Quantum-Mechanical
Theory of the Nonlinear Optical Susceptibility
Contents:

3.1. Introduction

3.2. Schrödinger Calculation of Nonlinear Optical Susceptibility

3.3. Density Matrix Formulation of Quantum Mechanics

3.4. Perturbation Solution of the Density Matrix Equation of Motion

3.5. Density Matrix Calculation of the Linear Susceptibility

3.6. Density Matrix Calculation of the Second-Order Susceptibility

3.7. Density Matrix Calculation of the Third-Order Susceptibility

3.8. Electromagnetically Induced Transparency

3.9. Local-Field Corrections to the Nonlinear Optical Susceptibility
In this chapter, we use the laws of quantum mechanics to derive explicit expressions for the nonlinear optical susceptibility.

• (1) these expressions display the functional form of the nonlinear optical susceptibility and hence show how the susceptibility depends on material parameters such as dipole transition moments and atomic energy levels

• (2) these expressions display the internal symmetries of the susceptibility

• (3) these expressions can be used to make predictions of the numerical values of the nonlinear susceptibilities.
The idea behind resonance enhancement of the nonlinear optical susceptibility is shown schematically in Fig. 3.1.1 for the case of third-harmonic generation.

**Figure 3.1.1** Third-harmonic generation described in terms of virtual levels (a) and with real atomic levels indicated (b).
The idea behind resonance enhancement of the nonlinear optical susceptibility is shown schematically in Fig. 3.1.1 for the case of third-harmonic generation.

third-harmonic generation in terms of the virtual levels introduced in Chapter 1

real atomic levels, indicated by solid horizontal lines
Three possible strategies for enhancing the efficiency of third-harmonic generation through the technique of resonance enhancement are illustrated in Fig. 3.1.2.

**Fig. 3.1.2** Three strategies for enhancing the process of third-harmonic generation.

- **(a)** The one-photon transition is nearly resonant.
- **(b)** The two-photon transition is nearly resonant.
- **(c)** The three-photon transition is nearly resonant.
Schrödinger Equation Calculation of the Nonlinear Optical Susceptibility

At first a review on quantum mechanics:

- the time-dependent Schrödinger equation

\[ i \hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \]

Hamiltonian for a free atom:

\[ \hat{H} = \hat{H}_0 + \hat{V}(t) \]

\[ \hat{V}(t) = -\mu \cdot \vec{E}(t) \]

\[ \hat{\mu} = -e\hat{r} \]
Energy Eigenstates:

For the case in which no external field is applied to the atom, the Hamiltonian $\hat{H}$ is simply equal to $\hat{H}_0$, and Schrödinger’s equation possesses solutions in the form of energy eigenstates. These states have the form:

$$\psi_n(r, t) = u_n(r)e^{-i\omega_nt}$$

By substituting this form into the Schrödinger equation $\hat{H}_0u_n(r) = E_nu_n(r)$,

$n$ is a label used to distinguish the various solutions. For future convenience, we assume that these solutions are chosen in such a manner that they constitute a complete, orthonormal set satisfying the condition

$$\int u_m^*u_n d^3r = \delta_{mn}$$

$$E_n = \hbar\omega_n$$
Perturbation Solution to Schrödinger’s Equation:

For the general case in which the atom is exposed to an electromagnetic field, Schrödinger’s equation, we replace the Hamiltonian by:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t)$$

where $0 \leq \lambda \leq 1$ corresponds to the actual physical situation.

We now seek a solution to Schrödinger’s equation in the form of a power series in $\lambda$:

$$\psi(\mathbf{r}, t) = \psi^{(0)}(\mathbf{r}, t) + \lambda \psi^{(1)}(\mathbf{r}, t) + \lambda^2 \psi^{(2)}(\mathbf{r}, t) + \cdots$$

By substituting this form into the Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

we obtain:

1. $$i\hbar \frac{\partial \psi^{(0)}}{\partial t} = \hat{H}_0 \psi^{(0)}$$
2. $$i\hbar \frac{\partial \psi^{(N)}}{\partial t} = \hat{H}_0 \psi^{(N)} + \hat{V} \psi^{(N-1)}, \quad N = 1, 2, 3 \ldots$$
gives the probability amplitude that, to Nth order in the perturbation, the atom is in energy eigenstate $|\psi^{(N)}\rangle$ at time $t$.

