An algorithm for the nonlinear optical susceptibilities of dipolar molecules, and an application to third harmonic generation

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Abstract.   It is well known that a simple transformation of the electric dipole interaction provides a convenient means for ascertaining the effects of permanent dipoles on the optical behaviour of systems with a response dominated by two energy levels. By establishing the general validity of the procedure for parametric processes such as harmonic generation, it is shown how the detailed structure of the optical susceptibilities associated with arbitrary forms of optical nonlinearity can be ascertained by an algorithmic method, based on a novel interpretation of the relevant quantum electrodynamical Feynman diagrams. Application of the algorithm to second and third harmonic generation illustrates its usefulness and simplicity, whilst also providing new results and revealing features, related to the role of permanent dipoles, which have not hitherto been apparent.

1. Introduction

In the description of optically parametric processes, one is concerned with phenomena mediated by a material which suffers no overall change; at the molecular level these may be termed 'elastic' processes. Familiar examples are optical harmonic generation and multiwave mixing, though the simplest (optically linear) example is forward Rayleigh scattering. Use of the electric dipole approximation in deriving the optical susceptibilities for such processes leads to expressions involving products of transition dipole moments along a connected route beginning and ending in the same, usually ground, state. The term 'transition moment' (used in this connection as a distinction from permanent moments) immediately needs qualifying, however. Each such transition moment embedded in an optical susceptibility tensor connects two *en route* states, at least one of which will be a virtual state. The usual prescriptions of perturbation theory require us to sum such states over the complete set of eigenstates for the unperturbed system, one of which must necessarily generate a diagonal matrix element corresponding to a permanent moment. In this sense, permanent electric dipole moments are particular cases of the transition moments, and they play a significant role (often unacknowledged, though see, for example, recent papers [1–4]) in the structure of any nonlinear susceptibility. The role of such permanent moments in *non*-parametric laser–molecule interactions is relatively well attested—see for example [5–8] and citations therein.

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For polar molecules, it proves [9, 10, 7] that a singular role is played by the vector *difference* or *displacement* between excited and ground-state dipole moments, traditionally given the symbol d. Though such a permanent dipole displacement can be defined for all excited states, for many systems the optical response is dominated by just one excited state, and this is the case we shall consider here. One aim of our work is to verify the general applicability of employing a suitably transformed interaction Hamiltonian which directly isolates terms driven by such a dipole difference—the general validity of such a procedure with regard to parametric processes has not previously been established, and is the first issue to be addressed in this paper. With this result proven, our second aim is to demonstrate through its application a convenient and calculationally expedient way to discover the dependence of nonlinear optical susceptibilities on the dipole displacement.

Specific applications to second- and third-harmonic generation reveal a number of new features, while also serving to illustrate the usefulness and simplicity of the procedure. With the correct choice of convention for the inclusion of resonance damping—see for example [11, 12]—the new algorithm leads directly to results which exhibit proper symmetry with respect to time reversal. Our results for harmonic generation clarify the relative roles of single- and multi-photon resonances; more importantly, they serve to demonstrate that the permanent dipole displacement d can prove the major factor in determining the magnitude of the susceptibility tensor elements, and hence the strength of nonlinear optical response. For third harmonic generation in particular, new effects related to the role of permanent dipoles are discussed. Such results are of particular importance to the many 'push–pull' (giant dipole) organic materials currently being investigated in the pursuit of higher efficiencies for laser frequency conversion [13–17].

2. Parametric processes and the interaction transformation

2.1. Quantum electrodynamical formulation

Consider first the full quantum electrodynamical Hamiltonian in multipolar form:

$$H = H_{\text{rad}} + \sum_\xi H_{\text{mol}}(\xi) + \sum_\xi H_{\text{int}}(\xi). \tag{1}$$

The leading term is the radiation Hamiltonian, the second a sum of the unperturbed Hamiltonian operators for each molecule or site ξ with distinct electronic integrity, and the last a sum of the interaction operators, whose explicit form we detail below, for each of these species with the radiation field. The sum of the first two terms in equation (1) represents a Hamiltonian $H_{\text{sys}}^{(0)}$ whose eigenstates, products of the eigenstates of H_{rad} with those of each $H_{\text{mol}}(\xi)$, form a basis set of *system states* for the standard perturbative treatment in powers of the terms $H_{\text{int}}(\xi)$. In the usual electric dipole approximation we have†

$$H_{\text{int}}(\xi) = -\mu(\xi) \cdot e^\perp(\mathbf{R}_\xi), \tag{2}$$

whereby a molecule at position $\mathbf{R}_\xi$ undergoes dipolar interaction with the transverse electric field of the radiation at that position, $e^\perp(\mathbf{R}_\xi)$. To employ the above interaction Hamiltonian we implement the following mode expansion of the electric field:

$$e^\perp(\mathbf{r}) = \mathrm{i} \sum_{\mathbf{k},\lambda} \left(\frac{\hbar ck}{2\varepsilon_0 V} \right)^{1/2} \{ e^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} - \bar{e}^{(\lambda)}(\mathbf{k}) a^{+(\lambda)}(\mathbf{k}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \}. \tag{3}$$

† Here the interaction is cast in terms of the electric field rather than the electric displacement, to avoid possible confusion in over-use of the symbol d.

Here photon creation and annihilation operators, $a^{+(\lambda)}(\mathbf{k})$ and $a^{(\lambda)}(\mathbf{k})$ respectively, are associated with each radiation mode of wavevector $\mathbf{k}$ and polarization vector $\mathbf{e}^{(\lambda)}$: V is the quantization volume and ε_0 the vacuum permittivity. A key property is that $H_{\mathrm{int}}(\xi)$ is linear in $a^{+(\lambda)}(\mathbf{k})$ and $a^{(\lambda)}(\mathbf{k})$.

To address cases of nonlinear optical response, in general we need to evaluate a probability amplitude or optical parametric signal field A given by [18, 19]

$$A \sim \sum_{\xi} \langle f_{\mathrm{sys}} | \{ H_{\mathrm{int}}(\xi) + H_{\mathrm{int}}(\xi) T_{\mathrm{sub}}(\xi) H_{\mathrm{int}}(\xi) \} | i_{\mathrm{sys}} \rangle, \tag{4}$$

where $T_{\mathrm{sub}}(\xi)$ is the resolvent operator for a subsystem comprising the radiation and molecule ξ alone. The subscript on both the initial and final state labels, i_{sys} and f_{sys}, shows that system states are referred to—and as energy is conserved, both have the same energy, $E_{\mathrm{sys}}^{(0)}$. Moreover for parametric interactions, energy is separately conserved by both the molecular and radiation parts of the system; each summand matrix element on the right-hand side of equation (4) is thus diagonal in the molecular basis but, save in the trivial case of forward Rayleigh scattering or its higher-order analogues, nondiagonal in the radiation basis. Since all molecules other than ξ provide vanishing contributions to each summand, equation (4) can be written as

$$A \sim \sum_{\xi} \langle f_{\mathrm{sub}} | H_{\mathrm{int}} + H_{\mathrm{int}} T_{\mathrm{sub}} H_{\mathrm{int}} | i_{\mathrm{sub}} \rangle_{\xi} \equiv \sum_{\xi} S_{\xi}, \tag{5}$$

given that all states, operators and energies within the Dirac bracket now implicitly refer to the subsystem comprising the radiation and molecule ξ. In fluid media, two-centre interference terms in the signal to be derived from $|A|^2$ survive for all parametric processes, and thus reflect their coherent nature [20].

