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Quantum field representation of photon-molecule interactions

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Abstract

In reporting and explaining the interactions of light with atoms and molecules, a photon-based description is not only appropriate but clearly essential when electronic or other kinds of quantum transition ensue. However, textbook treatments frequently go no further than the Planck relation, in representing the quantum nature of the light itself – often resorting to classical principles when discussing mechanism. Complete consistency and rigour can be achieved by treating both the matter and the radiation in a fully quantised form, which requires the electromagnetic fields to be cast in a quantum field representation. It proves possible to develop a rigorous approach to this theory that is simple to convey and apply, and which lends itself to a significantly enhanced level of appreciation of mechanism. This paper lays a concise foundation and exemplifies the application in three specific cases: absorption, emission and scattering. It is also shown how this formulation affords a basis for applications in higher-order, multiphoton and nonlinear optical processes.

1. Introduction

To describe the physics behind the simplest kinds of optical interaction, which involves light with atoms and molecules, the use of the photon concept is clearly essential and it is especially important for processes that directly involve transitions between quantum energy levels. Nonetheless, to go beyond use of the Planck relation $\Delta E = h\nu$ – whose origins lie in the quantum theory that pre-dated fully fledged quantum mechanics – it is surprisingly common to find the quantum nature of the radiation itself underplayed in favour of an essentially classical wave representation. To cultivate a proper understanding of the mechanisms for photon absorption, emission and scattering requires the introduction of simple principles from the field theory engaged in quantum optics and electrodynamics. This framework not only affords answers to many of the most obvious questions of mechanism; it also directly paves the way to comprehend higher-order processes, such as those in the sphere of nonlinear optics [1-3].

Customarily, and perfectly correctly, the introduction to a quantum representation of electrodynamics is formally developed from a starting point exhibiting its basis in Maxwell’s equations – whose operator implementation has exactly the same form as its original, classical counterpart [4-7]. Given the incontrovertible status of these equations, and secure in the knowledge that all the major constructs of QED (quantum electrodynamics) are fully consistent with them, it is expedient from an applications perspective to more directly approach the subject from a higher, and in a sense simpler, level. A true and physically comprehensible representation of the key interaction
mechanisms can, therefore, begin by considering engagement between the electromagnetic fields of optical radiation, and the fundamental nuclear and electronic charges of which all material particles are made. In fact, although the magnetic field of light may also come into play in a range of subtle effects – especially those where chiral properties rise to the fore – its direct effects are generally much weaker, and much more experimentally challenging to measure, than the corresponding electric field [8]. Accordingly, all of the most prominent features in optical interactions with atoms and molecules trace their origin to the electric field of radiation.

The following account develops theory from a starting point beyond the well-trodden descriptions that work up from Maxwell’s equations and the intricacies of gauge theory [1, 2, 5, 9, 10]. We begin (Section 2) with a generic depiction of a quantised light-plus-matter system, moving on through identification of the standard time-dependent perturbation method for dealing with interactions. We then introduce a physically intuitive operator framework, laying a simple but complete foundation for detailed description of simple optical interactions. The account that follows then exemplifies applications in three specific cases: photon absorption and emission (Section 3), and Rayleigh scattering (Section 4). These are the three forms of optical interaction responsible for almost every feature in our visual world; they also operate at the heart of most kinds of spectroscopy, illumination and imaging science. Section 5 summarises and indicates how the approach may readily be extended to higher-order processes.

2. Key QED equations

For optical systems, it is appropriate to use the molecular representation of quantum electrodynamics. This differs from the full relativistic form of QED only in recognition that the charges comprising matter generally move at significantly sub-luminal speeds in almost all optics and photonics applications. In a molecular QED analysis of light-matter interactions, the matter and the light are treated as twin components of a fully quantised system [11-14], and the theory is developed from the formulation of a Hamiltonian $H$, the energy operator of the system. The system Hamiltonian comprises operators for: (i) the matter, for which the state wavefunctions are secured as eigenstates of a material Hamiltonian $H_{\text{mat}}$; (ii) the quantised radiation with Hamiltonian $H_{\text{rad}}$, which introduces the quantity known as a photon that is absent from any semiclassical description (where light is presumed to be a classical wave); (iii) the interaction between the matter and radiation, with energy operator $H_{\text{int}}$.