If $\star$ is substituted into equation 2, we find that the probability amplitudes obey the system of Equations:

$$i\hbar \sum_l \dot{a}_l^{(N)} u_l(r) e^{-i\omega_l t} = \sum_l a_l^{(N-1)} \hat{V} u_l(r) e^{-i\omega_l t}$$
To simplify this equation, we multiply each side from the left by $U^*_m$ and we integrate the resulting equation over all space. Then through use of the orthonormality condition, we obtain the equation:

$$a_m^{(N)}(t) = (i\hbar)^{-1} \sum_l a_l^{(N-1)}(t) V_{ml}(t)e^{i\omega_{ml} t}$$

$$V_{ml} \equiv \langle u_m | \hat{V} | u_l \rangle = \int u_m^* \hat{V} u_l d^3r$$

$$\omega_{ml} \equiv \omega_m - \omega_l$$

Once the probability amplitudes of order $N-1$ are determined, the amplitudes of the next higher order ($N$) can be obtained by straightforward time integration. In particular, we find that:

$$a_m^{(N)}(t) = (i\hbar)^{-1} \sum_l \int_{-\infty}^{t} dt' V_{ml}(t') a_l^{(N-1)}(t')e^{i\omega_{ml} t'}$$
To determine the first-order amplitudes $a^{(1)}_m(t)$ we set $a^{(0)}_l$ in equal to $\delta_{lg}$, corresponding to an atom known to be in state $g$ in zeroth order.

We represent the optical field $\tilde{E}(t)$ as a discrete sum of (positive and negative) frequency components as:

$$\tilde{E}(t) = \sum_p E(\omega_p) e^{-i\omega_p t}$$

Through use of $\star$ & $\hat{V}(t) = -\hat{\mu} \cdot \tilde{E}(t)$ we can then replace $V_{ml}(t')$ by:

$$V_{ml}(t') = - \sum_p \mu_{ml} \cdot E(\omega_p) \exp(-i\omega_p t')$$

$\mu_{ml} = \int u^*_m \hat{\mu} u_l d^3r$ (electric dipole transition moment)
\[ V_{ml}(t') \]

\[ a_m^{(N)}(t) = (i\hbar)^{-1} \sum_l \int_{-\infty}^{t} dt' V_{ml}(t') a_l^{(N-1)}(t') e^{i\omega_{ml}t'} \]

\[ \text{N=1} \]
\[ a_m^{(1)}(t) = \frac{1}{\hbar} \sum_p \frac{\mu_{mg} \cdot E(\omega_p)}{\omega_{mg} - \omega_p} e^{i(\omega_{mg} - \omega_p)t} \]

\[ \text{N=2} \]
\[ a_n^{(2)}(t) = \frac{1}{\hbar^2} \sum_p \sum_q \sum_m \frac{[\mu_{nm} \cdot E(\omega_q)][\mu_{mg} \cdot E(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} e^{i(\omega_{ng} - \omega_p - \omega_q)t} \]

\[ \text{N=3} \]
\[ a_v^{(3)}(t) = \frac{1}{\hbar^3} \sum_p \sum_q \sum_r \sum_{mn} \frac{[\mu_{vn} \cdot E(\omega_r)][\mu_{nm} \cdot E(\omega_q)][\mu_{mg} \cdot E(\omega_p)]}{(\omega_{vg} - \omega_p - \omega_q - \omega_r)(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \times e^{i(\omega_{vg} - \omega_p - \omega_q - \omega_r)t} \]
Linear Susceptibility

- According to the rules of quantum mechanics, the expectation value of the electric dipole moment is given by:

\[
\langle \tilde{p} \rangle = \langle \psi | \hat{\mu} | \psi \rangle
\]

the lowest-order contribution to \( \langle \tilde{p} \rangle \)

\[
\langle \tilde{p}^{(1)} \rangle = \langle \psi^{(0)} | \hat{\mu} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{\mu} | \psi^{(0)} \rangle
\]