For each molecule–radiation subsystem the resolvent operator of equations (4) and (5) can be cast in terms of $T_0 = (E_0 - H_0)^{-1}$ and expressed [18] as

$$T_{\mathrm{sub}} = (E_0 - H)^{-1} = (E_0 - H_0 - H_{\mathrm{int}})^{-1} = (E_0 - H_0)^{-1} + (E_0 - H_0)^{-1} H_{\mathrm{int}} (E_0 - H_0)^{-1}$$

$$+ \cdots = \sum_{p=0}^{\infty} [T_0 H_{\mathrm{int}}]^p T_0 \tag{6}$$

where H_0 is the Hamiltonian whose eigenstates are products of the eigenstates of H_{rad} with $H_{\mathrm{mol}}(\xi)$; $H_{\mathrm{int}}(\xi)$ is the operator for the coupling of the radiation and molecular states and E_0 is the corresponding ground-state energy. Then, the probability amplitude S_{ξ} is

$$S_{\xi} \sim \langle f_{\mathrm{sub}} | H_{\mathrm{int}} + \sum_{p=0}^{\infty} \{ H_{\mathrm{int}} [T_0 H_{\mathrm{int}}]^p T_0 H_{\mathrm{int}} \} | i_{\mathrm{sub}} \rangle_{\xi}. \tag{7}$$

Since each operation of H_{int} produces a change by one in photon number, for the case of an n-photon process the result for S_{ξ} has as its leading contribution:

$$S_{\xi}^{(n)} \sim \langle f_{\mathrm{sub}} | H_{\mathrm{int}} (T_0 H_{\mathrm{int}})^{n-1} | i_{\mathrm{sub}} \rangle_{\xi}. \tag{8}$$

Calculation normally proceeds by introducing the completeness relation for the subsystem states:

$$S_{\xi}^{(n)} = \langle f_{\mathrm{sub}} | H_{\mathrm{int}} \prod_{j=1}^{n-1} \left\{ \sum_{s_{\mathrm{sub}}^{(j)}} T_0 | s_{\mathrm{sub}}^{(j)} \rangle \langle s_{\mathrm{sub}}^{(j)} | H_{\mathrm{int}} \right\} | i_{\mathrm{sub}} \rangle_{\xi}. \tag{9}$$

In the above equation the sum over each set of virtual intermediate states represented by $| s_{\mathrm{sub}}^{(j)} \rangle$ comprises all molecular and radiation eigenstates of H_0. Again the linearity of H_{int} ensures that for each operation it either creates or destroys a photon; explicitly effecting in equation (9)

the sum over all intermediate states, and the product over j, singles out the various sequences of allowed routes between the initial and final radiation state corresponding to the familiar time-orderings—see for example [21]. Substituting for the explicit form of H_{int} allows the result for the signal amplitude from each molecule to be represented as the tensor inner product of a radiation tensor $\underline{\gamma}$ and a nonlinear susceptibility tensor $\underline{O}^{fi(\eta\omega)}(\xi)$:

$$S_\xi \equiv \gamma^{(k)}_{\alpha_1\ldots\alpha_n} O^{fi(\eta\omega)}_{\alpha_1\ldots\alpha_n}(\xi), \tag{10}$$

in which there is implied summation over the set of Cartesian indices $\alpha_1\ldots\alpha_n$. The structure of the radiation tensor $\gamma^{(k)}$ is that of an outer product of the beam polarization vectors $e^{(\lambda)}(k)$—according to equation (3), taking the complex conjugate for emitted photons. This tensor also carries factors relating to other beam parameters—which, in the signal derived from $|A|^2$, will manifest the dependence on beam intensities and degrees of coherence [20]. These need concern us no further here.

Our interest is in the nonlinear susceptibility tensor $\underline{O}^{fi(\eta\omega)}(\xi)$, wherein the superscript $(\eta\omega)$ represents a parametric dependence on each beam frequency ω_j, with the multiplier $\eta_j = +1$ for emission and $\eta_j = -1$ for absorption. Dropping the label ξ on each side of the following equation for simplicity, the susceptibility tensor can neatly and concisely be expressed in the following form [22] (in which $\{s\}$ signifies the set of molecular intermediate states and $\{\alpha\}$ the Cartesian indices; $\pi\{\alpha\}$ and $\pi(\eta\omega)$ are a shorthand notation for parallel (linked) permutations of the indices and frequency parameters):

$$O^{fi(\eta\omega)}_{\{\alpha\}} = \sum_{\pi\{\alpha\},\{s\}} \frac{N^{\pi\{\alpha\}\{s\}}_{fi}}{D^{\pi\{\eta\omega\}\{s\}}_{fi}}, \tag{11}$$

with

$$N^{\{\alpha\}\{s\}}_{fi} \equiv \mu^{f s_{n-1}}_{\alpha_n} \mu^{s_{n-1} s_{n-2}}_{\alpha_{n-1}} \cdots \mu^{s_1 i}_{\alpha_1}, \tag{12}$$

$$D^{\{\eta\omega\}\{s\}}_{fi} = \prod_{j=1}^{n-1} \left[E_i - E_{s_j} - \hbar \sum_{i=1}^{j} \eta_{\pi(i)}\omega_{\pi(i)} \right], \tag{13}$$

i.e. a sum of quotients for each of which the numerator is a product of dipole transition moment components, and the denominator is a product of energy factors. It is convenient at this point to give a more compact notation for the algebraic frequency sum $\sum_{i=1}^{j} \eta_{\pi(i)}\omega_{\pi(i)}$, that is $\Omega_\pi(j, 1)$; in those cases where there is no permutation involved the subindex π may be dropped. As so defined, the tensor $\underline{O}^{fi(\eta\omega)}$ differs from common forms of the nonlinear susceptibility $\underline{\chi}$ only through a trivial sign factor $(-)^{n-1}$.

Where any molecular excited state differs from the initial state by an amount similar to the net energy of a subset of the participating photons, it is necessary to properly account for the finite resonance enhancement and the detailed dispersion behaviour. Here it is traditional to include phenomenologically based damping in the energy factors to extend applicability to those frequency regions where such (nonsecular†) resonances occur. There are, nonetheless, two conflicting but equally current conventions concerning the sign of the imaginary addenda which represent the damping, which can lead to physically different results. One dictates, for example, that in the case of harmonic generation the damping should carry opposite signs for interactions preceding and following emission; the other convention dictates that all signs should be the same—see for example [11, 12]. A recent detailed assessment of their legitimacy, on the basis of time-reversal symmetry, unequivocally confirms the latter convention [23]. This

† Secular resonances involve the ground state, and since this has no decay channel it suffers no damping. See, for example, [3].

can be denoted by the introduction of a tilde on E_{s_j}, representing $\tilde{E}_{s_j} \equiv E_{s_j} - \mathrm{i}\Gamma_{s_j}$ where Γ_{s_j} is the damping factor. Notice that the product of sums in equation (9) is here finally reduced to a qualified sum of products, as given by equations (11)–(13), reflecting inclusion only of the permitted time-orderings—the distinguishable permutations of the beam interaction sequence.

2.2. Employment of the fluctuation dipole operator

We now address the implications of employing a transformed electric dipole interaction for treating the nonlinear optical response of systems dominated by two electronic levels. It has been established in a series of recent works that a transformation of the electric dipole interaction is valid for deriving various optical characteristics of molecular systems with a response dominated by two electronic states [5–10, 24, 25]. This procedure relates to the employment of a *fluctuation* dipole operator [26, 3] as given by

$$H'_{\mathrm{int}} = -[\underline{\mu} - \underline{\mu}^{00}] \cdot e^{\perp}, \tag{14}$$

in which the subtracted moment is the permanent dipole of the initial molecular state—usually the ground state; the absence of state superscripts on $\underline{\mu}$ serves as a reminder of its operator status. In the following we shall show how the adoption of (14) for the form of the interaction operator leads to a new and expedient algorithm for the calculation of the requisite nonlinear optical susceptibilities, to be summarized at the end of the section. The reader intent only on direct applications can move directly to that summary.

