}}\}$ and $\{\bar{c}_{\text{M}}\}$. For example, the rate of absorption of left-handed circularly polarized light by one specific enantiomer of a chiral substance will equal the rate of absorption of right-handed light by the corresponding mirror-image enantiomer. Identifying the potential origins of chiral differentiation therefore rests upon considerations of how parity inversion affects $\{c_{\text{R}}\}$ and $\{c_{\text{M}}\}$ individually. For example, with a molecule of one specific enantiomeric form, one can experimentally invert the circularity of all the photons: the net effect is clearly different from parity inversion of the system as a whole. To identify terms that can support the sought chiral discrimination, one needs to invoke the parity signatures of the electric and magnetic fields—which are also, of course, those of the electric and magnetic multipole moments.

Gyrotropic processes [57] occur because parity is not a good quantum number for the wavefunctions and properties of chiral species. Accordingly, electronic transitions can occur between electronic states that are coupled by both even-parity and odd-parity multipoles. In circular dichroism, for example, the quadratic dependence of the rate equation on the matrix element M_{FI} leads to a sum of contributions including interferences between different terms.

Chiral molecules support real transitions, between electronic ground and excited states, that are both $E1$ and $M1$ allowed. The rate equation thus contains terms that are products of $\mathbf{T}(E1)$ and $\bar{\mathbf{T}}(M1)$, and also the corresponding complex conjugate product. Necessarily, these interference terms also contain the corresponding radiation tensor products $\mathbf{S}(E1)\bar{\mathbf{S}}(M1)$ and its conjugate, respectively, so that the overall rate contribution preserves parity. But changing the handedness of the radiation (but not the molecule), $\{c_R\} \rightarrow \{\bar{c}_R\}$, changes the sign of this (albeit relatively minor) contribution to the rate. This signifies that a given stereoisomer will display a differential absorption of left- and right-handed light.

A similar feature arises in light scattering, involving a second-order interaction. Here, virtual transitions couple the electronic ground state to other states, as in the conventional ($E1^2$) dynamic polarizability. Chiral molecules enable every coupling that is electric dipole allowed to be also magnetic dipole allowed, such that one of these forms of coupling may be associated with the incoming photon annihilation and the other with creation of the emergent photon. The $\mathbf{T}(E1M1)$ tensor accommodating this feature is formally of odd parity under P , and the corresponding $\mathbf{S}(E1M1)$ radiation tensor is also odd under P , so that the product of these two tensors preserves parity as an energy term should. But again, in consequence, reversing the handedness of the radiation (but not the molecule) changes the sign of this contribution to M_{FI} , signifying chiral differentiation. The manifestations of this feature are observed not only in the quadratic interference terms that arise in the light scattering rate equation (circular differential Rayleigh scattering), but also where they appear linearly, in the energy shift experienced by a chiral molecule in a circularly polarized beam.

Having established the general principles, we now return to the formulation of theory for a specific case, focusing on a chirally sensitive optical trap.

5. Forms of optical discrimination in the chiral system

As mentioned earlier, the photonic mechanism that describes optical trapping at the molecular level is forward-Rayleigh scattering, although it might also be understood semiclassically as a manifestation of a dynamic (ac) Stark effect. An optical trap involves an energy shift of the molecule (specifically, a position-dependent lowering of energy) on application of the irradiating beam, and the alternating electric field of the input radiation may be interpreted as producing a dynamic Stark shift to the ground state energy of the molecule. In quantum electrodynamical terms, however, such a shift (quadratically dependent on the electric field strength of the light) has to originate in the coupled annihilation and creation of identical photons, in exact correspondence with forward-Rayleigh scattering—namely, the concerted single absorption and single emission of photons with identical energy and wave-vector. In both representations, the irradiating laser beam delivers photons whose wavelengths are within the transparent region of the molecule and, hence, there is no net absorption—i.e. the laser beam emerges unaltered.

