

Chapter 2

Response Functions

2.1 Causal Response

Response functions form a wide class of both classical and quantum quantities. Synonyms of response functions are linear and non-linear susceptibilities of different kinds, as well as polarizability and hyperpolarizabilities. The defining characteristic of a response function $\chi(t)$ is causality of a map that it establishes between perturbing quantity $E(t)$ and a responding quantity $P(t)$.¹ In case of a linear response function, it is accomplished by an integral relation:

$$P(t) = \int_0^{\infty} \chi^{(1)}(\tau) E(t - \tau) d\tau. \quad (2.1)$$

One may examine by inspection that (2.1) guarantees that values of $E(t)$ at times earlier than t_0 do not contribute to $P(t_0)$. It also allows for response $P(t_0)$ to persist for all times $t > t_0$ even if field $E(t)$ is zero at these times. For example, taking time profile as delta function for $E(t) = E \delta(t)$, and taking $\chi^{(1)}$ as being non-zero only on an interval $0 < t < t_M$ leads to the following response $P(t)$:

$$P(t) = \begin{cases} E\chi^{(1)}(t) & \text{if } 0 < t < t_M \\ 0 & \text{if } t > t_M \end{cases} \quad (2.2)$$

Multiplying (2.1) by $e^{i\omega t}$, integrating in time t from $-\infty$ to ∞ , changing variable in left hand side (LHS) $t' = t - \tau$ and using definition of Fourier Transforms one gets frequency domain representation of linear response:

$$P(\omega) = \chi^{(1)}(\omega) E(\omega), \quad (2.3)$$

¹ Both $P(t)$ and $E(t)$ are assumed to be observable (i.e. real).

where linear response function is:

$$\chi^{(1)}(\omega) = \int_0^{\infty} \chi^{(1)}(t) e^{i\omega t} dt. \quad (2.4)$$

Sometimes it is convenient to replace (2.4) with a conventional Fourier Transform by multiplying $\chi^{(1)}(t)$ by step function $\theta(t)$ and extending limits of integration to $-\infty$. Generalizations of (2.1) and (2.3) to higher order response are:

$$P^{(n)}(t) = \int_0^{\infty} \dots \int_0^{\infty} \chi^{(n)}(\tau_1, \dots, \tau_n) E(t - \tau_1) \dots E(t - \tau_n) d\tau_1 \dots d\tau_n, \quad (2.5)$$

$$P^{(n)}(\omega) = \frac{1}{(2\pi)^{(n-1)}} \int_0^{\infty} \dots \int_0^{\infty} \chi^{(n)}(\omega; \omega_1, \dots, \omega_n) E(\omega_1) \dots E(\omega_n) \times \delta(\omega - \omega_1 - \dots - \omega_n) d\omega_1 \dots d\omega_n. \quad (2.6)$$

Delta function appearing in (2.6) enforces conservation of energy.

2.2 Kramers-Kronig

Causality of response functions leads to several properties that are intrinsic to this class of functions.² For linear response, from (2.4) it follows that $\chi^{(1)}(-\omega) = (\chi^{(1)}(\omega))^*$. If ω is complex, then it turns into:

$$\chi^{(1)}(-\omega^*) = (\chi^{(1)}(\omega))^*. \quad (2.7)$$

Kramers-Kronig dispersion relations are the consequence of (2.7). Kramers-Kronig relations connect real and imaginary parts of $\chi^{(1)}$ via a Hilbert Transform:

$$\Re(\chi^{(1)}(\omega)) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Im(\chi^{(1)}(\xi))}{\xi - \omega} d\xi, \quad (2.8)$$

$$\Im(\chi^{(1)}(\omega)) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Re(\chi^{(1)}(\xi))}{\xi - \omega} d\xi. \quad (2.9)$$

² The proof of these relations could be found in [1].

These are routinely used in calculations as well as in experimental work, where they are used for optical data inversion, for example for deducing dispersion from absorption spectra.