The obvious corollary to the modification of the interaction Hamiltonian according to equation (14) is the inclusion in H_0 of a counterpart set of terms with opposite sign:

$$H'_0 = H_0 - \delta, \tag{15}$$

defining by δ the extra operator term introduced in equations (14) and (15):

$$\delta = \underline{\mu}^{00} \cdot e^{\perp}. \tag{16}$$

This leaves the overall Hamiltonian of equation (1) unchanged, and signals a recasting of the resolvent operator (6), in terms of $T'_0 = (E_0 - H'_0)^{-1}$, as follows:

$$T_{\mathrm{sub}} = (E_0 - H)^{-1} = (E_0 - H'_0 - H'_{\mathrm{int}})^{-1} = (E_0 - H'_0)^{-1} + (E_0 - H'_0)^{-1} H'_{\mathrm{int}} (E_0 - H'_0)^{-1}$$

$$+ \cdots = \sum_{p=0}^{\infty} T'_0 [T'_0 H'_{\mathrm{int}}]^p \tag{17}$$

in which the factorization is purposely cast in a different form from equation (7), to expedite the development below. Instead of the later equation, we now have an expression in terms of H'_0, H'_{int} and H_{int}:

$$S_{\xi} \sim \langle f_{\mathrm{sub}} | H_{\mathrm{int}} + \sum_{p=0}^{\infty} \{ H_{\mathrm{int}} T'_0 [H'_{\mathrm{int}} T'_0]^p H_{\mathrm{int}} \} | i_{\mathrm{sub}} \rangle_{\xi}, \tag{18}$$

which can be written in terms of H'_{int} and H_0 by further expanding the factor T'_0 in terms of T_0 and δ:

$$T'_0 = (E_0 - H_0)^{-1} + (E_0 - H_0)^{-1}(-\delta)(E_0 - H_0)^{-1} + \cdots = \sum_{m=0}^{\infty} (-1)^m T_0 [\delta T_0]^m. \tag{19}$$

The probability amplitude can then be rewritten as

$$S_{\xi} \sim \langle f_{\mathrm{sub}} | (H'_{\mathrm{int}} - \delta) | i_{\mathrm{sub}} \rangle_{\xi}$$

$$+ \langle f_{\mathrm{sub}} | (H'_{\mathrm{int}} - \delta) \sum_{l,m,p=0}^{\infty} \{ T_0 [(-\delta) T_0]^l [H'_{\mathrm{int}} T_0 [(-\delta) T_0]^m]^p \} (H'_{\mathrm{int}} - \delta) | i_{\mathrm{sub}} \rangle_{\xi}.$$

$$\tag{20}$$

This expression accommodates every order of n (the number of photons involved in the process). For l, m and p (non-negative integers) such that $l + p(m + 1) + 2 = n$, it follows that the leading contribution for an n-photon process is

$$S \sim \langle f_{\text{sub}}|H'_{\text{int}}[T_0 H'_{\text{int}}]^{n-1}|i_{\text{sub}}\rangle + \sum_{p=1}^{n} L^{fi}_{n,p}, \tag{21}$$

where for simplicity we drop the subindex ξ. The first term of equation (21) is the equivalent of equation (8), where the interaction Hamiltonian H_{int} has been replaced with the transformed one, H'_{int}. As it transpires, the $L^{fi}_{n,p}$ terms are all exactly zero—the general proof and explicit expressions for the $L^{fi}_{n,p}$ are given in the appendix.

As an example, let us consider the simple two-photon process of Rayleigh scattering. From equation (20) the probability amplitude is given by

$$S^{(2)} = \langle f_{\text{sub}}|H'_{\text{int}}T_0 H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|(-\delta)T_0 H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|H'_{\text{int}}T_0(-\delta)|i_{\text{sub}}\rangle$$
$$+ \langle f_{\text{sub}}|(-\delta)T_0(-\delta)|i_{\text{sub}}\rangle, \tag{22}$$

and it can be shown that the last three terms vanish. Specifically, the second and third terms in equation (22) can be expressed as

$$\sum_{s_{\text{sub}}} \langle f_{\text{sub}}|(-\delta)T_0|s_{\text{sub}}\rangle \langle s_{\text{sub}}|H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|H'_{\text{int}}T_0|s_{\text{sub}}\rangle \langle s_{\text{sub}}|(-\delta)|i_{\text{sub}}\rangle$$

$$= \sum_{s_s=0,u} \left(\frac{\hbar ck}{2\varepsilon_0 V}\right) \{m(m-1)\}^{1/2} e_i \bar{e}_j$$

$$\times \left\{ \frac{\mu_i^{00} d_j^{s0}}{E_0 - E_s - \hbar\omega} + \frac{\mu_j^{00} d_i^{s0}}{E_0 - E_s + \hbar\omega} + \frac{d_i^{0s} \mu_j^{00}}{E_0 - E_s - \hbar\omega} + \frac{d_j^{0s} \mu_i^{00}}{E_0 - E_s + \hbar\omega} \right\} \delta_{0,s} \tag{23}$$

where s denotes the molecular state of the intermediate state s_{sub} and $d^{s0} = \langle s|\underline{\mu} - \underline{\mu}^{00}|0\rangle$. The fact that the matrix element $\langle 0|(\underline{\mu} - \underline{\mu}^{00})|0\rangle$ is identically zero could be used to justify the null contribution of equation (23). In the more general context of employing transformed Hamiltonians, it is nevertheless expedient to proceed without explicitly invoking this result. For the right-hand side of equation (23) we then have

$$\left(\frac{\hbar ck}{2\varepsilon_0 V}\right) \{m(m-1)\}^{1/2} e_i \bar{e}_j \left\{ \frac{\mu_i^{00} d_j^{00}}{-\hbar\omega} + \frac{d_j^{00} \mu_i^{00}}{\hbar\omega} + \frac{\mu_j^{00} d_i^{00}}{\hbar\omega} + \frac{d_i^{00} \mu_j^{00}}{-\hbar\omega} \right\}$$

$$= \left(\frac{\hbar ck}{2\varepsilon_0 V}\right) \{m(m-1)\}^{1/2} e_i \bar{e}_j \frac{(\hbar\omega - \hbar\omega)}{(-\hbar\omega)(\hbar\omega)} (\mu_i^{00} d_j^{00} + \mu_j^{00} d_i^{00}). \tag{24}$$

Expression (24) is equal to zero not only because the matrix element $d^{00} = \langle 0|(\underline{\mu} - \underline{\mu}^{00})|0\rangle$, but also because it is proportional to the difference in energy between the initial and final state:

$$E_{\text{initial}} - E_{\text{final}} = (E_0 + m\hbar\omega) - (E_0 + (m - 1 + 1)\hbar\omega) = \hbar\omega - \hbar\omega \equiv 0. \tag{25}$$

The fourth term in equation (22) is also proportional to the difference in energy of the initial and final states:

$$\langle f_{\text{sub}}|(-\delta)T_0(-\delta)|i_{\text{sub}}\rangle = \sum_{s_{\text{sub}}} \langle f_{\text{sub}}|(-\delta)T_0|s_{\text{sub}}\rangle \langle s_{\text{sub}}|(-\delta)|i_{\text{sub}}\rangle$$

$$= \left(\frac{\hbar ck}{2\varepsilon_0 V}\right) \{m(m-1)\}^{1/2} \left\{ \frac{\mu_i^{00} \mu_j^{00}}{\hbar\omega} + \frac{\mu_j^{00} \mu_i^{00}}{(-\hbar\omega)} \right\}$$

$$= \left(\frac{\hbar ck}{2\varepsilon_0 V}\right) \{m(m-1)\}^{1/2} \frac{\mu_i^{00} \mu_j^{00}}{(\hbar\omega)^2} \{\hbar\omega - \hbar\omega\}. \tag{26}$$

Therefore the probability amplitude reduces to the first term of equation (22) alone. With this we conclude the application to Rayleigh scattering.

Returning to the most general case, the development of theory described above justifies the adoption of the following single prescription for susceptibility calculations:

$$\underline{\mu}^{uu} \rightarrow \underline{\mu}^{uu} - \underline{\mu}^{00} = \boldsymbol{d}; \qquad \underline{\mu}^{00} \rightarrow 0 \tag{27}$$

whilst the transition dipoles remain unchanged. *When the various time-orderings for any optical processes of interest are drawn up, application of this rule enables expressions involving a connected route which entails any ground-state dipole μ^{00} to be discarded, so long as those entailing the excited-state dipole μ^{uu} are reinterpreted to invoke $\boldsymbol{d}$.* This is the algorithm whose illustrative applications are described in the following section. The method has been explicitly validated for all parametric and nonparametric processes, both degenerate and fully nondegenerate, of rank n. In every case its implementation leads in a matter of lines to results identical to those previously established by substantially more laborious means: for example, see [2, 6].

