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Role of magnetic and diamagnetic interactions in molecular optics and scattering

Kayn A. Forbes[*]
School of Chemistry, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, United Kingdom

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This paper aims to explicitly clarify the role and interpretation of diamagnetic interactions between molecules and light in quantum electrodynamics. In contrast to their electric and magnetic counterparts, the diamagnetic couplings between light and matter have received relatively little interest in the field of molecular optics. This intriguing disregard of an interaction term is puzzling. The diamagnetic couplings possess unique physical properties that warrant their inclusion in any multiphoton process, and the lack of gauge invariance for paramagnetic and diamagnetic susceptibilities necessitates their inclusion. Their role and importance within nonrelativistic molecular quantum electrodynamics in the Coulomb gauge is illuminated, and it is highlighted how for any multiphoton process their inclusion should be implicit. As an indicative example of the theory presented, the diamagnetic contributions to both forward and nonforward Rayleigh scattering are derived and put into context alongside the electric and magnetic molecular responses. The work represents clarification of diamagnetic couplings in molecular quantum electrodynamics, which subsequently should proffer the study of diamagnetic interactions in molecular optics due to their unique physical attributes and necessary inclusion in multiphoton processes.

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I. INTRODUCTION

Electromagnetic interactions with matter permeate throughout the natural sciences, ranging from being responsible for a plethora of biological processes, such as vision and photosynthesis [1,2], to the van der Waals interactions that give rise to intermolecular forces [3,4]. Contemporary utilization includes the burgeoning fields of photonics [5] and plasmonics [6,7]. Light-matter interactions pervade virtually all of science to most of our daily lives, and their importance cannot be overemphasized.

It can therefore be argued that being able to understand the underlying physical mechanisms behind these interactions, and the subsequent manipulation and exploitation, is paramount. The problematic issues of studying light-matter interactions using classical methods is well known, the discrete nature of molecular transitions being incompatible with the theory of light acting as a wave. One of the most obvious examples of this failure of classical methods is the explanation of spontaneous emission [8]. The logical step to apply to this semiclassical theory, where the material component of the light-matter system is quantized, but the radiation field is not, is to use a fully quantized theory of the electrodynamics. The most suitable theoretical framework to account for light-matter interactions is therefore quantum electrodynamics (QED) [9]. In contrast to its semiclassical predecessor, in QED not only is the material part of the total system subjected to the postulates of quantum mechanics, but the electromagnetic field and its interaction with the matter is also quantized [8]. This quantization process leads to the concept of the photon [10], so prevalent in science that a multitude of research fields hinges upon its existence [5]. Justification of adopting the theory is straightforward as not only has it proven remarkably adept at giving pronounced physical insight and unrivaled precision in matching experimental data [11–13], it sits at the forefront of being able to predict and explain certain physical phenomena [14], and in specific cases it appears to have no rival in this regard [15,16].

The work presented herein is concerned with the electromagnetism of molecules, and as such the most suitable theory to adopt is molecular quantum electrodynamics (MQED) [9]. In this theory, the coupling of photons with charged particles is derived in a noncovariant formulation because the nuclei and outer electrons of atoms and molecules are of low energy, and therefore a nonrelativistic approach leads to convenient methods for calculating photon-molecule interactions. The Hamiltonian used to describe the electrodynamics is cast in a form that couples the fundamental electric and magnetic fields to the molecule's electric polarization, magnetization, and diamagnetization fields. It is the latter two of these interactions between the molecules and the electromagnetic field with which this paper is concerned. Recent work [17] has identified that the less-well known diamagnetic couplings to the radiation field lead to interesting and unique characteristics to optical rates in nonlinear and scattering processes. This insight invites an appraisal and clarification of diamagnetic interactions in molecular optics: they are either unknown or not fully understood.

The aim of this work is to establish the physically unique diamagnetic coupling between molecules and photons. When studying magnetic interactions in molecular optics their inclusion is necessary if one is to calculate gauge-invariant optical rates and energy shifts that depend on the total magnetic susceptibility. The work also provides further evidence of the efficacy of the Power-Zienau-Woolley (PZW) Hamiltonian

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[*] k.forbes@uea.ac.uk

in molecular optics [18], explicitly showing that the theory accounts for even the more subtle aspects of electromagnetic-molecule interactions. The paper begins with an outline of the general MQED theory, PZW Hamiltonian, and diamagnetic couplings; this is followed by a discussion of molecular susceptibility tensors; and finally the total magnetic contributions to both forward and nonforward Rayleigh scattering are derived, explicitly highlighting the diamagnetic coupling.