Analogue of (2.7) for general nonlinear case exists for real frequencies

$$\chi^{(n)}(-\omega_1, \dots, -\omega_n) = (\chi^{(n)}(\omega_1, \dots, \omega_n))^*, \quad (2.10)$$

and for some nonlinear processes for complex frequencies. It has been shown that analogs of Kramers-Kronig (2.8 and 2.9) for nonlinear processes in form of multidimensional Hilbert Transforms do not generally exist. The cases for which they exist include all orders of higher harmonic generation, for which KK takes the following form:

$$\Re(\chi^{(n)}(-n\omega; \omega, \dots, \omega)) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Im(\chi^{(n)}(-n\omega'; \omega', \dots, \omega'))}{\omega' - \omega} d\omega', \quad (2.11)$$

$$\Im(\chi^{(n)}(-n\omega; \omega, \dots, \omega)) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Re(\chi^{(n)}(-n\omega'; \omega', \dots, \omega'))}{\omega' - \omega} d\omega'. \quad (2.12)$$

A further discussion of application of Kramers-Kronig relations to nonlinear optics could be found in [2].

2.3 Symmetry Relations

In this section we specialize to the response functions that describe electronic polarization by external electric fields \mathbf{E} . These functions are tensors of $(n + 1)$ rank, where n is the order of nonlinearity. Besides symmetry relation (2.10) that follows from causality of response, there are two other kinds of symmetries: one related to structural symmetry of material and another to permutation properties of response function.³

2.3.1 Permutation Symmetries

The most general of permutation symmetries is Intrinsic Permutation Symmetry. It follows from the fact that one can not distinguish physical order of the fields appearing in expressions of the following form:

$$\chi_{ij_1 j_2 \dots j_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) E_{j_1}(\omega_1) E_{j_2}(\omega_2) \dots E_{j_n}(\omega_n).$$

³ In depth discussion of this subject could be found in [3].

From this follows property that allows us to permute indices j_k simultaneously with the corresponding frequency ω_k :

$$\chi_{ij_1j_2\dots j_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) = \chi_{ij_2j_1\dots j_n}^{(n)}(-\omega_\sigma; \omega_2, \omega_1, \dots, \omega_n). \quad (2.13)$$

As a result, number of distinct permutations enters as a factor for the series of equivalent terms in calculations of polarization response. For example, $\chi_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) = \chi_{ikj}^{(2)}(-\omega_\sigma; \omega_2, \omega_1)$ and second order polarization will become:

$$P_i^{(2)}(-\omega_\sigma) = \frac{1}{2\pi} \frac{1}{2!} \sum_{jk} D \int \chi_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) \times E_j(\omega_1) E_k(\omega_2) \delta(\omega_\sigma - \omega_1 - \omega_2) d\omega_2,$$

where $D = 2$ is a number of distinct permutations of fields $E(\omega)$, $2!$ —coefficient of Taylor expansion, and 2π is Fourier Transform factor.

In case of lossless media $Im(\chi^{(n)}) = 0$ and IPS becomes Full Permutation Symmetry, where all indices can be permuted simultaneously with corresponding frequencies:

$$\begin{aligned} \chi_{ij_1j_2\dots j_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) &= \chi_{j_nj_2j_1\dots i}^{(n)}(-\omega_n; \omega_2, \omega_1, \dots, -\omega_\sigma) \\ &= \chi_{j_1j_2i\dots j_n}^{(n)}(-\omega_1; \omega_2, -\omega_\sigma, \dots, \omega_n). \end{aligned} \quad (2.14)$$

In case of lossless $Im(\chi^{(n)}) = 0$ and dispersionless media $Re(\chi^{(n)}) = const.$ one has Kleinman Symmetry which allows one to permute indices without regard to frequencies:

$$\begin{aligned} \chi_{ij_1j_2\dots j_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) &= \chi_{j_nj_2j_1\dots i}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) \\ &= \chi_{j_1j_2i\dots j_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n). \end{aligned} \quad (2.15)$$