As stated in section 3, it is the $E1$ – $E1$ contribution that is the leading term and, ordinarily, this would be the sole consideration in optical trapping calculations. However, as has been shown using symmetry arguments in section 4, for optical trapping with circularly polarized light this term gives identical results for molecules of opposite handedness—whereas a differential response is elicited from the $E1$ – $E2$ and $E1$ – $M1$ contributions. Therefore, in the two photon–molecule couplings of forward-Rayleigh scattering, the mechanisms of key interest are

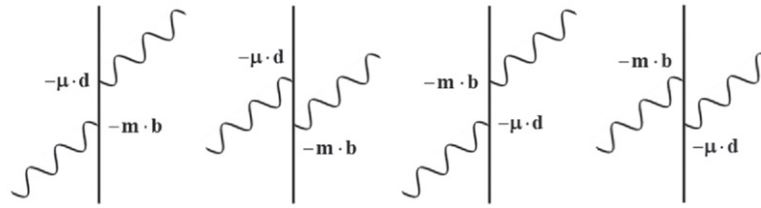


Figure 1. Feynman diagrams of forward-Rayleigh scattering mediated by a transition electric dipole ($-\boldsymbol{\mu} \cdot \mathbf{d}$) and magnetic dipole ($-\mathbf{m} \cdot \mathbf{b}$), namely the $E1$ – $M1$ contribution.

those where one coupling is mediated by a transition electric dipole and the other by a transition magnetic dipole or electric quadrupole. The $E1$ – $M1$ contribution is illustrated by the Feynman diagrams of figure 1; here the relevant term of equation (5) labels an interaction mediated by either the transition electric or magnetic dipole.

Closely related to optical trapping of a chiral molecule is optical rotation, which involves the rotation of plane polarized light on its passage through a liquid containing chiral molecules (*not*, to be clear, molecular rotation). The mechanism that describes optical rotation is also Rayleigh scattering, although the singly absorbed and emitted photons are no longer identical since the output polarization is, by definition, modified. As a result of this mechanistic similarity the equations that follow for optical trapping of a chiral molecule, and the optical discrimination effects that may arise, are intimately connected to those for optical rotation. Another closely related phenomenon is circular differential Rayleigh scattering, where the intensity of left and right circularly polarized incident light differ slightly following scattering from an optically active molecule [58–61]. In contrast, the process of circular dichroism (necessarily associated with the conveyance of momentum to the molecule) is completely unconnected and incongruent with an optical trapping force, despite suggested links [15]. Indeed, the common use of counterpropagating beams in optical trapping experiments is designed to prevent overall ‘downstream’ motion of the trapped particles through radiation pressure imparted by the linear momentum of absorbed (or scattered) photons [11].

Returning to equation (8), assuming a circularly polarized irradiating beam of either specific handedness, the explicit form of the potential energy for optical trapping of a chiral molecule is determined from equation (4) by insertion of the appropriate terms of (5)–(7), so that

$$\Delta E^{(L/R)} = \text{Re} \left\{ - \left(\frac{I}{2\epsilon_0 c^2} \right) \left(c \bar{e}_i^{(L/R)} e_j^{(L/R)} \right) \right. \\ \times \left(\alpha_{ij}(\omega) + ik_k (A_{ijk}(\omega) - A_{jik}(\omega)) \right) \\ \left. + \bar{e}_i^{(L/R)} b_j^{(L/R)} G_{ij}(\omega) + \bar{b}_i^{(L/R)} e_j^{(L/R)} \bar{G}_{ji}(\omega) \right\}, \quad (10)$$

in which a dependence on position \mathbf{r} is implicit in the beam irradiance I (given by $n\hbar c^2 k/V$). In equation (10), $\mathbf{e}^{(L/R)}$ and $\mathbf{b}^{(L/R)}$ are the circular polarization of the electric and magnetic field, respectively,—which is either left- or right-handed as denoted by the superscript—and $\alpha_{ij}(\omega)$ is the polarizability tensor; \mathbf{k} is the wavevector of the input beam. It is noteworthy to state that an identical expression to equation (10) is found for plane polarized light, except that the linear