II. THEORY

A. Quantum electrodynamics

To describe the coupling between photons and molecules, we start with the multipolar PZW interaction Hamiltonian [19–26].

$$\begin{aligned} H_{\mathrm{int}} = \sum_{\xi} \big[&-\varepsilon_0^{-1} \boldsymbol{\mu}(\xi)\cdot \boldsymbol{d}^{\perp}(\boldsymbol{R}_{\xi}) - \varepsilon_0^{-1} Q_{ij}(\xi)\nabla_j d_i^{\perp}(\boldsymbol{R}_{\xi}) \\ &- \boldsymbol{m}(\xi)\cdot \boldsymbol{b}(\boldsymbol{R}_{\xi})\big] \\ &+ \frac{e^2}{8m}\sum_{\xi,\alpha}[(\boldsymbol{q}_{\alpha}(\xi) - \boldsymbol{R}_{\xi})\times \boldsymbol{b}(\boldsymbol{R}_{\xi})]^2 + \dots, \end{aligned} \tag{1}$$

where for a molecule ξ positioned at $\boldsymbol{R}_{\xi}$, $\boldsymbol{\mu}$ is the electric dipole moment operator; $\boldsymbol{Q}$ is the electric quadrupole moment operator; $\boldsymbol{m}$ is the magnetic dipole moment operator; the final term in (1) is the leading-order diamagnetic interaction term: D1 term. In (1), $\boldsymbol{q}_{\alpha}(\xi)$ is the position vector of an electron α possessing a charge $-e$ and mass m. The first term in (1) is the E1 coupling, the second is the E2, and the third is the M1; $\boldsymbol{d}^{\perp}(\boldsymbol{R}_{\xi})$ is the electric displacement field and $\boldsymbol{b}(\boldsymbol{R}_{\xi})$ is the magnetic field, whose vacuum mode expansions are given as

$$\begin{aligned} \boldsymbol{d}^{\perp}(\boldsymbol{r}) = i\sum_{\boldsymbol{k},\eta}\left(\frac{\hbar c k \varepsilon_0}{2V}\right)^{1/2} \\ \times [\boldsymbol{e}^{(\eta)}(\boldsymbol{k})a^{(\eta)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{e}}^{(\eta)}(\boldsymbol{k})a^{\dagger(\eta)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}], \end{aligned} \tag{2}$$

and

$$\begin{aligned} \boldsymbol{b}(\boldsymbol{r}) = i\sum_{\boldsymbol{k},\eta}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} \\ \times [\boldsymbol{b}^{(\eta)}(\boldsymbol{k})a^{(\eta)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{b}}^{(\eta)}(\boldsymbol{k})a^{\dagger(\eta)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}], \end{aligned} \tag{3}$$

respectively. In (3), $\boldsymbol{e}^{(\eta)}(\boldsymbol{k})$ and $\boldsymbol{b}^{(\eta)}(\boldsymbol{k})$ are the generalized electric and magnetic polarization unit vectors, respectively, and V is an arbitrary quantization volume defined as containing n number of photons; for a photon in a mode $(\eta,\boldsymbol{k})$, where η designates the polarization state and $\boldsymbol{k}$ the wave vector, $a^{(\eta)}(\boldsymbol{k})$ and $a^{\dagger(\eta)}(\boldsymbol{k})$ are photon annihilation and creation operators, respectively.

This fully quantized Hamiltonian provides distinct advantages over other frameworks, such as the well-known minimal coupling method, due to being cast in transverse electromagnetic fields which directly couple to matter through the electric polarization, magnetization, and diamagnetization fields [9,27]. Since there are no terms in (1) dependent on the electromagnetic scalar and vector potentials, the Hamiltonian is independent of gauge; the coupling due to transverse electromagnetic fields gives interactions between molecules through the exchange of transverse photons propagating with speed c, and as such the Hamiltonian gives fully retarded results. There is also no separate term accounting for the intermolecular Coulomb interactions, as these are fully accounted for through the exchange of transverse photons. The multipolar Hamiltonian and minimal coupling Hamiltonian are related by a canonical transformation [18], and for any optical processes or phenomena that conserve the energy of the total system (i.e., on the energy shell) they give the exact same quantum amplitude. However, describing interactions between photons and molecules is best suited to working within the Coulomb gauge, and dealing with retardation in this gauge with the minimal coupling Hamiltonian is laborious and cumbersome. For this reason, and the others stated above, the multipolar Hamiltonian offers distinct advantages in MQED.

It is worth emphasizing that the mode expansions in (2) and (3) are cast in their vacuum forms, where the quantum field description applies only to the molecule that is directly interacting with the photons, and no other matter is present. However, in general, interacting molecules are surrounded by other atoms and molecules, whose electronic properties modify the fields experienced and produced by the interacting optical center of interest. In the quantum electrodynamical theory, the influence of the surrounding medium is naturally accommodated for within the field operators $\boldsymbol{d}^{\perp}$ and $\boldsymbol{b}$ [28–31]. This is in contrast to the semiclassical formalism, where material-induced field corrections are accommodated for within the macroscopic susceptibilities in an *ad hoc* approach [32]. Through a rigorous theory describing QED couplings in terms of polaritons, the modifications of the electromagnetic fields in the condensed phase due to refractive and dissipative effects are explicitly taken account of.

Similarly, the issue of the small radiative damping forces is easily accounted for within MQED [33,34]. This is an important aspect when dealing with scattering processes due to the problematic infinities in the molecular response tensors when approaching resonance frequencies. In an analogous manner to the classical theory of harmonic oscillators, a finite energy width of the excited electronic states of the molecule can be incorporated into the theory, thus allowing a finite lifetime. In this work we will persist with the vacuum formulation, neglecting both media and radiative damping corrections on the basis that the key physics of the work presented is not altered by their presence, and they can easily be accounted for within the theory.