2.3.2 Structural Symmetries

Spatial arrangement of atoms in molecules and solids is frequently symmetric. The point group of material structural symmetry \mathcal{S} is a finite subgroup of the full symmetry group of Hamiltonian. It can be shown that the related response functions must also possess the same point group. Let $S_{nm}^{(g)}$ be a matrix representing g th element of this group. Since a response function of n th order is a tensor of $n + 1$ rank, it transforms according to:

$$\chi_{p i \dots, j}^{(n)} = \sum_{s k \dots, m} \chi_{s k \dots, m}^{(n)} S_{ps}^{(g)} S_{ik}^{(g)} \dots S_{jm}^{(g)}. \quad (2.16)$$

If the order of the group is N_g then, there exist N_g constraints of type (2.16) that can be used to reduce the number of independent elements. As an illustration consider inversion symmetry that is an element of T_h , O_h and other point groups. Its matrix representation is $S_{ij}^{(inversion)} = -\delta_{ij}$. In case of even order (nonlinear) response function, from (2.16) follows:

$$\chi_{p i \dots, j}^{(2n)} = - \sum_{s k \dots, m} \chi_{s k \dots, m}^{(2n)} \delta_{ps} \delta_{ik} \dots \delta_{jm} = -\chi_{p i \dots, j}^{(2n)} = 0. \quad (2.17)$$

Therefore even orders of nonlinear response vanish if the material possesses inversion symmetry. The tables indicating non-vanishing elements for the first, second and third order response functions for several point groups may be found in [4].

2.4 Quantum Field Theory Response Formalism

Typically, (hyper) polarizabilities are defined as coefficients of Taylor series expansion of polarization $P(t)$:

$$P(t) = \chi^{(1)} E(t) + \frac{1}{2!} \chi^{(2)} E^2(t) + \dots \quad (2.18)$$

In this expansion, the hyperpolarizabilities are formally partial derivatives of the “total”, generally time dependent polarization in respect to the electric field $E(t)$:

$$\chi_{ijk}^{(2)} = \frac{D}{2!} \frac{\partial^2 P_i}{\partial E_j \partial E_k}, \quad (2.19)$$

where D is degeneracy factor. This definition is purely classical and is frequently supplemented by a qualification such as “...if the series converge, then the hyperpolarizabilities could be defined as (2.18) ...”. Since convergence of (2.18) generally requires electric field to be small $E \ll 1$, it raises a question whether the classical definition has any relevance in Nonlinear optics, because in practice the electric field has to be strong in order for the nonlinear phenomena to appear. One may even go as far as to question the existence and the applicability of response functions to the description of any strong field phenomena. In this section we try to address this issue. We define the optical response functions through the quantum density–density response functions that are in turn related to higher order density fluctuations.

To underline the quantum mechanical nature of nonlinear optical response we need to extend the textbook theory of linear response [5] to higher orders. The many-body Hamiltonian is taken in second quantization:

$$\hat{H} = \int d^3x \hat{\psi}^\dagger(x) T(x) \hat{\psi}(x) + \frac{1}{2} \int \int d^3x d^3x' \hat{\psi}^\dagger(x) \hat{\psi}^\dagger(x') \times \frac{e}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}(x') \hat{\psi}(x) + \hat{H}^{ext} \quad (2.20)$$

where $x = (\mathbf{x}, t, spin)$, c_k, c_k^\dagger are field annihilation and creation operators, $\psi_k(x)$ are single particle states and $\hat{\psi}, \hat{\psi}^\dagger$ are field operators: $\hat{\psi}(x) = \sum_k \psi_k(x) c_k$, $\hat{\psi}^\dagger(x) = \sum_k \psi_k^\dagger(x) c_k^\dagger$. The external interaction is described in general by $\hat{H}^{ext} = \int d^3x \hat{n}(x) \phi^{ext}(x)$, where $\hat{n}(x)$ is density operator $\hat{n}(x) = \hat{\psi}^\dagger(x) \hat{\psi}(x)$. Taking external potential as $\phi^{ext}(x) = e \mathbf{r} \cdot \mathbf{E}(t)$ leads to one of the forms of dipole approximation for photon-electron interaction:

$$\begin{aligned} \hat{H}^{ext} &= e \sum_{ij} \langle i | \mathbf{r} \cdot \mathbf{E}(t) | j \rangle c_i^\dagger c_j = \int d^3x \hat{\psi}^\dagger(x) e \mathbf{r} \cdot \mathbf{E}(t) \hat{\psi}(x) \\ &= e \int d^3x \hat{n}(x) \mathbf{r} \cdot \mathbf{E}(t). \end{aligned} \quad (2.21)$$

Next, we expand the many-body state vector $|\Psi_S(t)\rangle$ in terms of time ordered products of external interaction $T(H^{ext}(t') \dots H^{ext}(t'_{\dots}))$

$$\begin{aligned} |\Psi_S(t)\rangle &= e^{-\frac{iHt}{\hbar}} \left(1 - \frac{i}{\hbar} \int dt' H^{ext}(t') \right. \\ &\quad \left. - \frac{1}{2! \hbar^2} \int dt' dt'' T(H^{ext}(t') H^{ext}(t'')) + \dots \right) |\Psi_S(0)\rangle \end{aligned} \quad (2.22)$$

and use it to compute the density fluctuation $\delta\langle\hat{n}(x)\rangle$:

$$\delta\langle\hat{n}(x)\rangle = \langle\Psi_S(t)|\hat{n}_S(x)|\Psi_S(t)\rangle - \langle\Psi_S(0)|\hat{n}_S(x)|\Psi_S(0)\rangle = \langle\hat{n}(x)\rangle - \langle\hat{n}(x)\rangle_0. \quad (2.23)$$

We observe that the density fluctuation could be represented as a series with k th term being a function of k th power of external potential ϕ^{ext} :

$$\delta\langle\hat{n}(\mathbf{x}, t)\rangle = \sum_k \delta\langle\hat{n}^{(k)}(\mathbf{x}, t; (\phi^{ext})^k)\rangle. \quad (2.24)$$

The non-linear response starts with the second order contribution

$$\begin{aligned} \delta\langle\hat{n}^{(2)}(x)\rangle &= \frac{1}{2! \hbar^2} \int d^4x' d^4x'' \phi^{ext}(x') \phi^{ext}(x'') \\ &\quad \times \langle\Psi_S(0)|[[\hat{n}_H(x'), \hat{n}_H(x'')], \hat{n}_H(x)]|\Psi_S(0)\rangle. \end{aligned} \quad (2.25)$$

Introducing the second order density-density response function $\Xi^{(2)}$

$$\Xi^{(2)}(x; x', x'') = \theta(t - t')\theta(t' - t'') \frac{\langle \Psi_S(0) | [[\hat{n}_H(x'), \hat{n}_H(x)], \hat{n}_H(x'')] | \Psi_S(0) \rangle}{\hbar^2 \langle \Psi_S(0) | \Psi_S(0) \rangle}, \quad (2.26)$$

the second order density fluctuation could be written as

$$\delta \langle \hat{n}^{(2)}(\mathbf{x}, \omega) \rangle = \frac{1}{4\pi} \int \Xi^{(2)}(\omega; \omega', \omega'', \mathbf{x}, \mathbf{x}', \mathbf{x}'') \phi^{ext}(\omega', \mathbf{x}') \phi^{ext}(\omega'', \mathbf{x}'') \times \delta(\omega - \omega' - \omega'') d^3 x' d^3 x'' d\omega' d\omega''. \quad (2.27)$$