equivalent of the circular polarization vectors are employed. The frequency-dependent tensors $G_{ij}(\omega)$ and $A_{ijk}(\omega)$ are an electric-magnetic dipolar scattering tensor and an electric dipolar–quadrupolar analogue, both of which arise in optical rotation expressions but not circular dichroism [45]. The former tensor has the same physical connotation as the complex mixed electric–magnetic dipole polarizability χ deployed in semiclassical theory [62]. With the inclusion of the resonance damping to be considered below, these two tensors are explicitly given by

$$G_{ij}(\omega) = \sum_r \left\{ \frac{\mu_i^{0r} m_j^{r0}}{E_{r0} - \hbar\omega - i\hbar c\gamma_r} + \frac{m_j^{0r} \mu_i^{r0}}{E_{r0} + \hbar\omega \pm i\hbar c\gamma_r} \right\}, \quad (11)$$

$$A_{ijk}(\omega) = \sum_r \left\{ \frac{\mu_i^{0r} Q_{jk}^{r0}}{E_{r0} - \hbar\omega - i\hbar c\gamma_r} + \frac{Q_{jk}^{0r} \mu_i^{r0}}{E_{r0} + \hbar\omega \pm i\hbar c\gamma_r} \right\}, \quad (12)$$

where μ_i^{ba} and m_i^{ba} are components of the transition electric and magnetic dipoles, for the transition $b \leftarrow a$ respectively, and Q_{ij}^{ba} are components of the electric quadrupolar moment; $E_{r0} = E_r - E_0$ is the energy difference between the intermediate and ground state, $\hbar\omega$ is the energy of the input photon.

The damping factor γ_r introduced in the above equations is associated with a Lorentzian lineshape with a full width at half-maximum linewidth of $2\gamma_r$. It represents the consequences of spectral damping due to features including the manifold of vibrational states within an electronic excited state and the finite lifetime of such an electronic state. The inclusion of the damping correction in the denominator of $G_{ij}(\omega)$ and $A_{ijk}(\omega)$ is essentially pragmatic and phenomenological [63]: its exclusion from some standard texts reflects the fact that such damping is not strictly rigorous, since it effectively compromises the time-reversal invariance of the even-parity system Hamiltonian, thereby introducing a non-Hermitian character and a sign ambiguity. In the first term of equations (11) and (12) the negative sign on the damping correction is indisputable, and leads to the Lorentzian lineshape. In contrast, a number of opinions have arisen on the sign for the correction in the second term [64–66], although physically the results of different choices cannot be experimentally differentiated. For this reason, the sign on the damping correction in equations (11) and (12) is left unspecified. Prominent chiral effects in surface second harmonic generation [67–70] are one example of the physically observed consequences that can emerge from an approach to resonance conditions, where damping effects become most relevant. Nonetheless, over wavelength regions that are remote from resonance, time-reversal arguments still retain value as guides to the key terms in a quantum amplitude, capable of generating a chirality-specific optical response.

On examination of equation (10) it is clear that the dipolar-quadrupolar terms are null for cases where the input beam is within the transparent region of the molecule, since $A_{ijk}(\omega)$ and $A_{jik}(\omega)$ then become essentially real quantities; these terms are, therefore, no longer considered here, since their role could only be significant under circumstances within the range of an absorption band where real (energy-conserving) electronic transitions occur. To determine an expression for optical discrimination, i.e. the difference in potential energy for left-handed compared to right-handed circular polarization, the identities $\mathbf{b}^{(L/R)} = \mp i\mathbf{e}^{(L/R)}$ and $\bar{e}_i^{(L)} e_j^{(L)} - \bar{e}_i^{(R)} e_j^{(R)} = i\epsilon_{ijm} \hat{k}_k$ are employed, so that equation (10) is recast as

$$\begin{aligned} \Delta E^{(L)} - \Delta E^{(R)} = & i \left(\frac{I}{2\epsilon_0 c^2} \right) \left(\bar{e}_i^{(L)} e_j^{(L)} + \bar{e}_i^{(R)} e_j^{(R)} \right) \\ & \times \left(G_{ij}(\omega) - \bar{G}_{ji}(\omega) \right), \end{aligned} \quad (13)$$