Being derived in a nonrelativistic framework, the PZW Hamiltonian does not account for relativistic spin. This leads to a Hamiltonian (1) without a spin Hamiltonian for the electron. Of course, the addition of the so-called Pauli term can be accounted for in a phenomenological manner, allowing for the temperature-dependent spin-paramagnetic susceptibility to be accommodated for in molecules possessing unpaired electrons [35]. However, in general, nonrelativistic Hamiltonians cannot accurately model atoms and molecules possessing a degree of spin [36]. In this work we are clearly confined to the nonrelativistic limit by enacting the PZW Hamiltonian, dealing with coupling energies between the molecules and radiation that are much weaker than the Coulombic binding energies, and to maintain the scope originally laid out we apply the theory to molecules with zero spin.

The method of QED theory to be implemented in this work is often termed "diagrammatic perturbation theory": the optical rates and energy shifts of processes being calculated with the aid of time-ordered Feynman diagrams [37,38]. Another key point is that all time dependence is contained within the states of the system, the operators being time-independent: the representation of quantum mechanics more formally known as the Schrödinger picture [39]. There does exist, however, another formulation of QED—-the field-theoretic approach—-cast in terms of the Heisenberg picture, where the states are fixed in time, but the dynamical variables represented as operators are dependent on time [40–47]. To this point, it is worth stating that both theories are related to one another through a suitable unitary transformation, and of interest to us here is the fact that the field-theoretic viewpoint pays full heed to diamagnetic interactions. As such, one may choose either method to study and illuminate diamagnetic couplings in light-matter interactions; however, we will proceed with adopting the Schrödinger method as it leads to simpler equations that will help to make clearer the role of diamagnetic couplings.

Although the distinct and clear advantages of the multipolar Hamiltonian have been put forward, there still appears to be confusion over some of the more subtle aspects of it: namely the diamagnetic term and its application in the theory of MQED. It is borne out at the same order of interaction as the commonly studied magnetic M1 and quadrupole E2 interactions, and possesses a unique quadratic dependence on electric charge and magnetic field. It is therefore puzzling as to why it has received relatively little interest, and the legitimacy of its inclusion in any multiphoton processes will now be outlined.

B. Diamagnetic interactions

The physical significance of the diamagnetic term has its origins in correctly accounting for the overall magnetic susceptibility response of a molecule. The magnetic susceptibility is a gauge-invariant property that manifests itself in two-photon interactions and is always experimentally measurable. The total magnetic susceptibility can be partitioned into two distinct contributions: the paramagnetic and the diamagnetic [48–50]. The diamagnetic susceptibility, as well as the paramagnetic susceptibility, are not independent of the gauge, and therefore such compartmentalization has little meaning in a general sense. However, in the Coulomb gauge they are legitimately separable physical quantities, so long as it is understood that only when they are combined do they give useful gauge-invariant physical predictions. This is the main reason why diamagnetic couplings should always be included in multiphoton processes.

At the lowest-order diamagnetic D1 and magnetic dipole coupling M1 for two-photon processes, we produce the leading terms to the diamagnetic susceptibilities and paramagnetic susceptibilities. The Dn and Mn couplings, where $n > 2$, give rise to higher-order corrections to these susceptibilities, but are so small in magnitude they warrant very little motivation for their inclusion.

Once computed, the D1 and M1M1 terms are combined to give the overall magnetic-interaction contribution to the specified optical process. If the D1 contribution is larger than the M1M1, then the molecule is said to be diamagnetic: the other way around, then it is paramagnetic. The vast majority of molecules are diamagnetic and therein lies another reason that in molecular QED it is extremely important to include the diamagnetic couplings terms. Indeed, it has been shown that a particular example where diamagnetic couplings become important and prominent is in the Casimir-Polder dispersion forces between ground-state molecules [51,52]. However, for molecules that possesses a nonzero spin, the spin-paramagnetic behavior can dominate the overall magnetic susceptibility—-of course, the diamagnetic contributions still require accounting for [53].

C. Molecular response tensors

A molecule exposed to external electromagnetic fields, both static and dynamic, will respond through its molecular susceptibilities (or response tensors), acquiring electric and magnetic multipole moments in the process [54]. When the electromagnetic field disrupts a charge distribution, electric multipole moments are acquired; perturbation of current distributions produces magnetic multipole moments. The external fields can either be in the form of free radiation as produced by a laser, for example, or when considering intermolecular interactions, another molecule [26]. Static response tensors are derived through time-independent perturbation theory, due to static electric and magnetic fields. However, for oscillating radiation fields which vary with time, the corresponding time-dependent theory yields dynamic polarizabilities, which are dependent on the external field frequency. When the frequency of the external field tends to zero, the static result is recovered. In QED, an electrodynamical theory, the dynamic molecular susceptibilities fall out of the theory naturally.