For the finite systems, such as molecules, we can use the density fluctuation to directly compute polarization \mathbf{P} (in practice only a change in polarization $\Delta \mathbf{P}(t)$ is relevant)

$$\mathbf{P} = \int d^3 x \mathbf{x} \delta \langle \hat{n}(x) \rangle, \quad (2.28)$$

which could also be written as a series analogous to (2.24) :

$$\mathbf{P}(t) = \sum_k \mathbf{P}^{(k)}(t, (E)^k). \quad (2.29)$$

The second term corresponds to the second order nonlinear optical response:

$$\mathbf{P}^{(2)}(t) = \int d^3 x \mathbf{x} \delta \langle \hat{n}^{(2)}(\mathbf{x}, t) \rangle = \frac{1}{2!} \int \chi_{ijk}^{(2)}(t; t', t'') E_j(t') E_k(t'') dt' dt'', \quad (2.30)$$

where $\chi_{ijk}^{(2)}$ is the first hyperpolarizability. Fourier transforming (2.30) yields

$$P_i^{(2)}(\omega) = \mathcal{K} \int \chi_{ijk}^{(2)}(\omega; \omega', \omega'') E_j(\omega') E_k(\omega'') \delta(\omega - \omega' - \omega'') d\omega' d\omega'', \quad (2.31)$$

where \mathcal{K} is factor from Table 5.2. Comparing (2.27) and (2.31) we see that optical susceptibilities could be obtained directly from density-density response function:

$$\chi^{(2)}(\omega; \omega', \omega'') = \int \Xi^{(2)}(\omega; \omega', \omega'', \mathbf{x}, \mathbf{x}', \mathbf{x}'') \mathbf{x} \mathbf{x}' \mathbf{x}'' d^3 x d^3 x' d^3 x''.$$

The Eqs. (2.29) and (2.18) are both the expansions of the total polarization in the external electric fields, and therefore the terms with the same power of electric field must be equal. This should convince the reader that the hyperpolarizabilities obtained via a classical expansion of the total polarization are in fact quantum mechanical quantities. Their existence and properties are governed by the mechanisms of photon-electron interaction that is specific for a system. Each k th term is related to k -photon process, and the number of the terms is restricted by the energy conservation. Therefore, the classical expansion (2.18) should be viewed as a finite polynomial rather than series, and the question of its convergence is not relevant.

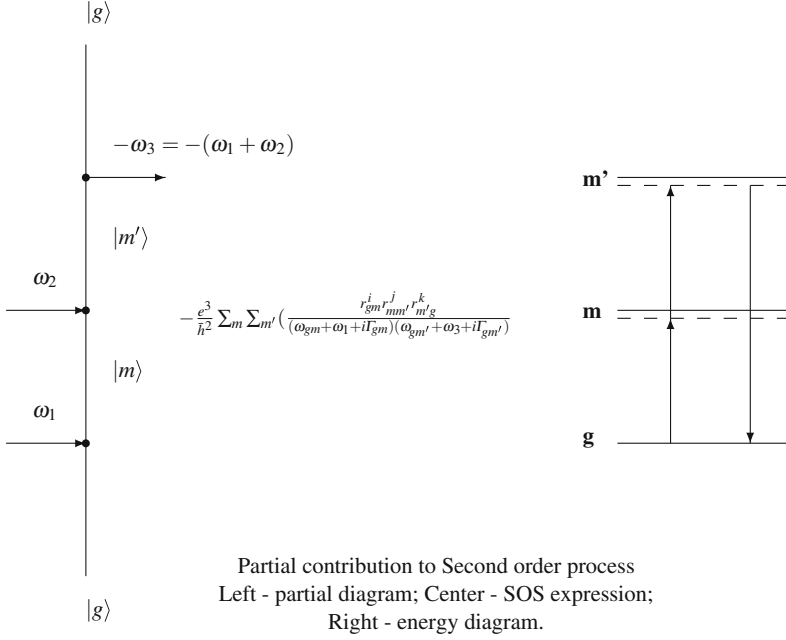


Fig. 2.1 A partial diagram for second order process: $\chi^{(2)}(-\omega_3; \omega_1, \omega_2)$. $|m\rangle$ and $|m'\rangle$ are virtual states