Before launching into the detail, it is worth flagging up one of the signal advantages of a full quantum field treatment of light-matter interactions. If we focus on the optical processes exhibited by individual molecules then – although thermodynamic concepts are inapplicable to systems at this level – the light and matter together constitute the core of a technically closed system. Furthermore, this system is in fact an isolated system during the course of any distinct interaction; the Hamiltonian is, therefore, Hermitian and it ensures time-reversal invariance. The implications of any energy exchange or losses to other components of a more physically extended system can be dealt with by developing the following expression [9, 15, 16]:

...
where $\xi$ designates each electronically distinct component – such as an atom, molecule, quantum dot, chromophore etc. It is immediately worth emphasising that the expression is *exact*: there are no cross-terms to signify coupling between different components, since every such electrodynamic coupling is now properly cast as engaging the electromagnetic field – including the vacuum field. Therefore, the system Hamiltonian differs from a semiclassical one, in three respects: the presence of $H_{\text{rad}}$, the formulation of $H_{\text{int}}$ as an operator on both material and radiation states, and the absence of any inter-component coupling terms [16-18].

For application to a wide range of simple optical processes, the Hamiltonian (1) can be regarded as encapsulating the core elements of a closed system of interaction for each representative molecule $\xi = A$, through;

$$H = H_{\text{rad}} + \sum_{\xi} H_{\text{mol}}(\xi) + \sum_{\xi} H_{\text{int}}(\xi),$$  \hspace{1cm} (1)

where the latter two summations represent surroundings, sometimes called the ‘bath’, that can as a first approximation be excluded from the closed system under consideration. For example, the extraneous matter may be responsible for a local electronic environment that shifts peak absorption or emission wavelengths [19, 20], but which do not remove a clear correlation to states and energies of the isolated components. Equally, in the course of any optical process, the closed sub-system may behave as an isolated system until the interaction is over – at which point energy may exchange with other parts of the full system. For example, such an exchange may occur through resonance energy transfer, following photon absorption [21, 22]; a QED description, presented at a similar level to the present work, is to be found in a previous article [17]. The closed system Hamiltonian is decomposed into these three simple parts (supressing the dependence on molecule $A$ for convenience), *i.e.*;

$$H = H_{\text{mol}} + H_{\text{rad}} + H_{\text{int}}.$$

In most situations, the energies associated with the operator $H_{\text{int}}$ are much smaller than those represented by $H_{\text{mol}}$ and $H_{\text{rad}}$. Hence, light-matter interactions only perturb the system represented by $H_0 = H_{\text{mol}} + H_{\text{rad}}$ [23]. (This presumes a typically weak coupling between the matter and the light; at ultra-high laser intensities above $10^{21}$ W cm$^{-2}$, for example, non-perturbative methods should be employed.) Based on the perturbation, the general expression for the matrix element, $M_{F'I'}$ – for progression from an initial system state $|I\rangle$ to a final state $|F\rangle$ – is then developed. This is a formulation where a matrix describes all the couplings between a full set of initial and final states, which is determined from the following general expression [2, 3, 24]:
where $|R\rangle$, $|S\rangle$, $|T\rangle$ and so on are virtual intermediate states, and $E_R$, $E_S$ and $E_T$ are the energies of these states. Determining the matrix element for a given process usually requires only a single term of this expression – the leading non-zero term, which depends on the number of light-matter interactions of the examined process. As we shall see, the form of $H_{int}$ and the nature of its field operator determines that for each term in equation (4), the number of times $H_{int}$ appears essentially represents the number of light-matter interactions. Therefore, for example, the second term in equation (4) is used to describe both two-photon absorption and light scattering, which involves an input and an output photon. The latter is examined in detail in Section 4.

Proceeding further, we now identify an explicit expression for $H_{int}$. Although an alternative ‘minimal coupling’ formulation exists, we employ the widely used multipolar form of coupling here: this is an issue we return to below. As observed in the Introduction, the electric field of radiation is the strongest form of coupling with discrete atoms and molecules in the optical region. The electric field of light engages with the charges of these atoms and molecules, enabling quantum transitions to occur when resonant conditions are met, so that Planck’s relation is satisfied. However, for such processes to occur a secondary issue must also be satisfied, relating to the associated selection rules. The spherical symmetry of atoms and some molecules (and the lower but still significant symmetry of many small molecules) has a strong bearing on which electronic transitions may occur – not only in the ultraviolet and visible region, but also in the infrared and microwave regions where nuclear states of motion are involved. In nearly all major optical phenomena, it is accurate and customary to express light-matter interactions in terms of an electric dipolar coupling with the electric field of the radiation, i.e.;

$$H_{int} = -\mu \cdot E$$

(5)

Here, both $\mu$ and $E$ are operators – the former acting on matter states and the latter on radiation states. Throughout this article, standard subscript notation will be employed – i.e. Einstein summation over indices is implied [25] – meaning that equation (5) has invoked:
\[ \sum_{i=x,y,z} \mu_i E_i = \mu_x E_x + \mu_y E_y + \mu_z E_z = \mathbf{\mu} \cdot \mathbf{E} . \]  

(6)