Using standard perturbation techniques, the quantum amplitude M_{fi} for any optical processes or phenomenon can be calculated with the aid of H_{int}:

$$M_{fi} = \langle f|H_{\mathrm{int}}|i\rangle + \sum_r \frac{\langle f|H_{\mathrm{int}}|r\rangle\langle r|H_{\mathrm{int}}|i\rangle}{E_i - E_r} + \dots . \qquad (4)$$

In (4) the first term relates to processes that are first-order in H_{int}; these include single-photon absorption and emission of which diamagnetic interactions do not contribute, nor do they directly depend on the molecular susceptibilities. The second term corresponds to two-photon interaction processes, which do depend on molecular susceptibilities. The molecular response tensors can be seen to come from the transition moment operators in (1)—$\boldsymbol{\mu}(\xi)$ for example—-acting upon the energy states of the molecule $|E_i(\xi)\rangle$. As a relevant example, in the dipole approximation, for any two photons "a" and "b" involved in an optical process the molecular susceptibility is defined as

$$\Theta_{ij}^{fi}(\pm\omega_a, \pm\omega_b) = \sum_r \left\{ \frac{\tau_i^{fr}\tau_j^{ri}}{E_{ri} \mp \hbar\omega_a} + \frac{\tau_j^{fr}\tau_i^{ri}}{E_{ri} \mp \hbar\omega_b} \right\}, \qquad (5)$$

where τ_i^{ri} represents either the electric or magnetic transition dipole moment, and dependent on what transition moments are calculated, $\Theta_{ij}^{fi}(\pm\omega_a, \pm\omega_b)$ represents the frequency-dependent molecular susceptibility: it would be the well-known polarizability tensor $\alpha_{ij}^{fi}(\pm\omega_a,\pm\omega_b)$ if τ_i^{ri} were electric dipole transition moments; the orbital paramagnetic susceptibility tensor $\chi_{ij}^{fi}(\pm\omega_a,\pm\omega_b)$ for magnetic dipole transition moments; and a mixture of electric and magnetic dipole transition moments yields the mixed electric-magnetic susceptibility tensor $G_{ij}^{fi}(\pm\omega_a,\pm\omega_b)$, important in chiroptical interactions [55,56].

D. Magnetic susceptibility

As discussed, the total magnetic susceptibility χ_{tot} is a combination of both diamagnetic and paramagnetic contributions:

$$\chi_{\text{tot}} = \underbrace{\chi_{\text{dia}} + \chi_{\text{para}}}_{\text{orbital}} + \underbrace{\chi_{\text{para}}}_{\text{spin}}, \qquad (6)$$

where the first two terms are the orbital contributions to the diamagnetic and paramagnetic susceptibilities, both of which are derived in MQED through the method outlined above. All molecules, regardless of their spin state, possess both orbital contributions to their magnetic susceptibility. The final term is the already-discussed relativistic spin-paramagnetic susceptibility, applicable only for molecules with spin, with which we are not concerned. The spin-paramagnetic susceptibility is a temperature-dependent quantity, whereas the orbital-paramagnetic term is not—-which is why it is sometimes called the temperature-independent paramagnetic susceptibility (TIP susceptibility) [57,58]. Furthermore, it is worth mentioning at this stage that the orbital paramagnetic susceptibility is alternatively known as the “high-frequency” term. This comes from the fact that, as can be seen from (5), when the incident radiation is of a similar frequency to that of the molecular transition, preresonance enhancement leads to the TIP susceptibility taking on a large value. This ability to tune the input beam into a preresonance frequency is well exploited in laser optics, where optical rates and energy shifts depend on molecular response tensors. However, of interest to us here is the unique property that diamagnetic interactions offer no such preresonance enhancement as there forms do not possess a frequency dependence: this characteristic will be explicitly highlighted in the proceeding sections.

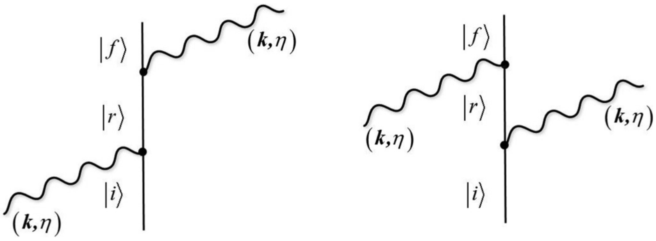

FIG. 1. Two topologically distinct time-ordered Feynman graphs representing the scattering of an incident photon into an output photon of the same mode $(\boldsymbol{k},\eta)$. For nonforward scattering the output mode $(\boldsymbol{k}',\eta')$ is not equal to that of the input $(\boldsymbol{k},\eta)$.

III. RAYLEIGH SCATTERING

A. Forward Rayleigh scattering

To provide a demonstration of the theory outlined in the previous section, we apply the QED calculation procedure to the process of forward Rayleigh scattering. Optical trapping is one of the most important tools in the field of optomechanical forces and particle manipulation [59–61]. It allows the control and maneuvering of particles using the noncontact forces produced by intense laser beams. Indeed, recent theoretical and experimental studies have looked at utilizing discriminatory trapping forces to separate chiral molecules as an alternative to the standard chemical methods used to resolve enantiomers [62]. The mechanism of optical trapping is built from two distinct photon-molecule interactions: one-photon absorption (gradient force) and forward Rayleigh scattering (scattering force). As stated, in one-photon absorption forces there is no diamagnetic contributions, so we restrict our interest to the scattering force.