2.5 Diagrammatic Technique for Susceptibilities

In this section we present rules that facilitate drawing pictorial representation of n th order of polarization expansions of type (2.31) and writing down corresponding expressions for matrix elements $\chi_{ij\dots k}^{(n)}$. This diagrammatic technique is analogous to construction of non-relativistic Feynman Diagrams [6, 7]. The resulting expressions for $\chi^{(n)}$ are essentially the same as those one would obtain from matrix elements of electric dipole operator using wavefunctions calculated to n th order of perturbation theory. For n th order process

1. Draw a (vertical) line. On the line draw $n + 1$ vertices.
2. This will partition line into $n + 2$ segments. Label first and the last segments with initial $|g\rangle$ and final states $|g'\rangle$. Label remaining segments with intermediate (generally virtual) states: $|m\rangle, |m'\rangle, \dots$
3. Each vertex corresponds to a matrix element of external potential, that in case of electric dipole interaction becomes $\langle m'|e r_j|m\rangle = e r_{m'm}^j$. Here r_j is j th Cartesian component of position operator \hat{r} . Distribute components over vertices.
4. Draw a (horizontal) arrow in/out of each vertex. Label arrows pointing to vertex with $+\omega$. This corresponds to absorption of photon with energy $\hbar\omega$. Label arrows pointing out of vertex with $-\omega'$. This corresponds to emission of photon with energy $\hbar\omega'$.

5. For each intermediate state $|m\rangle$ write down propagator $\frac{1}{\Delta_{mg} - i\Gamma_{mg}}$ where Δ_{mg} is energy of state $|m\rangle$: $\Delta_{mg} = E_m - E_g + \hbar \sum_i \pm \omega_i$, and Γ_{mg} is line width of $|m\rangle \rightarrow |g\rangle$ transition
6. Write down expression corresponding to the diagram by summing up over all intermediate states m products of $n + 1$ vertices with n propagators.
7. Repeat the steps above for all permutations of frequencies ω_i , sum up resulting expressions.

For example, for a second order process that starts at ground state, then absorbs two photons with energies $\hbar\omega_1$ and $\hbar\omega_2$, then emits a photon with energy $\hbar\omega_3 = \hbar(\omega_1 + \omega_2)$ and ends at ground state one gets diagram (Fig. 2.1) with corresponding expression:

$$-\frac{e^3}{\hbar^2} \sum_{mm'} \frac{r_{gm}^i r_{mm'}^j r_{m'g}^k}{(\omega_{gm} + \omega_1 + i\Gamma_{gm})(\omega_{gm'} + \omega_3 + i\Gamma_{gm'})}. \quad (2.32)$$

Diagrams resulting in permutation of ω_1, ω_2 and ω_3 are shown on diagram (Fig. 2.2), and the summed expression is

$$\begin{aligned} \chi_{ijk}^{(2)}(-\omega_3; \omega_1, \omega_2) = & -\frac{e^3}{\hbar^2} \sum_m \sum_{m'} \left(\frac{r_{gm}^i r_{mm'}^j r_{m'g}^k}{(\omega_{gm} + \omega_1 + i\Gamma_{gm})(\omega_{gm'} + \omega_3 + i\Gamma_{gm'})} \right. \\ & + \frac{r_{gm}^j r_{mm'}^k r_{m'g}^i}{(\omega_{gm} + \omega_1 + i\Gamma_{gm})(\omega_{gm'} - \omega_2 + i\Gamma_{gm'})} \\ & + \frac{r_{gm}^k r_{mm'}^j r_{m'g}^i}{(\omega_{gm} - \omega_3 + i\Gamma_{gm})(\omega_{gm'} - \omega_2 + i\Gamma_{gm'})} \\ & + \frac{r_{gm}^j r_{mm'}^i r_{m'g}^k}{(\omega_{gm} + \omega_2 + i\Gamma_{gm})(\omega_{gm'} + \omega_3 + i\Gamma_{gm'})} \\ & + \frac{r_{gm}^i r_{mm'}^k r_{m'g}^j}{(\omega_{gm} + \omega_2 + i\Gamma_{gm})(\omega_{gm'} - \omega_1 + i\Gamma_{gm'})} \\ & \left. + \frac{r_{gm}^k r_{mm'}^i r_{m'g}^j}{(\omega_{gm} - \omega_3 + i\Gamma_{gm})(\omega_{gm'} + \omega_1 + i\Gamma_{gm'})} \right). \quad (2.33) \end{aligned}$$