3. Applications

3.1. Second-harmonic generation

Interesting features emerge in the first case with any significant complexity: second-harmonic generation. Here there are three time-ordered diagrams [27], as illustrated in figure 1. The route of molecular states between the initial (ground) state and the final (also ground) state runs through two virtual states, s_1 and s_2, and in the two-level approximation each of these is summed to represent one of two possibilities, either the ground state 0 or the excited state u. The $(0 \rightarrow s_1 \rightarrow s_2 \rightarrow 0)$ sequences which arise are thus concisely expressible as 0000, 00u0, 0u00, 0uu0. From the three time-orderings we therefore have $3 \times 2^2 = 12$ contributions—each a product of three 'transition' dipoles (one or more of which may be permanent—see the introduction), divided by a product of two energy factors.
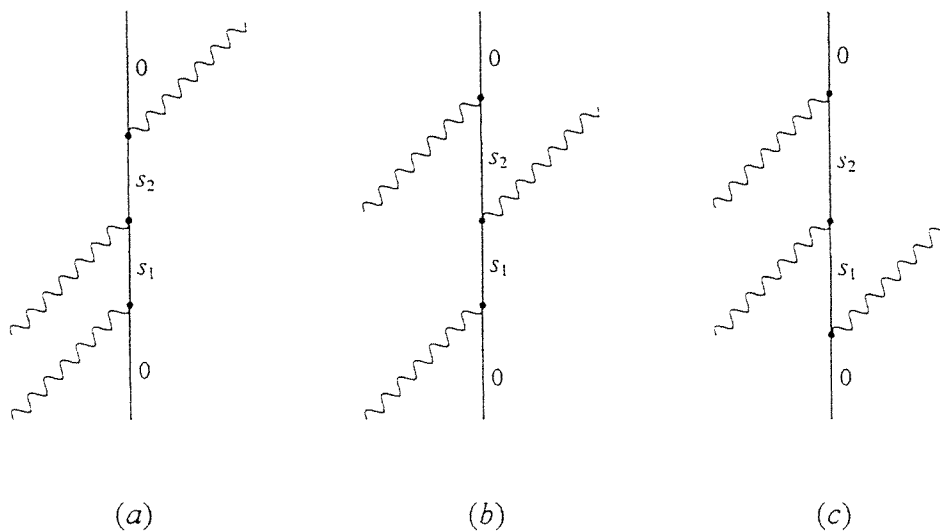

Figure 1. The three time-ordered diagrams for second-harmonic generation.

Application of the algorithm determines that only the state sequence $0uu0$ need be considered in a suitable reinterpretation of the three time-ordered diagrams, since each of the other possibilities includes a 00 segment. From figure 1 we therefore have a two-level hyperpolarizability tensor given by:

$$
O^{00}_{\alpha_1\alpha_2\alpha_3}(-2\omega,\omega,\omega) \equiv \beta_{\alpha_1\alpha_2\alpha_3} = \frac{\mu^{u0}_{\alpha_1} d_{\alpha_2} \mu^{u0}_{\alpha_3}}{(E_0 - E_u + 2\hbar\omega + i\Gamma_u)(E_0 - E_u + \hbar\omega + i\Gamma_u)}
$$
$$
+ \frac{\mu^{u0}_{\alpha_2} d_{\alpha_1} \mu^{u0}_{\alpha_3}}{(E_0 - E_u - \hbar\omega + i\Gamma_u)(E_0 - E_u + \hbar\omega + i\Gamma_u)}
$$
$$
+ \frac{\mu^{u0}_{\alpha_2} d_{\alpha_3} \mu^{u0}_{\alpha_1}}{(E_0 - E_u - \hbar\omega + i\Gamma_u)(E_0 - E_u - 2\hbar\omega + i\Gamma_u)}. \tag{28}
$$

In passing we note that in any application the index-symmetrized form $\beta_{\alpha_1(\alpha_2\alpha_3)} \equiv \frac{1}{2}(\beta_{\alpha_1\alpha_2\alpha_3} + \beta_{\alpha_1\alpha_3\alpha_2})$ would necessarily be invoked because of the corresponding symmetry in the radiation tensor—with which it is eventually contracted to give a result for the signal as in equation (10). It is instructive to compare the above result (28) with that given in our earlier work. In equation (11) of that work [2], a result of almost identical form is presented: trivial differences relate to taking the negative of each denominator factor, writing $(E_u - E_0)$ as E_{u0}, and taking $\Gamma_u \equiv \frac{1}{2}\hbar\gamma_u$. For example, with the first denominator of equation (28) we have $(E_0 - E_u + 2\hbar\omega + i\Gamma_u)(E_0 - E_u + \hbar\omega + i\Gamma_u) \equiv (E_{u0} - 2\hbar\omega - \frac{1}{2}i\hbar\gamma_u)(E_{u0} - \hbar\omega - \frac{1}{2}i\hbar\gamma_u)$, which is identical to that occurring in the corresponding first term from [2]. The sign of the damping in the antiresonant terms—the second and third terms of both corresponding equations being associated with time-ordered diagrams 1(*b*) and (*c*)—was in that work determined by the prevailing convention of opposite signs for interactions preceding and following emission [28, 11]. By adopting in our earlier derivation the convention of a constant sign for damping [12, 23, 29, 30], the result coincides exactly with equation (28), and now without the need to assume that the linewidth is small compared to the harmonic frequency.

3.2. Third-harmonic generation

The second application of our algorithm serves both to illustrate its power and to draw out some new physics. The process of third-harmonic generation is a frequency up-conversion technique currently attracting significant interest for the study of thin films [31–34] and in scanning laser microscopy [35]—one of its attractions being that it is mediated by a susceptibility of even rank, supported by all materials irrespective of their intrinsic symmetry. To derive the form of the susceptibility tensor one employs four time-ordered diagrams, as shown in figure 2. The state route connecting the initial and final (ground) states here runs through three virtual states, s_1, s_2 and s_3, and the two-level approximation requires each to be either the ground or the excited state. In this case, from the four time-orderings we get a total of $4 \times 2^3 = 32$ contributions, each a product of four transition or permanent dipoles divided by three energy quotients.

With the benefit of the algorithmic method delineated above, we can take the four time-orderings and dispense with all but two of the following state sequences; 00000, 000u0, 00u00, 00uu0, 0u000, 0u0u0, 0uu00, 0uuu0: specifically, discarding each sequence which includes the segment 00, we retain only 0u0u0 and 0uuu0. With proper reinterpretation of these remaining cases we thus immediately obtain the following explicit result comprising only eight terms, of which each successive pair results from the successive time-ordered diagrams
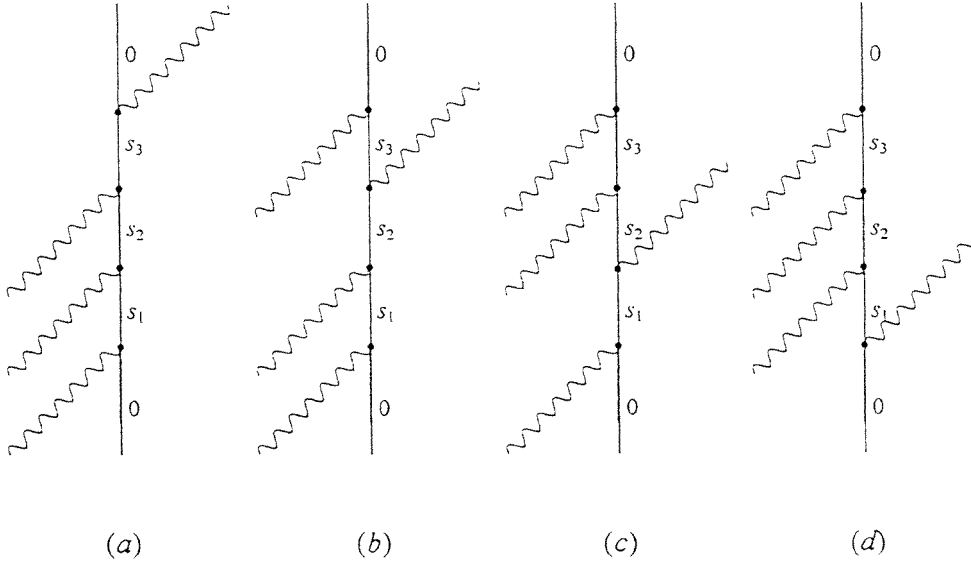
Figure 2. The four time-ordered diagrams for third-harmonic generation.