We begin by computing the purely magnetic dipole contribution. As a two-photon scattering process (Fig. 1), it can be designated by the shorthand notation M1M1. In forward Rayleigh scattering, the initial and final states of the system are identical: $|i\rangle = |f\rangle = |E_0; n(\boldsymbol{k},\eta)\rangle$. Therefore, second-order time-dependent perturbation theory is required, with the perturbing radiation field causing shifts of the eigenvalues of the unperturbed Hamiltonian. As such, the calculation of the matrix element corresponds to the energy shift for the phenomena:

$$\Delta E = \sum_r \frac{\langle E_0; n| -\boldsymbol{m}(\xi)\cdot\boldsymbol{b}(\boldsymbol{R}_\xi)|E_r; n-1\rangle\langle E_r; n-1| -\boldsymbol{m}(\xi)\cdot\boldsymbol{b}(\boldsymbol{R}_\xi)|E_0; n\rangle}{E_i - E_r}, \qquad (7)$$

where the photon mode is implicit. With the aid of the Feynman graphs in Fig. 1, and carrying out the operations in (7), the energy shift takes the form

$$\Delta E^{\text{M1M1}} = -\left(\frac{\hbar k}{2\varepsilon_0 cV}\right) n b_i \bar{b}_j \times \sum_r \left[\frac{m_i^{0r} m_j^{r0}}{E_{r0} - \hbar ck} + \frac{m_j^{0r} m_i^{r0}}{E_{r0} + \hbar ck}\right], \qquad (8)$$

where $m_i^{0r} = \langle 0|m_i|r\rangle$. The term in square brackets represents a molecular response tensor, namely the frequency-dependent TIP orbital paramagnetic susceptibility

$$\chi_{ij}^{\text{para(orb)}}(\omega,-\omega) = \sum_r \left[\frac{m_i^{0r} m_j^{r0}}{E_{r0} - \hbar ck} + \frac{m_j^{0r} m_i^{r0}}{E_{r0} + \hbar ck}\right]. \qquad (9)$$

Therefore, the M1M1 contribution to forward Rayleigh scattering can be written as

$$\Delta E^{\text{M1M1}} = -\frac{I}{2\varepsilon_0 c^3} b_i \bar{b}_j \chi_{ij}^{\text{para(orb)}}(\omega,-\omega), \qquad (10)$$

where we have written it in terms of the input laser beam intensity $I = n\hbar c^2 k/V$. This contribution to the scattering force takes on a very similar form to that of the leading-order E1E1 coupling:

$$\Delta E^{\mathrm{E1E1}} = -\frac{I}{2\varepsilon_0 c} e_i \bar{e}_j \alpha_{ij}(\omega,-\omega), \tag{11}$$

where $\alpha_{ij}(\omega,-\omega)$ is the frequency-dependent polarizability. This connection is expected since the TIP paramagnetic susceptibility is the magnetic analog to the electric polarizability. In general, the magnetic contribution is much smaller in magnitude than its electric counterpart: matrix elements for a magnetic dipole interaction are typically on the order of the fine-structure constant smaller than the equivalent electric dipole term. However, such magnetic interactions can be important, such as in molecules with small electric polarizabilities and relatively large magnetic susceptibilities, for example.

As it stands, the result (10) applies to molecules with a fixed orientation, such as in solids, and therefore has little relevance to standard optical trapping experiments where interest lays in the liquid phase. To secure an energy shift applicable to liquid (and gases) we therefore perform a rotational average of (10), which gives the shift for a system of freely tumbling molecules. The average entails contraction of the molecular tensor (9) above with the corresponding isotropic tensor of the same rank [63], namely the Kronecker delta; the result is secured as

$$\langle \Delta E \rangle^{\mathrm{M1M1}} = -\frac{I}{2\varepsilon_0 c^3} \chi^{\mathrm{para(orb)}}(\omega,-\omega), \tag{12}$$

where $\chi^{\mathrm{para(orb)}}$ is now the isotropic TIP paramagnetic susceptibility, and a factor of 1/3 which comes from the averaging that has been included within it.

The next step is to calculate the leading-order D1 diamagnetic contribution to the energy shift. A key difference in diamagnetic couplings compared to their magnetic and electric counterparts is that a single D1 interaction term is quadratic in the magnetic field and electric charge; E1 and M1 are linearly dependent on the electric and magnetic field, respectively. Therefore, although the E1E1 and M1M1 contributions to two-photon processes, such as Rayleigh scattering, require second-order perturbation theory, the D1 contributions to two-photon processes require perturbation theory that is first order in H_{int}: $\Delta E = \langle f|H_{\mathrm{int}}|i\rangle$. Interestingly, it can be highlighted at this point where the unique frequency *independence* of the diamagnetic interactions originate from in the theory: There are no virtual intermediate states in diamagnetic couplings, and therefore the molecule's response possesses no frequency dependence through the denominator as in standard polarizabilities, highlighted in (5).