For the interested reader it is worth highlighting that there exists a whole class of equivalent interaction Hamiltonians that may be deployed in QED. Two of the most frequently implemented are a multipolar expansion (the interaction Hamiltonian (5) is this type) and a ‘minimal coupling’ representation. The former describes light-matter interactions in terms of direct coupling between the electromagnetic field and transition multipole moments of the matter (e.g. the electric dipole). The latter deals in the less physically intuitive conjugate momentum of the material particles and, to represent the field, a vector potential \( \mathbf{A} \) (whose nature depends on a choice of electromagnetic gauge – as opposed to the experimentally identifiable electric field \( \mathbf{E} \)). Of key importance to us here is that, although these different interaction Hamiltonians provide equivalent results in non-relativistic QED, the multipolar form (5) is not only more direct; it also furnishes results that are immediately interpretable in relation to molecular symmetry. This simplicity is especially pertinent when studying higher-order photon interactions such as light scattering \([3, 16, 26-28]\).

Continuing, for each optical mode – with a given wave-vector \( \mathbf{k} \) and specific polarisation \( \eta \) – the electric field of the light can be rewritten in a Fourier expansion, in terms of a Hermitian operator, which is given by:

\[
\mathbf{E}(\mathbf{r}) = i \left( \frac{\hbar c k}{2 e_0 V} \right)^{1/2} \left\{ \mathbf{e} \cdot \mathbf{a} e^{i \mathbf{k} \cdot \mathbf{r}} \underbrace{- e^{i \mathbf{k} \cdot \mathbf{r}} \mathbf{e}^\dagger} \right\},
\]

(7)

where \( \hbar c k = \hbar \omega \) and \( \mathbf{e} \) are the photon energy and polarisation, respectively, and the overbar denotes a complex conjugate; the phase factors are given by \( e^{i \mathbf{k} \cdot \mathbf{r}} \); in this section (and the next) dealing with single-component processes, an expedient simplification is to assume they occur at the origin of an arbitrary spatial frame, \( \mathbf{r} = 0 \). Moreover, for each mode, the corresponding photon annihilation \( \mathbf{a} \) and creation \( \mathbf{a}^\dagger \) (lowering and raising) operators act on the radiation states through;

\[
a|n\rangle = n^{1/2} |n-1\rangle ,
\]

(8)

\[
a^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle ,
\]

(9)

respectively, in which \( n \) is the number of photons. Analogous to equation (4), only one term of equation (7) is required per \( H_{\text{int}} \) – thus, either equation (8) or (9) is used – because a single dipolar light-matter interaction cannot involve both photon creation and annihilation. In consequence, each action of \( H_{\text{int}} \) either creates or destroys a photon. For this reason, the first term in equation (4) is the significant term for describing single-
photon absorption or emission (the subject of the next section). In passing, we note the single-mode operator commutator relationship;

\[
[a, a^\dagger] = aa^\dagger - a^\dagger a = 1 ,
\]

whose form is consistent with the integer spin of photons, signifying that the theory deeply embeds the fact that they are bosons. It is the fact that photons carry unit spin that leads to the selection rules mentioned earlier: as standard textbooks make clear, all the key selection rules for electronic spectroscopy owe their origin to the photon spin, and cannot be readily understood on any other basis – see, for example, ref. [29].

To determine an experimentally verifiable quantity from equation (4), the time-averaged rate \( \Gamma \) of any specific process involves taking the modulus squared of the matrix element \( M_{FI} \) so that, via the Fermi Rule, we have;

\[
\Gamma = \frac{2\pi}{h} |M_{FI}|^2 \rho ,
\]

where \( \rho \) represents the density of states – a much misunderstood quantity signifying the number of quantum states per unit energy interval. In principle – in both QED and semiclassical formulations – this should be taken as a convolution over the minimum measurable linewidth, of four state densities: those for the initial and final states of the matter, and of the radiation field, \( i.e.; \)

\[
\rho = \int \int \int \rho_{\text{mol}}^{(i)}(E_{\text{mol}}^{(i)}) \rho_{\text{mol}}^{(f)}(E_{\text{mol}}^{(f)}) \rho_{\text{rad}}^{(i)}(E_{\text{rad}}^{(i)}) \rho_{\text{rad}}^{(f)}(E_{\text{rad}}^{(f)}) \delta(E_{\text{mol}}^{(i)} + E_{\text{mol}}^{(f)} - E_{\text{rad}}^{(i)} - E_{\text{rad}}^{(f)}) dE_{\text{mol}}^{(i)} dE_{\text{mol}}^{(f)} dE_{\text{rad}}^{(i)} dE_{\text{rad}}^{(f)}
\]