By substituting \( \psi^{(0)} \) & \( \psi^{(1)} \) we find that:

\[
\langle \tilde{p}^{(1)} \rangle = \frac{1}{\hbar} \sum_p \sum_m \left( \frac{\mu_{gm} \cdot \mathbf{E}(\omega_p)}{\omega_{mg} - \omega_p} e^{-i\omega_p t} + \frac{[\mu_{mg} \cdot \mathbf{E}(\omega_p)]^* \mu_{mg}}{\omega_{mg}^* - \omega_p} e^{i\omega_p t} \right)
\]

\[
\omega_{mg} = \frac{(E_m - E_g)}{\hbar} - i\frac{\Gamma_m}{2}
\]

the population decay rate of the upper level \( m \)
we formally replace \( \omega_p \) by \(-\omega_p\) in the second term, in which case the expression becomes:

\[
\langle \tilde{p}^{(1)} \rangle = \frac{1}{\hbar} \sum_p \sum_m \left( \frac{\mu_{gm} [\mu_{mg} \cdot \mathbf{E}(\omega_p)]}{\omega_{mg} - \omega_p} e^{-i \omega_p t} + \frac{[\mu_{mg} \cdot \mathbf{E}(\omega_p)]^* \mu_{mg}}{\omega_{mg}^* - \omega_p} e^{i \omega_p t} \right)
\]
\[ \chi_{ij}^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_m \left( \frac{\mu^i_{gm} \mu^j_{mg}}{\omega_{mg} - \omega_p} + \frac{\mu^j_{gm} \mu^i_{mg}}{\omega^*_{mg} + \omega_p} \right) \]

- Note that if \( g \) denotes the ground state, it is impossible for the second term to become resonant, which is why it is called the antiresonant contribution.
Second-Order Susceptibility

\[ \langle \tilde{\mathbf{p}}^{(2)} \rangle = \langle \psi^{(0)} | \hat{\mu} | \psi^{(2)} \rangle + \langle \psi^{(1)} | \hat{\mu} | \psi^{(1)} \rangle + \langle \psi^{(2)} | \hat{\mu} | \psi^{(0)} \rangle \]

By substituting \( \psi^{(0)}, \psi^{(1)} \) & \( \psi^{(2)} \) we find that:

\[
\langle \tilde{\mathbf{p}}^{(2)} \rangle = \frac{1}{\hbar^2} \sum_{pq} \sum_{mn} \left( \frac{\mu_{gn} \cdot [\mu_{nm} \cdot \mathbf{E}(\omega_q)] \cdot [\mu_{mg} \cdot \mathbf{E}(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} e^{-i(\omega_p + \omega_q)t} \right. \\
+ \left. \frac{[\mu_{ng} \cdot \mathbf{E}(\omega_q)]^* \cdot \mu_{nm} \cdot [\mu_{mg} \cdot \mathbf{E}(\omega_q)]}{(\omega_{ng} - \omega_q)(\omega_{mg} - \omega_p)} e^{-i(\omega_p - \omega_q)t} \right) \\
+ \frac{[\mu_{ng} \cdot \mathbf{E}(\omega_q)]^* \cdot [\mu_{nm} \cdot \mathbf{E}(\omega_p)]^* \cdot \mu_{mg}}{(\omega_{ng}^* - \omega_q)(\omega_{mg}^* - \omega_q - \omega_q)} e^{i(\omega_p + \omega_q)t} \right)
\]

As in the case of the linear susceptibility, this equation can be rendered more transparent by replacing \( \omega_q \) a transparent by replacing \( \omega_q \) by \(-\omega_q\) in the second term and by replacing \( \omega_q \) and \( \omega_p \) by \(-\omega_p\) in the third term:
\[
\langle \tilde{p}^{(2)} \rangle = \frac{1}{\hbar^2} \sum_{pq} \sum_{mn} \left( \frac{\mu_{gn} [\mu_{nm} \cdot E(\omega_q)] [\mu_{mg} \cdot E(\omega_p)]}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \right) \\
+ \frac{[\mu_{gn} \cdot E(\omega_q)] [\mu_{nm} \cdot E(\omega_p)]}{(\omega^*_{ng} + \omega_q)(\omega_{mg} - \omega_p)} \\
+ \frac{[\mu_{gn} \cdot E(\omega_q)] [\mu_{nm} \cdot E(\omega_p)] \mu_{mg}}{(\omega^*_{ng} + \omega_q)(\omega^*_{mg} + \omega_q + \omega_q)} e^{-i(\omega_p + \omega_q t)}
\]

\[
\tilde{P}^{(2)} = N \langle \tilde{p}^{(2)} \rangle
\]

\[
\tilde{P}^{(2)} = \sum_r P^{(2)}(\omega_r) \exp(-i\omega_r t)
\]