To make the procedure of calculating D1 couplings easier to follow, with the aid of $(\boldsymbol{a}\times\boldsymbol{b})_i = \varepsilon_{ijk} a_j b_k$ we can write the D1 interaction Hamiltonian term from (1) as

$$\begin{aligned} H_{\mathrm{int}}^{(\mathrm{D1})} = \frac{e^2}{8m} \varepsilon_{pij}\varepsilon_{pkl} \sum_{\substack{\boldsymbol{k},\eta \\ \boldsymbol{k}',\eta'}} \sum_{\xi,\alpha} \left(\frac{\hbar}{2\varepsilon_0 c V}\right)(kk')^{1/2} \\ \times [\boldsymbol{q}_\alpha(\xi) - \boldsymbol{R}_\xi]_i [\boldsymbol{q}_\alpha(\xi) - \boldsymbol{R}_\xi]_k \\ \times (b_j a e^{i\boldsymbol{k}\cdot\boldsymbol{R}_\xi} - \bar{b}_j a^\dagger e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_\xi}) \\ \times (b'_l a' e^{i\boldsymbol{k}'\cdot\boldsymbol{R}_\xi} - \bar{b}'_l a'^\dagger e^{-i\boldsymbol{k}'\cdot\boldsymbol{R}_\xi}), \end{aligned} \tag{13}$$

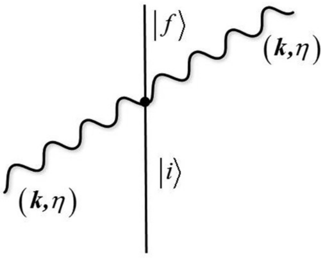

FIG. 2. Time-ordered Feynman graph representing the lowest-order diamagnetic scattering of an incident photon into an output photon of the same mode $(\boldsymbol{k},\eta)$. For nonforward scattering the output mode $(\boldsymbol{k}',\eta')$ is not equal to that of the input $(\boldsymbol{k},\eta)$.

where we have used the mode expansions for the magnetic field given by (3).

The initial and final states of the system are still equal as in the M1M1 calculation, and as it is forward scattering $k = k'$. By making use of the completeness relation to introduce a sum over the virtual intermediate states $|r\rangle$, together with defining the operator relation $-e\sum_\alpha [\boldsymbol{q}_\alpha(\xi) - \boldsymbol{R}_\xi]_i = \mu_i(\xi)$, the ensuing application of (13) gives the energy shift in terms of transition dipole moments. With the aid of the Feynman diagram in Fig. 2, and inserting (13) into the first-order time-dependent perturbation expression leads to

$$\Delta E = \frac{1}{8m}\varepsilon_{pij}\varepsilon_{pkl}\left(\frac{n\hbar k}{2\varepsilon_0 c V}\right) b_j \bar{b}_l \sum_r \mu_i^{0r}\mu_k^{r0}. \tag{14}$$

In (14) we have invoked the standard assumption that the photon creation and annihilation events relate to the same electron, and that its wave function is to a first approximation exactly separable from those of other electrons.

The energy shift can be further manipulated by using the identity $\varepsilon_{pij}\varepsilon_{pkl} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$ and expressing it in terms of the input beam intensity:

$$\begin{aligned} \Delta E^{\mathrm{D1}} \\ = \frac{I}{16 m \varepsilon_0 c^3} \sum_r \left(\mu_i^{0r}(\xi)\mu_i^{r0}(\xi) b_j \bar{b}_j - \mu_i^{0r}(\xi)\mu_j^{r0}(\xi)\bar{b}_i b_j\right). \end{aligned} \tag{15}$$

Using the same standard techniques as in the M1M1 case, the full rotationally averaged result of (15) above is

$$\begin{aligned} \langle \Delta E^{\mathrm{D1}} \rangle &= \frac{I}{16 m\varepsilon_0 c^3}\sum_r \left(\mu_\lambda^{0r}(\xi)\mu_\lambda^{r0}(\xi) - \frac{1}{3}\mu_\lambda^{0r}(\xi)\mu_\lambda^{r0}(\xi)\right) \\ &= \frac{I}{24 m\varepsilon_0 c^3}\sum_r \mu_\lambda^{0r}(\xi)\mu_\lambda^{r0}(\xi) \\ &= \frac{I}{24 m\varepsilon_0 c^3} D_{\lambda\lambda}^{00}(\xi), \end{aligned} \tag{16}$$

where we make the definition $\sum_r \mu_i^{0r}(\xi)\mu_j^{r0}(\xi) = D_{ij}^{00}(\xi)$, and it is once again highlighted that there exists no frequency dependence in the D1 contributions. It is also worth mentioning that with (16) being a positive quantity, the energy shift is therefore repulsive. Such behavior is well known for diamagnetic materials placed in an external electromagnetic field.

With recourse to (6), the total magnetic contribution to the scattering trapping force is the sum of the M1M1 and D1 terms, (12) and (16), respectively:

$$\begin{aligned}\langle \Delta E^{\chi_{\text{tot}}} \rangle &= -\frac{I}{2\varepsilon_0 c^3}\left[\chi^{00}_{\lambda\lambda}(\omega,-\omega) - \frac{1}{12m}D^{00}_{\lambda\lambda}(\xi)\right] \\ &= -\frac{I}{2\varepsilon_0 c^3}\chi^{00}_{\text{tot}},\end{aligned} \tag{17}$$

where the energy shift is secured in terms of the gauge-invariant isotropic total magnetic susceptibility χ^{00}_{tot}. Clearly, if the sign of (17) is positive the molecule is diamagnetic, and conversely a negative energy shift corresponds to a paramagnetic molecule.