of figures 2(*a*)–(*d*):

$$
\begin{aligned}
O^{00}_{\alpha_1\alpha_2\alpha_3\alpha_4}(-3\omega,\omega,\omega,\omega) =\ & \frac{\mu^{u0}_{\alpha_1}\mu^{u0}_{\alpha_2}\mu^{u0}_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u + 3\hbar\omega + \mathrm{i}\Gamma_u)(2\hbar\omega)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_1}d_{\alpha_2}d_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u + 3\hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u + 2\hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_1}\mu^{u0}_{\alpha_2}\mu^{u0}_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(2\hbar\omega)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_2}d_{\alpha_1}d_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u + 2\hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_1}\mu^{u0}_{\alpha_2}\mu^{u0}_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(-2\hbar\omega)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_2}d_{\alpha_2}d_{\alpha_1}\mu^{u0}_{\alpha_4}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u - 2\hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u + \hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_1}\mu^{u0}_{\alpha_2}\mu^{u0}_{\alpha_3}\mu^{u0}_{\alpha_4}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(-2\hbar\omega)(E_0 - E_u - 3\hbar\omega + \mathrm{i}\Gamma_u)} \\
&+ \frac{\mu^{u0}_{\alpha_2}d_{\alpha_3}d_{\alpha_4}\mu^{u0}_{\alpha_1}}{(E_0 - E_u - \hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u - 2\hbar\omega + \mathrm{i}\Gamma_u)(E_0 - E_u - 3\hbar\omega + \mathrm{i}\Gamma_u)}
\end{aligned}
$$

(29)

where once again it is the index-symmetrized form, here entailing all permutations of α_2, α_3 and α_4, which will feature in the observables.

One aspect of the result (29) which deserves comment is its amenability for the identification of resonances. Three-photon resonances are manifest in the first and second terms of (29); two-photon resonances feature in the second and fourth, and single-photon resonances in each of the first six. Since exploitation of the latter kind of resonance is in practice usually

avoided because of the competing linear absorption with which it is associated, it is the two- and three-photon resonances which are of the most interest. Under suitable conditions, the susceptibility is therefore in either of those cases largely driven by just two of the contributions to (29), other contributions representing minor corrections of much the same order of magnitude as those relating to the involvement of other molecular energy levels.

Other factors become evident when the relative magnitudes of the dipole difference $|d|$ and the transition dipole $|\mu^{u0}|$ are considered. One immediately striking feature is the observation that the second, fourth, sixth and eighth terms all disappear if $|d| = 0$, leaving only terms associated with virtual excitation routes. (Note that no such routes were manifest in the second-harmonic result. If $|d| = 0$ then the entire expression (28) becomes zero—any process involving an odd number of photons has to entail at least one 00 or uu segment in the interaction sequence). In the third-harmonic case, in particular, both terms associated with two-photon resonances disappear—in other words there can be no two-photon resonance enhancement of third-harmonic generation under such circumstances. This is consistent with the observation that two-photon absorption itself depends critically on the existence of d [5–8]. If, however, $|d| \gg |\mu^{u0}|$, then the even terms of (29) dominate the susceptibility—and in the case of three-photon resonance it is the second term which provides by far the leading contribution. Such considerations should play an important role in implementing strategies for the calculation of nonlinear susceptibilities—for example in the case just cited, the dominant term is of a form which has not previously been identified as representing the major contribution.

4. Conclusion

A procedure has been established for directly identifying the effects of permanent dipoles on the optically parametric behaviour of systems dominated by two energy levels. The method, based on a transformation of the interaction operator, leads to an algorithm involving reinterpretation of the conventional Feynman diagrams. Though illustrated specifically in terms of the electric dipole approximation—where the susceptibility for a process involving n photons is of $E1^n$ form (n electric dipoles)—the procedure is equally amenable to dealing with higher-order multipoles, since they too are linear functions of the photon creation and annihilation operators. Such extensions of the algorithm will prove useful in connection with parametric processes involving an odd number of photons, where the corresponding optical nonlinearities for centrosymmetric substances are dominated by susceptibilities of $E1^{n-1}E2$ (one electric quadrupole) or $E1^{n-1}M1$ (one magnetic dipole) form.

It has been shown how application of the algorithm to second- and third-harmonic generation swiftly leads to results which would otherwise demand considerable algebraic manipulation, even starting from the general Orr and Ward formulation [36], moreover it aids direct identification of the crucial dependence on the difference in dipole moments between the ground and excited state. The case of third-harmonic generation in particular illustrates how the method is amenable to the identification of resonances, and to calculational implementation. Both aspects represent major factors in the formulation, design and characterization of new nonlinear optical materials. Where higher orders of optical nonlinearity are concerned, as for example in the various five- and six-wave processes currently of interest [37–46], exploratory work shows that the algorithm will enormously simplify derivation of the appropriate susceptibilities.

Appendix

Equation (21) expresses the probability amplitude for an n-photon process $(n > 1)$, in the subsystem formed by *one* molecule and the radiation, in a form including the terms $L_{n,p}^{fi}$. The explicit form of these is as follows:

$$L_{n,p}^{fi} = \sum_{m_1=0}^{n-p} \sum_{m_2=0}^{n-p-\sigma(1)} \cdots \sum_{m_p=0}^{n-p-\sigma(p-1)} \left\{ \langle f_{\text{sub}}|[H'_{\text{int}}T_0]^{n-p-\sigma(p)} \right.$$

$$\left. \times \prod_{l=1}^{p-1}[(-\delta)T_0[H'_{\text{int}}T_0]^{m_l}](-\delta)[T_0H'_{\text{int}}]^{m_p}|i_{\text{sub}}\rangle \right\} \tag{A.1}$$

where the $\sigma(r)$ are defined for $1 \leqslant r \leqslant p$ as

$$\sigma(r) = \sum_{j=1}^{r} m_j. \tag{A.2}$$

The expression for $L_{n,p}^{fi}$, equation (A.1), is sufficiently intricate to warrant further analysis and exemplification, beyond the simple case in section 2.2, for which $n = 2$ and p has two possible values: 1 and 2. Consider the $n = 3$ case, where $p = 1, 2, 3$; the expressions for the different values of p are:

- $p = 1$

$$L_{3,1}^{fi} = \sum_{m_1=0}^{2} \langle f_{\text{sub}}|[H'_{\text{int}}T_0]^{2-m_1}(-\delta)[T_0H'_{\text{int}}]^{m_1}|i_{\text{sub}}\rangle \tag{A.3a}$$

- $p = 2$

$$L_{3,2}^{fi} = \sum_{m_1=0}^{1} \sum_{m_2=0}^{1-m_1} \langle f_{\text{sub}}|[H'_{\text{int}}T_0]^{1-m_1-m_2}(-\delta)T_0[H'_{\text{int}}T_0]^{m_1}(-\delta)[T_0H'_{\text{int}}]^{m_2}|i_{\text{sub}}\rangle \tag{A.3b}$$

- $p = 3$

$$L_{3,3}^{fi} = \sum_{m_1=0}^{0} \sum_{m_2=0}^{0-m_1} \sum_{m_3=0}^{0-m_1-m_2} \langle f_{\text{sub}}|[H'_{\text{int}}T_0]^{-m_1-m_2-m_3}(-\delta)T_0[H'_{\text{int}}T_0]^{m_1}(-\delta)T_0$$

$$\times [H'_{\text{int}}T_0]^{m_2}(-\delta)[T_0H'_{\text{int}}]^{m_3}|i_{\text{sub}}\rangle. \tag{A.3c}$$