where $G_{ij}(\omega)$ and $\bar{G}_{ji}(\omega)$ are imaginary quantities. It should be noted that situations where the input photon is left-handed circularly polarized and the output is right-handed polarized (or vice versa) are not included since the initial and final states are not identical and, therefore, those cases should be considered as processes. Moreover, the term related to the polarizability has also been omitted since it is not discriminatory; this is the term usually related to conventional optical trapping, i.e. the $-\alpha\mathcal{E}^2$ term [10] which, as has been shown in the previous section, is irrelevant in studies of chiral discrimination. This lack of chiral sensitivity is further reinforced by the fact that field helicity is identified with $n_L - n_R$ (i.e. the number of photons with left-handed polarization minus number of right-handed photons) [56, 71] and, therefore, chirality effects are null for plane polarized light since $n_L = n_R$ in such a situation.

The analysis up to this point centres on the principle that discrimination arises when a single enantiomer is irradiated with left-handed electromagnetic radiation compared to right-handed light. It is important to note that the same results form a basis for differentiation when a single circular polarization is applied to a left-handed chiral molecule relative to the right-handed enantiomer. (The reason is clear: one case—say left-handed light and a right-handed molecule—converts under space inversion to a system that must generate the same result—here, right-handed radiation and a left-handed molecule.) The latter scenario is significant in connection with the optical response of a mixture of enantiomers, as is often produced in synthetic chemistry. We shall exploit this equivalence when we return to a potential application of this principle in section 7.

6. Isotropic and partially oriented systems

Whilst the previous results have thus far been developed and defined for rigidly oriented systems, expressions can be constructed from them for systems such as liquids or solutions with bulk isotropy—in which individual molecules are free to tumble in the laboratory frame—or partially oriented systems, such as might typically be produced through the action of a static field. A rotational average corresponding to such situations is always performed on the observable: it cannot be executed on individual transition moments. It is important to recognize that, even in commonly isotropic media such as liquids and solutions, isotropy does not extend to the molecular scale at which scattering and other optical phenomena occur. The theory of all such phenomena, crucially including chiral response, has to be cast in a form that accommodates the molecular anisotropy. For example, the $\alpha_{ij}(\omega)$ and $G_{ij}(\omega)$ tensors are characterized not simply by a single scalar, but by a tensor with off-diagonal as well as diagonal elements—in the latter case all nine Cartesian components are independent and may be different.

The bulk isotropy of a free fluid is represented by applying an isotropic rotational average, in which each molecule is decoupled from the space-fixed frame into its own frame (a detailed description is found elsewhere [72]), equation (13) becomes

$$\begin{aligned}
\text{isotropic case: } \langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle &= i \left(\frac{I}{2\epsilon_0 c^2} \right) (\bar{e}_i^{(L)} e_j^{(L)} + \bar{e}_i^{(R)} e_j^{(R)}) \\
&\quad \times (G_{\lambda\mu}(\omega) - \bar{G}_{\lambda\mu}(\omega)) I_{ij\lambda\mu}^{(2)} \\
&= - \left(\frac{2I}{3\epsilon_0 c^2} \right) \text{Im} [G_{\lambda\lambda}(\omega)], \tag{14}
\end{aligned}$$

as a result of the relation $\bar{G}_{\lambda\lambda}(\omega) \equiv -G_{\lambda\lambda}(\omega)$. Here, $I_{ij\lambda\mu}^{(2)}$ denotes a second-rank rotational average, equating to $(1/3)\delta_{ij}\delta_{\lambda\mu}$, where the indices i, j denote components referring to the molecular frame and λ, μ , the laboratory frame. The term in square brackets of equation (14) is a trace of the $G_{ij}(\omega)$ tensor, precisely the parameter involved in optical rotation [45].