Diagrams with corresponding expressions are a useful tool in analysis of various nonlinear processes. However, the expressions obtained are virtually useless for calculations of susceptibilities of real materials. The reason is that it requires summation over an infinite number of states m, m', \dots These obviously include excited states, which are difficult to obtain for any systems except very few simple atoms and molecules. Actual application of this technique is known as Sum Over States

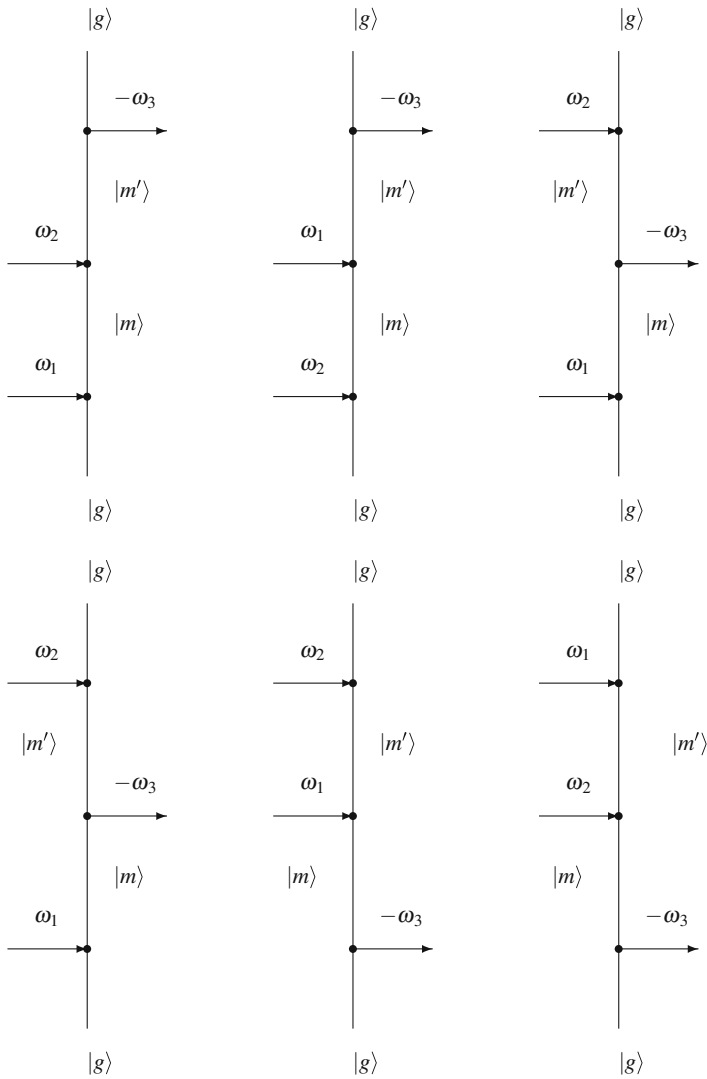


Fig. 2.2 Non-equivalent diagrams for second order process: $\chi^{(2)}(-\omega_3; \omega_1, \omega_2)$

approach, and involves additional approximations. A typical approximation is a truncation of infinite summation to just a few states, sometimes as little as two or three.

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