In equation (A.3c) the sums over m_1, m_2 and m_3 collapse to a single term in which these indices are identically zero. This characteristic occurs in any case where p is equal to n. When equations (A.3a)–(A.3c) are expanded the resulting expression for $S^{(3)}$ becomes

$$S^{(3)} = \langle f_{\text{sub}}|H'_{\text{int}}T_0H'_{\text{int}}T_0H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|H'_{\text{int}}T_0H'_{\text{int}}T_0(-\delta)|i_{\text{sub}}\rangle$$

$$+ \langle f_{\text{sub}}|H'_{\text{int}}T_0(-\delta)T_0H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|(-\delta)T_0H'_{\text{int}}T_0H'_{\text{int}}|i_{\text{sub}}\rangle$$

$$+ \langle f_{\text{sub}}|H'_{\text{int}}T_0(-\delta)T_0(-\delta)|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|(-\delta)T_0H'_{\text{int}}T_0(-\delta)|i_{\text{sub}}\rangle$$

$$+ \langle f_{\text{sub}}|(-\delta)T_0(-\delta)T_0H'_{\text{int}}|i_{\text{sub}}\rangle + \langle f_{\text{sub}}|(-\delta)T_0(-\delta)T_0(-\delta)|i_{\text{sub}}\rangle. \tag{A.4}$$
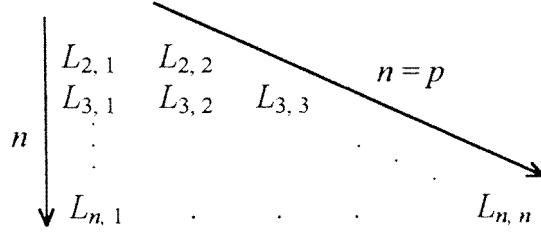
Figure A1. Induction scheme.

The probability amplitude $S^{(3)}$ is easier to understand when written explicitly, as in (A.4). It has a term with no δ operators present, three with a single δ operator, three with two δ operators and one with three δ operators. The probability amplitude for a *specific n*-photon process follows similar lines. The format of expression (A.4) is not useful for the general development, however. Then it is necessary to establish connections between the expressions of the different orders.

Casting results in terms of $L_{n,p}^{fi}$, it is possible to show by induction that each one of these terms is proportional to the difference in energy between the initial and final states of the subsystem, and which through energy conservation therefore do not contribute to the probability amplitude. For the special case when $p = (n-1)$, the $L_{n,n-1}^{fi}$ also cancels because it is proportional to the matrix element $\langle 0|(\mu - \mu^{00})|0\rangle$, but for generality we will conduct a proof for all n and $p (\leqslant n)$. Since $L_{n,p}^{fi}$ depends on two indices, it is helpful to follow a scheme where induction can be applied (figure A1). Supposing that for a given n and all $p \leqslant n$ the $L_{n,p}^{fi}$ is effectively proportional to the difference in energy, it is to be shown that it is also valid for $L_{n+1,p}^{fi}$. This proof will not be sufficient, it being also necessary to show that if for a given $n = p$ the $L_{n,n}^{fi}$ is proportional to the energy difference, so is $L_{n+1,n+1}^{fi}$ (diagonal in the scheme of figure A1).

Let us first establish a link between the expressions of $L_{n+1,p}$ and $L_{n,p}$. From (A.1) the $L_{n+1,p}^{fi}$ coefficient can be written as follows:

$$L_{n+1,p}^{fi} = \sum_{m_1=0}^{n+1-p} \cdots \sum_{m_p=0}^{n+1-p-\sigma(p-1)} \left\{ \langle f_{\text{sub}}|[H'_{\text{int}} T_0]^{n+1-p-\sigma(p)} \right.$$
$$\left. \times \prod_{l=1}^{p-1}\{(-\delta)T_0[H'_{\text{int}} T_0]^{m_l}\}(-\delta)[T_0 H'_{\text{int}}]^{m_p}|i_{\text{sub}}\rangle \right\}. \tag{A.5}$$

It is now necessary to express (A.5) in terms of $L_{n,p}^{si}$, where $s (\equiv s_{\text{sub}})$ is an intermediate state for the $(n+1)$-photon process. To do so let us consider the indices in the sums. If $m_1 = n+1-p$, the rest of the m_i indices (with $i = 2, \ldots, p$) are null, and $L_{n+1,p}^{fi}$ can be re-expressed as

$$L_{n+1,p}^{fi} = \langle f_{\text{sub}}|(-\delta)T_0[H'_{\text{int}} T_0]^{n+1-p}[(-\delta)T_0]^{p-2}(-\delta)|i_{\text{sub}}\rangle$$
$$+ \sum_{m_1=0}^{n-p} \cdots \sum_{m_p=0}^{n+1-p-\sigma(p-1)} \left\{ \langle f_{\text{sub}}|[H'_{\text{int}} T_0]^{n+1-p-\sigma(p)} \right.$$
$$\left. \times \prod_{l=1}^{p-1}\{(-\delta)T_0[H'_{\text{int}} T_0]^{m_l}\}(-\delta)[T_0 H'_{\text{int}}]^{m_p}|i_{\text{sub}}\rangle \right\}. \tag{A.6}$$

In a similar manner, for a given m_1, if the $m_2 = n + 1 - p - m_1$, the rest of the indices $(m_3, m_4, \ldots, m_p)$ will be zero. Repeating this argument for all indices, the final result is

$$
\begin{aligned}
L_{n+1,p}^{fi} = {}& \langle f_{\text{sub}}|(-\delta)T_0[H_{\text{int}}'T_0]^{n+1-p}[(-\delta)T_0]^{p-2}(-\delta)|i_{\text{sub}}\rangle \\
&+ \sum_{m_1=0}^{n-p}\{\langle f_{\text{sub}}|(-\delta)T_0[H_{\text{int}}'T_0]^{m_1}(-\delta)T_0[H_{\text{int}}'T_0]^{n+1-p-m_1}[(-\delta)T_0]^{p-3}(-\delta)|i_{\text{sub}}\rangle\} \\
&+ \cdots + \sum_{m_1=0}^{n-p}\cdots\sum_{m_r=0}^{n-p-\sigma(r-1)}\left\{\langle f_{\text{sub}}|\prod_{l=1}^{r}\{(-\delta)T_0[H_{\text{int}}'T_0]^{m_l}\}\right. \\
&\times (-\delta)[T_0H_{\text{int}}']^{n+1-p-\sigma(r)}[(-\delta)T_0]^{p-2-r}(-\delta)|i_{\text{sub}}\rangle\Bigg\} \\
&+ \cdots + \sum_{m_1=0}^{n-p}\cdots\sum_{m_{p-1}=0}^{n-p-\sigma(p-2)}\left\{\langle f_{\text{sub}}|\prod_{l=1}^{p-1}\{(-\delta)T_0[H_{\text{int}}'T_0]^{m_l}\}\right. \\
&\times (-\delta)[T_0H_{\text{int}}']^{n+1-p-\sigma(p-1)}|i_{\text{sub}}\rangle\Bigg\} \\
&+ \sum_{m_1=0}^{n-p}\cdots\sum_{m_p=0}^{n-p-\sigma(p-1)}\left\{\langle f_{\text{sub}}|[H_{\text{int}}'T_0]^{n+1-p-\sigma(p)}\right. \\
&\times \prod_{l=1}^{p-1}\{(-\delta)T_0[H_{\text{int}}'T_0]^{m_l}\}(-\delta)[T_0H_{\text{int}}']^{m_p}|i_{\text{sub}}\rangle\Bigg\}.
\end{aligned}
\tag{A.7}
$$

In the third line of (A.7) there are implicit terms whose general form is given in terms of r. These terms can be obtained following the arguments for the construction of the first and second term. Including the second and the fourth line, there are $(p-1)$ terms of this form, with $1 \leqslant r \leqslant (p-1)$.