Consideration of a partial orientation of the molecules with a static electric field, \mathbf{E}_0 , is achieved through use of a weighting factor $-\boldsymbol{\mu}^{00} \cdot \mathbf{E}_0$, where $\boldsymbol{\mu}^{00}$ is a static electric dipole, within the Boltzmann factor $\exp(\boldsymbol{\mu}^{00} \cdot \mathbf{E}_0/k_B T)$. A rotational average of this type [73] is applied to equation (13) using the following expression

$$\langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle = - \left(\frac{I}{\epsilon_0 c^2} \right) \text{Im} \left[G_{\lambda\lambda}(\omega) - \frac{\left\langle \hat{k}_i \hat{k}_j G_{ij}(\omega) e^{\frac{\boldsymbol{\mu}^{00} \cdot \mathbf{E}_0}{k_B T}} \right\rangle}{\left\langle e^{\frac{\boldsymbol{\mu}^{00} \cdot \mathbf{E}_0}{k_B T}} \right\rangle} \right], \tag{15}$$

where the identity $\bar{e}_i^{(L)} e_j^{(L)} + \bar{e}_i^{(R)} e_j^{(R)} \equiv \delta_{ij} - \hat{k}_i \hat{k}_j$ has been employed. On completion of the Boltzmann-weighted average on equation (15) the following expression is found

with static field orientation:

$$\begin{aligned}
\langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle &= - \left(\frac{I}{\epsilon_0 c^2} \right) \left\{ \frac{2}{3} \text{Im} [G_{\lambda\lambda}(\omega)] + \left(1 - \frac{3}{x} \coth(x) + \frac{3}{x^2} \right) \right. \\
&\quad \times P_2(\cos \theta) \text{Im} \left[G_{\lambda\mu}(\omega) \hat{\mu}_\lambda^{00} \hat{\mu}_\mu^{00} - \frac{1}{3} G_{\lambda\lambda}(\omega) \right] \left. \right\}, \tag{16}
\end{aligned}$$

where $x = \boldsymbol{\mu}^{00} \cdot \mathbf{E}_0/k_B T$ and $P_2(\cos \theta)$ is a Legendre polynomial, in which θ denotes the angle between $\hat{\mathbf{E}}_0$ and $\hat{\mathbf{k}}$. Examining equation (16), it is determined that the optimal value of θ for observation of optical discrimination is the ‘magic angle’, $\arccos(1/\sqrt{3})$. For fields whose effect is small compared to the forces of thermal redistribution, i.e. $x \ll 1$, a Taylor series of the coth function in (16) is appropriate, and the following simplified result emerges

weak alignment:

$$\begin{aligned}
\langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle &\simeq - \left(\frac{I}{3\epsilon_0 c^2} \right) \left\{ 2 \text{Im} [G_{\lambda\lambda}(\omega)] + \frac{1}{5} \left(\frac{\boldsymbol{\mu}^{00} \cdot \mathbf{E}_0}{k_B T} \right)^2 P_2(\cos \theta) \right. \\
&\quad \times \text{Im} \left[G_{\lambda\mu}(\omega) \hat{\mu}_\lambda^{00} \hat{\mu}_\mu^{00} - \frac{1}{3} G_{\lambda\lambda}(\omega) \right] \left. \right\}. \tag{17}
\end{aligned}$$

From this expression the isotropic case of equation (14) is easily recovered and corresponds to situations, for example at very high temperatures, when the static electric field has no influence (i.e. $x \rightarrow 0$). At the other extreme of strong molecular alignment with the field ($x \gg 1$), the following is obtained

strong alignment:

$$\begin{aligned} \langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle \simeq & - \left(\frac{I}{\epsilon_0 c^2} \right) \left\{ \frac{2}{3} \operatorname{Im} [G_{\lambda\lambda}(\omega)] + P_2(\cos \theta) \right. \\ & \left. \times \operatorname{Im} \left[G_{\lambda\mu}(\omega) \hat{\mu}_\lambda^{00} \hat{\mu}_\mu^{00} - \frac{1}{3} G_{\lambda\lambda}(\omega) \right] \right\}. \end{aligned} \quad (18)$$

On the assumption that the electric field is applied in the z -direction, so that $G_{\lambda\lambda}(\omega)$ is dominated by its zz -component, equation (18) simplifies to

$$\text{strong alignment: } \langle \Delta E^{(L)} \rangle - \langle \Delta E^{(R)} \rangle \simeq - \left(\frac{I}{3\epsilon_0 c^2} \right) (1 + 3 \cos^2 \theta) \operatorname{Im} [G_{zz}(\omega)]. \quad (19)$$

It is interesting to observe that to some extent similar effects might also be produced through dynamic interactions with an optical beam (i.e. through $-\alpha \mathcal{E}^2$)—including the beam directly used to create the optical trap. The corresponding theory involves a much more complicated form of rotational averaging [74] and it is a topic we shall analyse in detail in another article in preparation.