Generally, as will be evident, the result effectively simplifies to the single, significantly highest of the four densities of states – most obviously, in a limiting case where each of the other three reduces to a delta function. For example, in the absorption of a photon from essentially monochromatic laser light of frequency \( \omega \), by a molecule in its ground state \( E_{\text{mol}}^{(i)} \), where \( \rho_{\text{mol}}^{(i)}(E_{\text{mol}}^{(i)}) = \delta(E_{\text{mol}}^{(i)} - E_{\text{mol}}^{(i)}) \) and similarly \( \rho_{\text{mol}}^{(f)}(E_{\text{mol}}^{(f)}) = \delta(E_{\text{mol}}^{(f)} - E_{\text{mol}}^{(f)}) \), then implementing energy conservation, \( E_{\text{mol}}^{(i)} = E_{\text{mol}}^{(f)} + \hbar \omega \), leads to \( \rho = \rho_{\text{mol}}^{(i)}(E_{\text{mol}}^{(i)}) - \) which we can denote in shorthand as \( \rho_{\alpha} \), where \( \alpha \) signifies the molecular excitation state. More generally, in common with the classical take on the subject, it nonetheless remains the case that for zero, or extremely small linewidth transitions, it is impossible to secure a time-independent rate of the Fermi Rule form and Rabi oscillations arise. However, such effects are usually limited to the discrete energy level interactions of cold atoms with laser light.
3. Light absorption and emission

The easiest way to exhibit utilisation of the above equations is via examples, and the very simplest are one-photon absorption and emission. These can be visualised by energy level diagrams, in which one quantum of energy is transferred between the radiation and matter states; they are depicted in Figure 1(a) and Figure 2(a), respectively. These two figures are identical except the directions of the arrows are interchanged. In terms of QED, a more robust graphical aid is known as a Feynman diagram.

![Energy-level scheme for one-photon absorption](image1)

**Figure 1.** (a) Energy-level scheme depicting one-photon absorption: a quantum of light released from the radiation state excites the molecule (or atom), concurrently. (b) Feynman diagram for one-photon absorption. Vertical and wavy lines denote the matter and radiation, respectively, 0 is the ground state (blue line) and α is the excited state (red line); time, t, traverses up the graph, \( H_{\text{int}} \) denotes the light-molecule interaction and \((k, \eta)\) is the photon mode.

![Energy-level scheme for one-photon emission](image2)

**Figure 2.** (a) Energy-level scheme for one-photon emission: the relaxation of an excited molecule (or atom) releases a quantum of light into the radiation state, simultaneously. (b) Feynman diagram for one-photon emission. These are the time-inverse of Figure 1.
Using one-photon absorption as an example – as shown in Figure 1(b) – the vertical line represents the atom or molecule, which changes electronic state when the light is absorbed, and the wavy line is the photon. At the lower part of the diagram, matter is in its ground state and a photon is present in the system. After the annihilation of the photon (the upper part, in red), the matter is in an excited state and no light exists. With this in mind, and presuming an input of \( n \) photons, the initial and final states of this process can be decomposed into the following products of matter and radiation states:

\[
|I\rangle = |A^0\rangle |n\rangle \equiv |A^0; n\rangle ,
\]

|F\rangle = |A^\alpha\rangle |n-1\rangle \equiv |A^\alpha; n-1\rangle ,
\]

where \( A \) represents the matter in either its ground state, 0, or excited state, \( \alpha \), as denoted by the superscript, and the right-hand side of the expression depicts a change in notation for simplicity. Since one-photon absorption involves one light-matter interaction, its matrix element is determined from the first term of equation (4), and the \( H_{\text{int}} \) within it arises from the first term of equation (7), so that:

\[
M_{fi}^{\text{abs}} = \langle F | H_{\text{int}} | I \rangle = \langle A^\alpha; n-1 | -\mu \cdot E | A^0; n \rangle = -\langle A^\alpha | \mu | A^0 \rangle \langle n-1 | E | n \rangle
\]

\[
= -i \left( \frac{\hbar c \kappa}{2 \varepsilon_0 V} \right)^\frac{3}{2} \mu_0^\alpha 0 \langle n-1 | e \cdot a | n \rangle = \left( \frac{\hbar c \kappa}{2 \varepsilon_0 V} \right)^\frac{3}{2} \mu_0^\alpha 0 .
\]

Here, the photon energy \( \hbar c \kappa \) is equal to the energy required for electronic transition \( |\alpha\rangle \leftarrow |0\rangle \) (conventionally written in this way, i.e. backwards). Moving from left-to-right in this expression: (i) equations (5), (13) and (14) are inserted into the first term of equation (4); (ii) the matter operator acts on the matter states, to produce the transition dipole moment \( \mu_0^\alpha \), and the radiation operator acts on the radiation states; (iii) the first term of equation (7) is inserted into the radiation portion of the expression; (iv) the annihilation operator \( a \) acts on the radiation state following equation (8), which produces the result (noting that \( \langle n-1 | n-1 \rangle = 1 \), since quantum states with are orthonormal).