We can now express $L_{n+1,p}^{fi}$ in a simple and compact form. All the terms given by the subindex r (second, third and fourth lines of (A.7)) combined with the first line of equation (A.7) can be expressed in terms of $L_{n,p-1}^{si}$. On the other hand, the last line in equation (A.7) can be expressed in terms of $L_{n,p}^{si}$. The final expression is

$$
L_{n+1,p}^{fi} = \sum_{\pi}\left\{\sum_{s_{\text{sub}}}[\langle f_{\text{sub}}|(-\delta)T_0|s_{\text{sub}}\rangle L_{n,p-1}^{si}] + \sum_{s_{\text{sub}}}[\langle f_{\text{sub}}|H_{\text{int}}'T_0|s_{\text{sub}}\rangle L_{n,p}^{si}]\right\}.
\tag{A.8}
$$

In equation (A.8) the intermediate states s_{sub} have been introduced, by summing over the complete set of eigenstates of H_0. It is important to notice that, although s_{sub} is an intermediate state for $L_{n+1,p}^{fi}$, it is the final state for $L_{n,p'}^{si}$ ($p' = p, p - 1$). The expression (A.8) is completely general and no assumption has been made about the system: therefore it is valid for both parametric and nonparametric processes.

With an expression, (A.8), connecting the $L_{n+1,p}^{fi}$ from an $(n+1)$-photon process with $L_{n,p'}^{si}$ from an n-photon process, we now examine the specific form of the $L_{n,p'}^{si}$. In two-level systems whose initial molecular state is the ground state, the molecular part of the intermediate states s_{sub} can be either $|u\rangle$ or $|0\rangle$, and it is necessary to have expressions of $L_{n,p'}^{si}$ where these two possibilities are entertained. When the initial and final molecular states are the ground state the following identity is valid:

$$
L_{n,p'}^{00} = \sum_{\pi}\left\{\Theta_n^{fi} \times \frac{\mu_{i_n}^{0u}\{d;\mu^{u0}\}\mu_{i_{p'+1}}^{u0}}{\hbar\Omega_{\pi}(n,p'+1)\{\Delta E\}} \times \frac{\mu_{i_{p'}}^{00}\cdots\mu_{i_1}^{00}}{\prod_{r=1}^{p'}\hbar\Omega_{\pi}(r,1)} \times (E_{\text{initial}} - E_{\text{final}})\right\}
\tag{A.9}
$$

where the function Θ_n^{fi} accounts for the radiation parameters

$$\Theta_n^{fi} \equiv \prod_{l=1}^{n} \left[(-i) \left(\frac{\hbar c k_l}{2V\varepsilon_0} \right)^{1/2} g(m_l) \right]$$

(A.10)

and the function $g(m_l)$ is defined in terms of the number of photons of each mode, $m(\mathbf{k}_l, \lambda_l)$, participating in the process:

$$g(m_l) = \begin{cases} (m(\mathbf{k}_l, \lambda_l))^{1/2} e_l^{(\lambda_l)}(\mathbf{k}_l) & \text{for photon absorption} \\ (m(\mathbf{k}_l, \lambda_l) + 1)^{1/2} \bar{e}_l^{(\lambda_l)}(\mathbf{k}_l) & \text{for photon emission.} \end{cases}$$

(A.11)

In expression (A.9) the term in braces, $\{d; \mu^{u0}\}$, is a direct product of transition dipole moments between states u and 0 ($\mu^{u0} = \mu^{0u}$), and/or the d vector ($d = \underline{\mu}^{uu} - \underline{\mu}^{00}$), while $\{\Delta E\}$ is defined as the product of the energy difference between the intermediate states (i_{n-1} to $i_{p'+1}$) and the energy of the intermediate state $i_{p'}$. The sum over π denotes that all possible time-orderings are considered and $\Omega_\pi(k, l)$ is defined in the main text, following equation (13). A similar expression is also valid for the case where the final molecular state is the excited state u:

$$L_{n, p'}^{u0} = \sum_\pi \left\{ \Theta_n^{fi} \times \frac{d_{i_n}\{d; \mu^{u0}\}\mu_{i_{p'+1}}^{u0}}{(E_0 - E_u + \hbar\Omega_\pi(n, p'+1))\{\Delta E\}} \right.$$
$$\left. \times \frac{\mu_{i_{p'}}^{00} \cdots \mu_{i_1}^{00}}{\prod_{r=1}^{p'} \hbar\Omega_\pi(r, 1)} \times (E_{\text{initial}} - E_{\text{final}}) \right\}.$$

(A.12)

To unravel equation (A.8) we also need to cast the difference $(E_{\text{initial}} - E_{\text{final}})$ in terms of $\Omega_\pi(k, l)$:

$$E_{\text{initial}} - E_{\text{final}} = \left((E_{\text{mol}})_{\text{initial}} + \sum_p m_p \hbar\omega_p \right) - \left((E_{\text{mol}})_{\text{final}} + \sum_p m'_p \hbar\omega_p \right)$$
$$= (E_{\text{mol}})_{\text{initial}} - (E_{\text{mol}})_{\text{final}} + \sum_p (m_p - m'_p)\hbar\omega_p$$

(A.13)

where m_p and m'_p are initial and final occupation numbers of the mode $\mathbf{k}_p, \lambda_p$ ($|\mathbf{k}_p| = \omega_p/c$), and $\sum_p (m_p - m'_p)\hbar\omega_p = \sum_l \eta_l \hbar\omega_l$. In a parametric process, $(E_{\text{mol}})_{\text{initial}} = (E_{\text{mol}})_{\text{final}}$, and equation (A.13) reduces to

$$(E_{\text{initial}} - E_{\text{final}}) = \sum_l \eta_l \hbar\omega_l \equiv \hbar\Omega(n+1, 1).$$

(A.14)

Assuming that expressions (A.9) and (A.12) are valid for a certain n, expression (A.8) can be used to show that a similar result holds for $(n+1)$. First, when the initial and final molecular states are the ground state, equation (A.8) reduces to

$$L_{n+1, p}^{00} = \Theta_{n+1}^{fi} \sum_\pi \left\{ \frac{\mu_{i_p}^{00} \mu_{i_{n+1}}^{0u}\{d; \mu^{u0}\}\mu_{i_{p+1}}^{u0}}{\hbar\Omega_\pi(n+1, p+1)\{\Delta E\}} \frac{\mu_{i_{p-1}}^{00} \cdots \mu_{i_1}^{00}}{\prod_{r=1}^{p-1} \hbar\Omega_\pi(r, 1)} \right.$$
$$\left. + \frac{\mu_{i_{n+1}}^{0u}\{d; \mu^{u0}\}\mu_{i_{p+1}}^{u0}}{\{\Delta E\}} \frac{\mu_{i_p}^{00} \cdots \mu_{i_1}^{00}}{\prod_{r=1}^{p} \hbar\Omega_\pi(r, 1)} \right\}$$
$$= \Theta_{n+1}^{fi} \sum_\pi \frac{\mu_{i_{n+1}}^{0u}\{d; \mu^{u0}\}\mu_{i_{p+1}}^{u0}\mu_{i_p}^{00} \cdots \mu_{i_1}^{00}}{\hbar\Omega_\pi(n+1, p+1)\{\Delta E\} \prod_{r=1}^{p} \hbar\Omega_\pi(r, 1)}$$
$$\times \{\hbar\Omega_\pi(n+1, p+1) + \hbar\Omega_\pi(p, 1)\}.$$

(A.15)

Equation (A.15) is proportional to

$$\{\hbar\Omega_\pi(n+1,\,p+1)+\hbar\Omega_\pi(p,\,1)\}=\hbar\Omega_\pi(n+1,\,1)\equiv\hbar\Omega(n+1,\,1),\qquad\text{(A.16)}$$

which from equation (A.14) is identical to $(E_{\text{initial}}-E_{\text{final}})$. Therefore equation (A.15) is equivalent to (A.9).