7. Discussion

We shall conclude with an assessment of the quantitative measures and practicality of achieving enantiomeric separation based on forces associated with light scattering. Before doing so, it is interesting to compare the present analysis with other recently proposed optical methods for enantiomeric separation. For example, it has been shown experimentally practicable to effect the optomechanical separation of chiral microparticles of opposite handedness using chiral light fields, through the differential absorption of circularly polarized light [18]. Nonetheless, downscaling into molecular dimensions remains elusive. Although circular Bragg reflection [75] has been suggested as the possible basis for an experimental system, extensive complications due to thermal effects have been identified. Another potential setup has been described in theoretical work by Cameron *et al*, based on light scattering by chiral molecules subjected to overlapping beams of orthogonal linear polarization [16, 17]. The proposal is that such a system might be deployed as a discriminatory chiral diffraction grating. Viewed from a photonic perspective, however, it is notable that the mechanism seems not to satisfy the precepts presented in section 2. Any contributory scattering process has to involve the annihilation of a photon at one wavevector and creation of a photon at another (or else, two beams would not be required): therefore, since the initial and final states are typically not identical, energies and forces ought not to arise from necessarily off-diagonal matrix elements. One might consider as a possible exception a four-wave mixing case involving the paired annihilation and re-creation of photons from two crossed beams. However, on symmetry grounds, it becomes evident that no discriminatory effects can be supported by such a scenario.

The present analysis lays a solid ground, established in section 6, for determining specific conditions for the optical separation of enantiomers, using an optical trapping force. In principle one might consider the gas phase an ideal environment, to offset problems with local thermal agitation. However, for applications where the main prospective interest lies—namely to molecules of biological or pharmaceutical relevance—the typically large molecular size (mostly molecular masses well in excess of 0.2 kDa) means that vapour pressures will be small except at temperatures sufficiently high to produce thermal degradation and decomposition. Here, the scale of separation per passage across a laser beam focus suggests the need for repeated cycling of the mixture, akin to the early laser methods used in isotope separation. The scale of operation, given the necessarily extremely low levels of molecular throughput, would render any such scheme not remotely economic. Clearly, one has to confine attention to liquid or solution phase applications.

On examination of the isotropic liquid case from equation (14), using a typical value of 10^{12} W m^{-2} for the irradiance (at the focus of a modest intensity CW laser beam), and assuming molecular dimensions in the 10 nm range, the optical force for enantiomer separation is estimated to be $\sim 2 \times 10^{-16} \text{ N}$. This can be compared to the thermodynamic force associated with the diffusion-limited behaviour of molecules against a concentration gradient, in the absence of an applied electric field. Using Fick's first law of diffusion [76], it transpires that a force of this scale should be capable of sustaining a gradient of $\sim 6\%$ in the differential concentrations ($\Delta C/C$) of enantiomers with opposite handedness. This promising result has to be viewed in its context of a concentration difference that extends only across the small radial extent of the focused laser beam, perhaps a few cubic microns in total. However, the concentration figure could be significantly increased by, for example, exploiting pre-resonance enhancement of the \mathbf{G} tensor by the use of laser wavelengths in the outer span of an optical absorption band.

The method we have described, as well as the others cited by way of comparison, clearly suffer severe limitations on throughput, likely to render commercial application economically impractical. None appears to offer new methodologies that are genuinely viable to meet the aspirations of the pharmaceutical and allied industries, for new methods of separating enantiomers. However, ongoing studies in this area are undoubtedly revealing new kinds of chiroptical mechanism of fundamental interest, prompting further investigations in this renaissance of interest in molecular chirality.

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