Substituting \( M_{fi}^{\text{abs}} \) into the Fermi Rule of equation (11) obtains:

\[
\Gamma = \frac{\pi \varepsilon_0 \rho_\alpha}{\varepsilon_0} \left( \frac{n}{V} \right) |\mu_0^\alpha|^2 \cos^2 \theta ,
\]
where $\theta$ is the angle between the transition dipole, $\mu^{a\alpha}$, and the electric polarisation vector, $\varepsilon$, of the incident light; $\rho_{\alpha}$ is a density of states ascribed to the excited state, as discussed earlier. In this latter respect, we note a difference from textbook derivations of the Einstein $B$-coefficient, designed to exhibit a form originally conceived for application to blackbody radiation. Most of today’s applications, especially in the sphere of spectroscopy, deploy narrow-linewidth laser sources whose spectral breadth is far exceeded by any quantum states of the material: this is an aspect that should be common to both classical and quantum formulations. Next, by using the relationship between the ‘photon density’ $n/\nu$ and the irradiance (power per unit area) $I = (n/\nu)\hbar c \omega$, the final outcome is secured as follows:

$$\Gamma = \frac{\pi \rho_{\alpha} I |\mu^{a\alpha}|^2}{\hbar c \varepsilon_0} \cos^2 \theta . \quad (17)$$

Finally, for a fluid medium, a three-dimensional orientational average of the $\cos^2 \theta$ factor simply reduces to 1/3. It is noteworthy that the square of the transition dipole moment is the fundamental quantity that determines the photometric oscillator strength (see for example ref. [30], p. 432).

Moving to the case of emission, which is depicted by the Feynman diagram of Figure 2(b), it is supposed that the expressions are similar because emission is the time-inverse of absorption. For stimulated emission, this is indeed true. In this case, there is an initial radiation state (the input beam) containing $n$ photons resonant with the decay transition $|0\rangle \leftrightarrow |a\rangle$, so that the emission increases their number by one. The quantum states of stimulated emission are given by:

$$|I\rangle = |A^a; n\rangle \quad , \quad (18)$$

$$|F\rangle = |A^0; n+1\rangle . \quad (19)$$

Since one-photon emission again involves a single light-matter interaction, its matrix element is determined from the first term of equation (4), and the $H_{\text{int}}$ within it arises from the second term of equation (7) – rather than the first term used in photon absorption – to produce:

$$M_{fi}^{\text{stim}} = \langle F | H_{\text{int}} | I \rangle = \langle A^0; n+1 \rangle - \mu \cdot \mathcal{E} \langle A^a; n \rangle = i \left( \frac{\hbar c k}{2 \varepsilon_0 V} \right) \mu_{\alpha \alpha} \langle n+1 | \mathcal{E} \cdot a^\dagger | n \rangle$$

$$= i \left( \frac{(n+1)\hbar c k}{2 \varepsilon_0 V} \right) \mu_{\alpha \alpha} \cdot \mathcal{E} . \quad (20)$$
On the assumption of a sufficient number of photons in the absorbed beam so that \((n+1)/V \approx n/V\), the rate of stimulated emission emerges as:

\[
\Gamma = \frac{\pi \rho_a}{\hbar c e_o} [\mu^{\alpha\alpha}]^2 \cos^2 \theta .
\]  

(21)

The minor difference in results for absorption, i.e. equation (17), and stimulated emission, equation (21), is in fact illusionary, since the modulus square of the transition moments for excitation and decay are identical. The equivalence of the two expressions (again cast in a slightly different guise, in terms of ‘B coefficients’) is a feature first identified by Einstein [31]. This is where engagement with the wider system can more obviously come into play: molecules promoted to an excited state can lose their energy by many other means than stimulated emission. (These other routes for decay may, for example, include transfer of energy through collisional deactivation, resonance energy transfer, intramolecular vibrational redistribution etc.) So absorption dominates over stimulated emission unless population inversion is present, as in laser configurations. Conversely, however, in systems under thermal equilibrium where excited states persist beyond the timescale for excitation, then the initial number of photons \(n\) is zero. Thus, with the \((n+1)\) of equation (20) effectively replaced by unity, the result delivers a rate of spontaneous emission. Some further intricacies are necessary to secure a result accounting for the possibility of emission over \(4\pi\) steradians; it suffices to say that the non-zero result relates in a similar way to Einstein’s ‘A coefficient’.

Before moving on, one further observation should be highlighted. As noted earlier, the fact that quantum transitions result from discrete photon interactions is not simply a matter of demonstrating energy conservation – for once the Planck relation is deployed, semiclassical arguments can be made to support that principle. It needs emphasising that the engagement of photon spin is also a crucial element, as it accounts for the well-known angular momentum selection rules of conventional electronic spectroscopy. Moreover, the same principles extend to the significantly more intricate rules that apply to multiphoton transitions and multipole interactions [28, 32].