In the case where the final molecular state is the excited state we obtain the following expression:

$$
\begin{aligned}
L_{n+1,p}^{u0}=\Theta_{n+1}^{fi}\sum_\pi&\left\{\frac{\mu_{i_p}^{00}\mu_{i_{n+1}}^{u0}\{d;\mu^{u0}\}\mu_{i_{p+1}}^{u0}}{(E_0-E_u+\hbar\Omega_\pi(n+1,\,p+1))\{\Delta E\}}\frac{\mu_{i_{p-1}}^{00}\cdots\mu_{i_1}^{00}}{\prod_{r=1}^{p-1}\hbar\Omega_\pi(r,\,1)}\right.\\
&\left.+\frac{\mu_{i_{n+1}}^{u0}\{d;\mu^{u0}\}\mu_{i_{p+1}}^{u0}}{\{\Delta E\}}\frac{\mu_{i_p}^{00}\cdots\mu_{i_1}^{00}}{\prod_{r=1}^{p}\hbar\Omega_\pi(r,\,1)}\right\}\\
=\Theta_{n-1}^{fi}\sum_\pi&\frac{\mu_{i_{n+1}}^{u0}\{d;\mu^{u0}\}\mu_{i_{p+1}}^{u0}\mu_{i_p}^{00}\cdots\mu_{i_1}^{00}}{(E_0-E_u+\hbar\Omega_\pi(n+1,\,p+1))\{\Delta E\}\prod_{r=1}^{p}\hbar\Omega_\pi(r,\,1)}\\
\times&\{E_0-E_u+\hbar\Omega_\pi(n+1,\,p+1)+\hbar\Omega_\pi(p,\,1)\}.\qquad\text{(A.17)}
\end{aligned}
$$

The factor in equation (A.17) is the difference in energy between the initial and the final state

$$\{E_0-E_u+\hbar\Omega_\pi(n+1,\,p+1)+\hbar\Omega_\pi(p,\,1)\}=E_{0u}+\hbar\Omega_\pi(n+1,\,1)\equiv E_{0u}+\hbar\Omega(n+1,\,1)$$
$$\text{(A.18)}$$

as shown in equation (A.13). Therefore, equation (A.18) is the same as (A.12) for the $(n+1)$-photon process.

We have now proved that if any $L_{n,p}^{fi}$ is proportional to the energy difference between the final and the initial state, then this will be also true for $L_{n+1,p}^{fi}$. This allows us to 'move' downwards in the scheme of figure A1 (increasing n). To complete the proof it is necessary to show that if $L_{n,n}^{fi}$ is proportional to the difference in energy between the initial and the final molecular states, then so will be $L_{n+1,n+1}^{fi}$. The general expression for $L_{n,n}^{fi}$ is deduced from equation (A.1) by setting $p=n$,

$$L_{n,n}^{fi}=\langle f_{\text{sub}}|[(-\delta)T_0]^{n-1}(-\delta)|i_{\text{sub}}\rangle.\qquad\text{(A.19)}$$

This expression can be written in terms of the electric dipole moment of the ground state, by introducing intermediate states s_{sub}:

$$L_{n,n}^{fi}=\Theta_n^{fi}\sum_{\pi^n}\frac{\mu_{i_n}^{00}\cdots\mu_{i_1}^{00}}{\prod_{r=1}^{n-1}\hbar\Omega_{\pi^n}(r,\,1)}\delta_{f_{\text{mol}},i_{\text{mol}}}.\qquad\text{(A.20)}$$

This means that the term $L_{n,n}^{fi}$ can only be nonzero in a parametric process. Subject to these kinds of processes, it is easily shown that the expression (A.20) can be written as

$$l_{n,n}^{00}=\Theta_\pi^{fi}\frac{\mu_{i_n}^{00}\cdots\mu_{i_1}^{00}}{\prod_{r=1}^{n}\eta_r\hbar\omega_r}\hbar\Omega_{\pi^n}(n,\,1)\qquad\text{(A.21)}$$

which is identically zero ($\Omega_{\pi^n}(n,\,1)=\Omega(n,\,1)$ is independent of the permutation π^n, see equation (A.14)). For equation (A.21) to be valid, it is necessary to prove the following identity:

$$\sum_{\pi^n}\frac{1}{\prod_{r=1}^{n-1}\Omega_{\pi^n}(r,\,1)}=\frac{\Omega_{\pi^n}(n,\,1)}{\prod_{l=1}^{n}\Omega_{\pi^n}(l,\,l)}.\qquad\text{(A.22)}$$

For $n=2$ the identity is satisfied:

$$\sum_{\pi^2}\frac{1}{\prod_{r=1}^{1}\Omega_{\pi^2}(r,\,1)}=\frac{1}{\eta_1\omega_1}+\frac{1}{\eta_2\omega_2}=\frac{\eta_1\omega_1+\eta_2\omega_2}{\eta_1\omega_1\eta_2\omega_2}=\frac{\Omega_{\pi^2}(2,\,1)}{\prod_{l=1}^{2}\Omega_{\pi^2}(l,\,l)}.\qquad\text{(A.23)}$$

Now let us suppose that the identity is valid for an n-photon process, equation (A.22). Then the $(n + 1)$ case should be also valid. For the $(n + 1)$ case, it can be seen from equation (A.20) that $L_{n+1,n+1}^{fi}$ is proportional to

$$\sum_{\pi^{n+1}} \left[\prod_{r=1}^{n} \Omega_{\pi^{n+1}}(r, 1) \right]^{-1}. \tag{A.24}$$

Since the symbol π^{n+1} is the permutation of a set of $(n + 1)$ elements, equation (A.24) can be expressed differently, by partitioning the set into two subsets of n and 1 elements respectively and considering all possible partitions [47]:

$$\sum_{m=1}^{n+1} \sum_{\pi_m^{n+1}} \left[\prod_{r=1}^{n} \Omega_{\pi_m^{n+1}}(r, 1) \right]^{-1} = \sum_{m=1}^{n+1} \sum_{\pi_m^{n+1}} \left[(\Omega_{\pi_m^{n+1}}(n, 1)) \prod_{r=1}^{n-1} (\Omega_{\pi_m^{n+1}}(r, 1)) \right]^{-1}$$

$$= \sum_{m=1}^{n+1} (\Omega(m + n, m + 1))^{-1} \sum_{\pi_m^{n+1}} \left[\prod_{r=1}^{n-1} (\Omega_{\pi_m^{n+1}}(r, 1)) \right]^{-1} \tag{A.25}$$

where π_m^{n+1} is the permutation of n of the $(n + 1)$ photons present in the process, excluding $(\eta_m \omega_m)$. For example, the π_3^{n+1} embraces all the permutations of the following waves: $\eta_1\omega_1, \eta_2\omega_2, \eta_4\omega_4, \ldots, \eta_{n+1}\omega_{n+1}$. Rewriting equation (A.25) using the n case result, equation (A.22), we obtain

$$\sum_{m=1}^{n+1} (\Omega(m + n, m + l))^{-1} \left(\prod_{l=1}^{n} \eta_{m+l}\omega_{m+l} \right)^{-1} \Omega(m + n, m + l)$$

$$= \sum_{m=1}^{n+1} \left\{ \left(\prod_{l=1}^{n+1} \eta_{m+l}\omega_{m+l} \right)^{-1} \eta_{m+n+1}\omega_{m+n+1} \right\} \tag{A.26}$$

where we have defined $\eta_i\omega_i$ for $(n + 1 < i \leqslant 2(n + 1))$ as $\eta_{n+2}\omega_{n+2} = \eta_1\omega_1$, $\eta_{n+3}\omega_{n+3} = \eta_2\omega_2$, and so on. This last expression leads us to the desired identity

$$\sum_{\pi^{n+1}} \left[\prod_{r=1}^{n} \Omega_{\pi^{n+1}}(r, 1) \right]^{-1} = \left(\prod_{l=1}^{n+1} \Omega_{\pi^{n+1}}(l, l) \right)^{-1} \Omega_{\pi^{n+1}}(n + 1, 1). \tag{A.27}$$

Expressions (A.15), (A.17) and (A.21) prove that all the $L_{n,p}^{fi}$ are proportional to the energy difference between the initial and final states. Therefore, when energy conservation is imposed, the first contribution to the probability amplitude for an n-photon process is, as given by the first term of equation (21) in the main text, simply:

$$S^{(n)} \sim \langle f_{\text{sub}} | H_{\text{int}}' [T_0 H_{\text{int}}']^{n-1} | i_{\text{sub}} \rangle. \tag{A.28}$$

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