It is interesting to speculate on a "discriminatory" trapping force between paramagnetic and diamagnetic molecules. In the standard discriminatory trapping force [62], the difference is due to a chiral sensitivity to the handedness of the radiation and molecules. However, in this case there would be a different force acting upon paramagnetic and diamagnetic molecules in a mixture. Although in many cases the E1E1 energy shift (11) will dominate the magnetic contribution to scattering, it is still interesting to speculate on this approach to molecular separation. A further point worth bringing attention to is that, as stated previously, but now explicitly shown, a key difference between the M1M1 and D1 contributions to the total magnetic response is that the M1M1 paramagnetic susceptibility is frequency dependent, and therefore selecting a suitable input frequency one can exploit preresonance enhancement of this interaction term. It is therefore interesting to postulate whether a diamagnetic molecule under resonant conditions may in fact show paramagnetic behavior.

B. Nonforward scattering

In contrast to the well-known inelastic process of Raman scattering, any Rayleigh scattering process is elastic due to the energy of both the scatterer and the incident photon being conserved in the process, that is $|\boldsymbol{k}| = |\boldsymbol{k}'|$. In the forward Rayleigh scattering process discussed in the previous section, $\hat{\boldsymbol{k}} = \hat{\boldsymbol{k}}'$, however there exists another mechanism whereby $\hat{\boldsymbol{k}} \neq \hat{\boldsymbol{k}}'$, which leads to the scattered photon being in a different mode from that of the incident: this process is termed nonforward scattering. The process of nonforward scattering is slightly more complicated than the forward analog, occurring as an optical rate rather than an energy shift [61]. In the forward-scattering mechanism, the initial and final quantum states of the whole radiation-molecule system are identical, and therefore only diagonal matrix elements arise. In nonforward scattering, where initial and final states of the total system differ, off-diagonal matrix elements are the contributing terms.

Calculating the quantum amplitude using second-order perturbation theory as in the forward-scattering case, and inserting into the Fermi rate rule yields the M1M1 contribution in terms of the intensity of the scattered radiation:

$$I^{\text{M1M1}}(\boldsymbol{k}') = \frac{NIk^4}{16\pi^2\varepsilon_0^2 c^4}\bar{b}'_i b_j b'_k \bar{b}_l \langle \chi^{00}_{ij}(\omega,-\omega)\chi^{00}_{kl}(\omega,-\omega)\rangle, \tag{18}$$

where N represents the total number of molecules in the scattering sample. The molecular average in angular brackets in (18) once carried out using standard methods [63] is seen to be

$$I^{\text{M1M1}}(\boldsymbol{k}') = \frac{NIk^4}{480\pi^2\varepsilon_0^2 c^4}\left[A\chi^{00}_{\lambda\lambda}\bar{\chi}^{00}_{\sigma\sigma} + B\chi^{00}_{\lambda\sigma}\bar{\chi}^{00}_{\lambda\sigma} + C\chi^{00}_{\lambda\sigma}\bar{\chi}^{00}_{\sigma\lambda}\right], \tag{19}$$

where

$$A = 4|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 - |\boldsymbol{b}\cdot\boldsymbol{b}'|^2 - 1,\quad B = -|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 - |\boldsymbol{b}\cdot\boldsymbol{b}'|^2 + 4,\quad C = -|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 + 4|\boldsymbol{b}\cdot\boldsymbol{b}'|^2 - 1, \tag{20}$$

and the frequency dependence of the molecular tensors is assumed implicit for notational brevity. The molecular tensors in (19) can be further manipulated and expressed as a sum of irreducible tensors [64]. The paramagnetic susceptibility tenors in (19) are of rank 2, and can therefore be decomposed in three different weights (0), (1), and (2) as

$$\chi_{\lambda\sigma} = \chi^{(0)}_{\lambda\sigma} + \chi^{(1)}_{\lambda\sigma} + \chi^{(2)}_{\lambda\sigma},\quad \chi^{(0)}_{\lambda\sigma} = \tfrac{1}{3}\delta_{\lambda\sigma}\chi_{\nu\nu},\quad \chi^{(1)}_{\lambda\sigma} = \tfrac{1}{2}(\chi_{\lambda\sigma} - \chi_{\sigma\lambda}),\quad \chi^{(2)}_{\lambda\sigma} = \tfrac{1}{2}(\chi_{\lambda\sigma} + \chi_{\sigma\lambda}) - \tfrac{1}{3}\delta_{\lambda\sigma}\chi_{\nu\nu}. \tag{21}$$

Rewriting (19) in terms of the irreducible parts of χ^{00} we secure the following result:

$$I^{\text{M1M1}}(\boldsymbol{k}') = \frac{NIk^4}{1440\pi^2\varepsilon_0^2 c^4}\left[10|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2\chi^{(0)}_{\lambda\lambda}\bar{\chi}^{(0)}_{\sigma\sigma} + 3(3 - 2|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 + 3|\boldsymbol{b}\cdot\boldsymbol{b}'|^2)\chi^{(2)}_{\lambda\sigma}\bar{\chi}^{(2)}_{\lambda\sigma}\right]. \tag{22}$$