4. Rayleigh scattering

The single-photon absorption and emission processes discussed so far involve single light-matter interactions – they are, therefore, termed first-order interactions. In this section, we will deal with an important second-order interaction known as linear scattering. The principles and expressions employed in the previous sections are applied here but a number of additional complexities need to be considered for this higher order interaction.

In linear scattering, a single photon transfers its energy to a molecule – which excites it to a virtual intermediate state \(|r\rangle\) – that almost simultaneously releases the energy via the
emission of a photon, often into a different radiation mode (Figure 3). Thus, the radiation undergoes an overall transition \( |n-1\rangle_1 \rightarrow |1\rangle_2 \triangleleft |n\rangle_3 \rightarrow |0\rangle_z \), i.e. it loses a photon from the input mode 1 and generates one in an output mode 2. When the input and output radiation modes are identical, which is known as forward-Rayleigh scattering, the energy and direction of the photons are also identical. Non-forward Rayleigh scattering is when photons have identical energies but travel in different directions. The lifetime of the virtual intermediate states are of the order \( \omega^{-1} \), which allows us to invoke the time-energy uncertainty relation \( \Delta E \Delta t \geq h \) to rationalise that energy conservation does not measurably apply to these virtual states, over their ultrashort lifetimes.

![Energy-level scheme depicting non-forward Rayleigh (elastic) scattering](image)

Figure 3. Energy-level scheme depicting non-forward Rayleigh (elastic) scattering: a photon is absorbed from one radiation mode, and another is emitted into a different mode, at a molecule (or atom) that travels to and from a virtual intermediate state \( |r\rangle \).

In Rayleigh scattering, no net energy is transferred from the photon to the molecule; the scattered photon emerges with the same energy as the initial photon, that is \( k = k' \). It is for this reason that Rayleigh scattering is known as elastic scattering. In inelastic scattering, some energy is transferred from the input photon to the material, or alternatively the molecule can transfer energy to the scattered photon: \( k \neq k' \). Both of these inelastic phenomena leaves the scatterer in a final state that differs from the initial state, being manifestations of the Raman effect. More precisely the former results in the radiation being Stokes shifted, whilst the latter results in the radiation being anti-Stokes shifted. To give an indicative QED calculation of a second-order optical process, we will now derive the rate of Rayleigh scattering (understanding that Raman scattering can be developed along very similar lines).

To begin, we consider a molecule in the ground state \( |E_o\rangle \) that absorbs a photon of energy \( \hbar \omega = \hbar \omega' \) from a radiation field containing \( n \) photons of mode \( (k, \eta) \), leading to an intermediate state for the total system \( |R\rangle \), which then emits a photon of mode \( (k', \eta') \) and energy \( \hbar \omega' \) (remembering that for elastic scattering that \( k = k' \)) that returns the molecule to \( |E_o\rangle \). The initial \( |l\rangle \) and final \( |F\rangle \) system (matter and radiation) states are, respectively;
Because Rayleigh scattering involves the annihilation of a photon and creation of another, and thus the two light-matter interactions correspond to two operations of $H_{int}$, we require second-order perturbation theory to calculate the matrix element of the process; namely, the second term of equation (4). A significant difference from the earlier first-order calculations is that a summation over all possible virtual intermediate states, along with the computation of energy denominators, is required.

Figure 4: The two representative Feynman time-ordered diagrams required for the second-order perturbation theory calculation of the Rayleigh scattering of a photon of mode $(k, \eta)$ into mode $(k', \eta')$. Light-matter system states are represented by the kets, whilst the energy of each state (molecule plus radiation) for elastic scattering is highlighted in red.

In elastic scattering there are two distinct time-orderings, (a) and (b), as exhibited in Figure 4, where (as stated earlier) the virtual intermediate state is not subject to energy conservation, unlike the initial and final states. The intermediate states and their energies are provided in this Figure. The numerator of the matrix element, for the contribution from graph (a), is calculated from the following bra-kets:
\[ \langle R_o | H_{\text{int}} | l \rangle_\xi = \langle A^t; n-1, 0 | -\mu(\xi) \cdot E(R_{\xi}) | A^0; n, 0 \rangle = -i \left( \frac{nhck}{2e_0V} \right)^{\frac{1}{2}} e^{i\nu_{ij}(\xi)}e^{ikR_{\xi}}, \quad (24) \]

\[ \langle F | H_{\text{int}} | R_a \rangle_\xi = \langle A^0; n-1, 1 | -\mu(\xi) \cdot E(R_{\xi}) | A^t; n-1, 0 \rangle = i \left( \frac{hck}{2e_0V} \right)^{\frac{1}{2}} \bar{\sigma}_{ij}(\xi)e^{-ikR_{\xi}}, \quad (25) \]