Now concentrating on the D1 contribution to nonforward Rayleigh scattering, the rotationally averaged scattered intensity is seen to be

$$I^{\text{D1}}(\boldsymbol{k}') = \frac{NIk^4}{30\,720 m^2\varepsilon_0^2\pi^2 c^4}\left[(14|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 - |\boldsymbol{b}\cdot\boldsymbol{b}'|^2 - 1)D^{00}_{\lambda\lambda}\bar{D}^{00}_{\sigma\sigma} + (3 - 2|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 + 3|\boldsymbol{b}\cdot\boldsymbol{b}'|^2)D^{00}_{\lambda\sigma}\bar{D}^{00}_{\lambda\sigma}\right]. \tag{23}$$

Using the same techniques as for the M1M1 case, the scattered intensity (23) can be written in terms of the irreducible parts of the transition moments

$$I^{\text{D1}}(\boldsymbol{k}') = \frac{NIk^4}{92\,160 m^2\varepsilon_0^2\pi^2 c^4}\left[40|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 D^{(0)}_{\lambda\lambda}\bar{D}^{(0)}_{\sigma\sigma} + 3(3 - 2|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2 + 3|\boldsymbol{b}\cdot\boldsymbol{b}'|^2)D^{(2)}_{\lambda\sigma}\bar{D}^{(2)}_{\lambda\sigma}\right]. \tag{24}$$

In a similar fashion to the previous section, we can write the results in terms of the gauge-invariant total magnetic susceptibility for each different weight contribution. For weight (0) contributions

$$I^{\text{mag}(0)}(\boldsymbol{k}') = \frac{NIk^4}{144\pi^2\varepsilon_0^2c^4}|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2\left[\chi^{(0)}_{\lambda\lambda}\bar{\chi}^{(0)}_{\sigma\sigma}+\frac{1}{16m^2}D^{(0)}_{\lambda\lambda}\bar{D}^{(0)}_{\sigma\sigma}\right], \tag{25}$$

while the weight (2) contributions take the form of

$$I^{\text{mag}(2)}(\boldsymbol{k}') = \frac{NIk^4}{480\pi^2\varepsilon_0^2c^4}(3-2|\boldsymbol{b}\cdot\bar{\boldsymbol{b}}'|^2+3|\boldsymbol{b}\cdot\boldsymbol{b}'|^2)\left[\chi^{(2)}_{\lambda\mu}\bar{\chi}^{(2)}_{\lambda\mu}+\frac{1}{64m^2}D^{(2)}_{\lambda\sigma}\bar{D}^{(2)}_{\lambda\sigma}\right]. \tag{26}$$

The weight (0) contributions represent the isotropic contributions from the scalar scattering terms (25), while the weight (2) scattering contributions (26) are the anisotropic parts. The sum of both irreducible components, (25) and (26), produces an expression where it is possible to ascertain the scattered intensity for varying forms of polarized or unpolarized incident photons; such an analysis is standard for the E1E1 contribution to scattering [9].

IV. CONCLUSION

The manifestation of the well-known fact in Coulomb gauge molecular electromagnetism that the magnetic susceptibility is a sum of spin and orbital contributions has been explicitly highlighted in the framework of multipolar molecular quantum electrodynamics. In this noncovariant formulation of QED the spin-paramagnetic interaction Hamiltonian may be added in an *ad hoc* manner if dealing with the relatively limited examples of molecules possessing spin. For the majority of spin-less molecules, the theory clearly produces results dependent upon the total magnetic susceptibility which is a sum of the M1M1 orbital paramagnetic susceptibility and D1 diamagnetic susceptibility. Only when both these contributions are computed for any given multiphoton process do we secure gauge-invariant results: this is the main reason why diamagnetic couplings should be explicitly evaluated when studying magnetic interactions.

This work complements a recent Perspective article on the nature and validation of the multipolar PZW Hamiltonian [18], so prevalently utilized throughout chemical and optical physics. In this work it has been explicitly highlighted how the less well-known diamagnetic interactions take their place in light-matter interactions, their implementation and physical interpretation, and how the multipolar PZW takes full account of their existence. To highlight this clarification, the lowest-order magnetic coupling contribution to forward Rayleigh scattering (a mechanism responsible for the optical trapping force) was calculated, demonstrating the role that the M1M1 and D1 couplings play in yielding a result dependent on the total magnetic susceptibility—-a measurable physical parameter.

Although the main aim of this work was to put the diamagnetic and magnetic couplings in the PZW Hamiltonian on a firmer theoretical grounding, the role of magnetic couplings between radiation and light is fast becoming a flourishing field of research [65], specifically with the use of optical metamaterials leading to enhanced and observable magnetic light-matter interactions [66,67]. It is for this reason that an appropriate theoretical QED framework with suitable modifications to account for inhomogeneous and dispersive media [68,69], which highlights the significance of both the magnetic and diamagnetic contributions to these interactions in photonic nanostructures, is key to enable the further exploration in the ever-expanding field of molecular and optical physics. Indeed, exploratory work using macroscopic QED methods has highlighted the importance of diamagnetic interactions in a system of magnetodielectric bodies [70].

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