where the photon modes are suppressed for ease of use, and the energy denominator is given by;

\[ E_i - E_{R_a} = (E_0 + \hbar\omega) - E_r = -(E_{r_0} - \hbar\omega), \quad (26) \]

with the shorthand notation \( E_{r_0} = E_r - E_0 \). In equations (24) and (25) – for reasons that will become apparent when we consider coherence issues – a representative molecule \( \xi \) is specified, located at a position \( R_{\xi} \), meaning that the phase factors of the field expansion (7) are now retained. Next, combining equations (24), (25) and (26) as dictated by second-order perturbation theory, gives;

\[ M^a_{Ri}(\xi) = \frac{\langle F | H_{\text{int}} | R_o \rangle_\xi \langle R_a | H_{\text{int}} | l \rangle_\xi}{E_i - E_{R_a}} \]
\[ = -n^{\frac{1}{2}} \left( \frac{hck}{2e_0V} \right) \sum_r \mu_{ij}^{0r}(\xi) \bar{\sigma}_{ij} \left( \frac{1}{E_{r_0} - \hbar\omega} \right)e^{i(k-k)'R_{\xi}}. \quad (27) \]

Here, to succinctly denote the paired dot products that give rise to the second rank tensor form, we adopt the Einstein implied summation convention for summing over repeated Cartesian indices, with subscripts \( i, j \) each denoting \( x, y, z \). Carrying out the analogous procedure for graph (b) provides;

\[ \langle R_b | H_{\text{int}} | l \rangle_\xi = \langle A^t; n, 1 | -\mu(\xi) \cdot E(R_{\xi}) | A^0; n, 0 \rangle = i \left( \frac{hck}{2e_0V} \right)^{\frac{1}{2}} \bar{\sigma}_{ij}(\xi)e^{-ikR_{\xi}}, \quad (28) \]

\[ \langle F | H_{\text{int}} | R_a \rangle_\xi = \langle A^0; n-1, 1 | -\mu(\xi) \cdot E(R_{\xi}) | A^t; n, 1 \rangle = -i \left( \frac{nhck}{2e_0V} \right)^{\frac{1}{2}} e^{i\nu_{ij}(\xi)}e^{ikR_{\xi}}. \quad (29) \]
noting that the intermediate state is the only difference between graphs (a) and (b) – this corresponds to the two dissimilar states of \( |R \rangle \) in the second term of equation (4) for Rayleigh scattering, which produces the two terms in the final result below – and the energy denominator is given by;

\[
E_i - E_{R_0} = (E_0 + h\omega) - (E_r + 2h\omega) = -(E_{r_0} + h\omega) .
\]  

(30)

Thus, the matrix element contribution from graph (b) is;

\[
M_{R}^{b}(\xi) = \frac{\langle F|H_{\text{int}}|R_{b}\rangle \langle R_{b}|H_{\text{int}}|I \rangle}{E_i - E_{R_0}} = -\frac{n^2}{2e_0V} \sum_{r} \alpha_{i}^{0r}(\xi) \mu_{j}^{0r}(\xi) \bar{e}_{j} \left( \frac{1}{E_{r_0} - h\omega} \right) e^{i(k-k')\cdot R_i} .
\]  

(31)

Since QED requires deployment of both time-ordered diagrams, summing the contributions (a) and (b) gives the matrix element for Rayleigh scattering as;

\[
M_{R}^{\text{Rayleigh}}(\xi) = M_{R}^{a}(\xi) + M_{R}^{b}(\xi) = -\frac{n^2}{2e_0V} \sum_{r} \left[ \alpha_{i}^{0r}(\xi) \mu_{j}^{0r}(\xi) + \mu_{i}^{0r}(\xi) \mu_{j}^{0r}(\xi) \right] \left( \frac{1}{E_{r_0} - h\omega} \right) e^{i(k-k')\cdot R_i} .
\]  

(32)

where the quantity in square brackets on the right-hand side of equation (32) is a second-rank tensor known as the molecular polarisability \( \alpha_{ij}^{00}(\omega,-\omega,\xi) \), i.e.;

\[
\alpha_{ij}^{00}(\omega,-\omega,\xi) = \sum_{r} \left[ \alpha_{i}^{0r}(\xi) \mu_{j}^{0r}(\xi) + \mu_{i}^{0r}(\xi) \mu_{j}^{0r}(\xi) \right] \left( \frac{1}{E_{r_0} - h\omega} \right) e^{i(k-k')\cdot R_i} .
\]  

(33)

This important property, which is possessed by all forms of matter, plays a key role in many optical phenomena; for example, it determines the magnitude of the photon-molecule interactions and the dispersion characteristics. It is also the basis for the two-photon selection rules, rather than those for one-photon couplings related to \( \mu \) which is the origin of two-photon symmetry-allowed electronic transitions that may be forbidden by one-photon interactions. Furthermore, the tensorial nature of the polarisability means
that it has a distinct orientation dependence – a feature sometimes overlooked in the literature.

As in the case of single-photon absorption and emission, the matrix element can be used to calculate the rate of the optical process by using the Fermi rule. In this case of scattering, given molecules that remain in their ground state, the most extensive density of states is for the emergent radiation. So, we use the same formula given by emission above, allowing the differential scattering rate for \( N \) identical molecules to be written as:

\[
d\Gamma = \frac{2\pi n k^4 d\Omega' V}{h} \left( \frac{hc}{2\varepsilon_0 V} \right)^2 \left| \vec{e}_f e_j \sum_{\xi}^N \alpha_{ij}^{(\xi)} (\omega_i - \omega_r, \xi) e^{i(k-k') \cdot R_i} \right|^2 .
\]  

This rate can be converted into an infinitesimal cross section \( d\sigma \) by diving by the photon flux number \( (nc/V) \), from which the differential cross section \( d\sigma/d\Omega' \) immediately follows:

\[
I(k') = \frac{d\Gamma}{d\Omega} \frac{hc}{k'}
\]

\[
= \frac{16\pi k^4}{16\pi k_0^2} \left| \vec{e}_f e_j \sum_{\xi}^N \alpha_{ij}^{(\xi)} (\omega_i - \omega_r, \xi) e^{i(k-k') \cdot R_i} \right|^2 .
\]

At this juncture, the inclusion of phase factors in equation (35) rewards closer attention. Importantly, there is a need to distinguish between forward \( k = k' \) and non-forward scattering \( k \neq k' \). Clearly, in both forward and non-forward Rayleigh scattering \( |k| = |k'| \), but in non-forward scattering the scattering amplitudes are acutely sensitive on the distribution of the positions of the molecules, and the amplitudes from different molecules interfere randomly and the scattering rate is simply a sum of \( N \) independent scattering rates. Non-forward scattering is incoherent. In forward scattering, the scattering amplitudes from the different molecules interfere constructively, being independent of molecular position and, therefore, forward scattering is a coherent process proportional to \( N^2 \). A more detailed analysis of the importance of coherence and wave-vector matching in scattering processes can be found in ref. [3]. In general, for a random distribution of molecular positions \( R_i \), we observe that [33];
Carrying out the modulus square of equation (35), therefore, gives the scattered radiant intensity for non-forward scattering as;

\[
I(k')=\frac{N\delta_{k,0}}{16\pi^2\varepsilon_0}\varepsilon'_k\varepsilon'_l\varepsilon_i\varepsilon_j\alpha_{ij}^{00}(\omega,-\omega)\alpha_{kl}^{00}(\omega,-\omega).
\]  

(37)

It is noteworthy that the radiant intensity for Raman (inelastic) scattering has a similar expression; the main difference is that the initial or the final molecular state is not the ground state. So, unlike Rayleigh (elastic) scattering, the molecule states do not begin and end at the same lowest state: the process is therefore always incoherent, its measured, frequency-shifted scattering signal is linearly dependent on the number of molecules. Developing the theory to explain the selection rules, and how vibrational transitions depend on a change in polarisability during each vibration, requires a Born-Oppenheimer development – perfectly straightforward (see, for example, ref. [34]) – but separable from the present focus on photonic mechanism.

5. Conclusion

In this ‘Century of the Photon’ it is becoming clear that numerous technological innovations depend critically on the quantum nature of light. We have aimed to show that developing and applying the full quantum theory in the description of optical interactions is relatively straightforward – and perhaps it is simpler than is commonly supposed. Moreover, beyond the applications we have illustrated here, it affords a robust framework for conceiving, explaining and understanding many more intricate processes – including those that hinge on the photon for quantum informatics [35, 36].

In this paper, we have derived some of the simplest optical processes and provided some physical insights into what the theory show about them. The same principles can be applied to much more complex mechanisms as, for example, outlined in our recent review article [18]. An obvious but simple extension is the nonlinear, third-order interaction known as second-harmonic generation, in which two input laser photons with frequency \(\omega\) are converted into a single output photon of twice the incident frequency \(\omega' = 2\omega\) (or \(k' = 2k\)) through their interaction with matter. The QED theory follows similar lines to those discussed above; due to its three light-matter interactions, third-order perturbation theory is required – i.e. the third term of equation (4). A short cut to deriving
an expression for this, and other associated hyperpolarisabilities, may be found in another previous paper [37].

In conclusion, our account has aimed to illustrate and make a strong case for a more thorough and substantive account of photon-molecule interactions, and to show by illustration that the necessary quantum field methods are by no means beyond the reach of simple presentation.

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