\[
P_i^{(2)} = \epsilon_0 \sum_{jk} \sum_{(pq)} \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) E_j(\omega_q) E_k(\omega_p)
\]

\[
\chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p)
\]
\[ \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^2} \mathcal{P}_I \sum_{mn} \left( \frac{\mu^i_{gn} \mu^j_{nm} \mu^k_{mg}}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \right) \]

denotes the intrinsic permutation operator. This operator tells us to average the expression that follows it over both permutations of the frequencies \( \omega_p \) and \( \omega_q \) of the applied fields.
For the case of highly nonresonant excitation, such that the resonance frequencies $\omega_{mg}$ and $\omega_{ng}$ can be taken to be real quantities, the expression for $\chi^{(2)}$ can be simplified still further. In particular, under such circumstances above equation can be expressed as:

$$\chi^{(2)}_{ijk}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{\varepsilon_0 \hbar^2} \mathcal{P}_1 \sum_{mn} \left( \frac{\mu^{i}_{gn} \mu^{j}_{nm} \mu^{k}_{mg}}{(\omega_{ng} - \omega_p - \omega_q)(\omega_{mg} - \omega_p)} \right)$$

$$+ \frac{\mu^{j}_{gn} \mu^{i}_{nm} \mu^{k}_{mg}}{(\omega_{ng}^{*} + \omega_q)(\omega_{mg} - \omega_p)} + \frac{\mu^{j}_{gn} \mu^{k}_{nm} \mu^{i}_{mg}}{(\omega_{ng}^{*} + \omega_q)(\omega_{mg}^{*} + \omega_p + \omega_q)}$$

For the case of highly nonresonant excitation, such that the resonance frequencies $\omega_{mg}$ and $\omega_{ng}$ can be taken to be real quantities, the expression for $\chi^{(2)}$ can be simplified still further. In particular, under such circumstances above equation can be expressed as:

$$\chi^{(2)}_{ijk}(\omega_\sigma, \omega_q, \omega_p) = \frac{N}{\varepsilon_0 \hbar^2} \mathcal{P}_F \sum_{mn} \frac{\mu^{i}_{gn} \mu^{j}_{nm} \mu^{k}_{mg}}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_p)}$$

$$\omega_\sigma = \omega_p + \omega_q$$

full permutation operator, denoted six permutations:

$$(-\omega_\sigma, \omega_q, \omega_p) \rightarrow (-\omega_\sigma, \omega_p, \omega_q), (\omega_q, -\omega_\sigma, \omega_p), (\omega_q, \omega_p, -\omega_\sigma),$$

$$(\omega_p, -\omega_\sigma, \omega_q), (\omega_p, \omega_q, -\omega_\sigma).$$
Third-Order Susceptibility:

\[
\langle \hat{p}^{(3)} \rangle = \langle \psi^{(0)} | \hat{\mu} | \psi^{(3)} \rangle + \langle \psi^{(1)} | \hat{\mu} | \psi^{(2)} \rangle + \langle \psi^{(2)} | \hat{\mu} | \psi^{(1)} \rangle + \langle \psi^{(3)} | \hat{\mu} | \psi^{(0)} \rangle
\]

By substituting \( \psi^{(0)} \), \( \psi^{(1)} \), \( \psi^{(2)} \) & \( \psi^{(3)} \) we find that:

\[
\langle \hat{p}^{(3)} \rangle = \frac{1}{\hbar^3} \sum_{pqr} \sum_{mrv} \left( \mu_{gv} \left[ \mu_{vn} \cdot \mathbf{E}(\omega_r) \right] \left[ \mu_{nm} \cdot \mathbf{E}(\omega_q) \right] \left[ \mu_{mg} \cdot \mathbf{E}(\omega_p) \right] \right) \times e^{-i(\omega_p + \omega_q + \omega_r)t} \\
\times \left( \frac{1}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right) \\
+ \frac{[\mu_{vg} \cdot \mathbf{E}(\omega_r)]^* \mu_{vn} [\mu_{nm} \cdot \mathbf{E}(\omega_q)]^* \mu_{mg} \cdot \mathbf{E}(\omega_p)}{(\omega_{vg}^* - \omega_r)(\omega_{ng}^* - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \times e^{-i(\omega_p + \omega_q - \omega_r)t} \\
+ \frac{[\mu_{vg} \cdot \mathbf{E}(\omega_r)]^* [\mu_{nv} \cdot \mathbf{E}(\omega_q)]^* [\mu_{nm} \cdot \mathbf{E}(\omega_p)]^* \mu_{mg}}{(\omega_{vg}^* - \omega_r)(\omega_{ng}^* - \omega_r - \omega_q)(\omega_{mg}^* - \omega_r - \omega_q - \omega_p)} \times e^{-i(\omega_p - \omega_q - \omega_r)t} \\
+ \frac{[\mu_{vg} \cdot \mathbf{E}(\omega_r)]^* [\mu_{nv} \cdot \mathbf{E}(\omega_q)]^* [\mu_{mn} \cdot \mathbf{E}(\omega_p)]^* \mu_{mg}}{(\omega_{vg}^* - \omega_r)(\omega_{ng}^* - \omega_r - \omega_q)(\omega_{mg}^* - \omega_r - \omega_q - \omega_p)} \times e^{+i(\omega_p + \omega_q + \omega_r)t} \right)
\]
Since the expression is summed over all positive and negative values of $\omega_p$, $\omega_q$, and $\omega_r$, we can replace these quantities by their negatives in those expressions where the complex conjugate of a field amplitude appears. We thereby obtain the expression:

$$\langle \hat{p}^{(3)} \rangle = \frac{1}{\hbar^3} \sum_{pqr} \sum_{mnv} \left( \frac{[\mu_{gv} \cdot E(\omega_r)][\mu_{vn} \cdot E(\omega_q)][\mu_{nm} \cdot E(\omega_p)]}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right. $$

$$\times \left. \left( \frac{[\mu_{gv} \cdot E(\omega_r)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} + \frac{[\mu_{vn} \cdot E(\omega_q)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} + \frac{[\mu_{nm} \cdot E(\omega_p)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} + \frac{[\mu_{mg} \cdot E(\omega_p)]}{(\omega_{vg}^* + \omega_r)(\omega_{ng}^* + \omega_r + \omega_q)(\omega_{mg}^* + \omega_r + \omega_q + \omega_p)} \right) \right) $$

$$\times e^{-i(\omega_p + \omega_q + \omega_r)t}$$
\[ \langle \tilde{P}^{(3)} \rangle = \frac{1}{\hbar^3} \sum_{pqr} \sum_{mn} \sum_{n} \frac{\mu_{g} \cdot E(\omega_r) \mu_{v} \cdot E(\omega_q) \mu_{m} \cdot E(\omega_p)}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \]

\[ + \frac{\mu_{g} \cdot E(\omega_r) \mu_{v} \cdot E(\omega_q) \mu_{m} \cdot E(\omega_p)}{(\omega_{vg} + \omega_r)(\omega_{ng} + \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \]

\[ + \frac{\mu_{g} \cdot E(\omega_r) \mu_{v} \cdot E(\omega_q) \mu_{m} \cdot E(\omega_p)}{(\omega_{vg} + \omega_r)(\omega_{ng} + \omega_r + \omega_q)(\omega_{mg} + \omega_r + \omega_q + \omega_p)} \]

\[ \times e^{-i(\omega_p + \omega_q + \omega_r)t} \]

\[ \tilde{P}^{(3)} = N \langle \tilde{p}^{(3)} \rangle = \sum_{s} P^{(3)}(\omega_s) \exp(-i\omega_st) \]

\[ P_k(\omega_p + \omega_q + \omega_r) = \epsilon_0 \sum_{hij} \sum_{(pqr)} \chi^{(3)}_{kjih}(\omega_p, \omega_q, \omega_r, \omega_p) E_j(\omega_r) E_i(\omega_q) E_h(\omega_p) \]

\[ \chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p) \]
\[ \chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p) \]
\[ = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_l \sum_{mnv} \left[ \frac{\mu^k_{gv} \mu^j_{vn} \mu^i_{nm} \mu^h_{mg}}{(\omega_{vg} - \omega_r - \omega_q - \omega_p)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \right. \]
\[ + \frac{\mu^j_{gv} \mu^k_{vn} \mu^i_{nm} \mu^h_{mg}}{(\omega_{vg} + \omega_r)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)} \]
\[ + \frac{\mu^j_{gv} \mu^i_{vn} \mu^h_{nm} \mu^k_{mg}}{(\omega_{vg} + \omega_r)(\omega_{ng} + \omega_r + \omega_q)(\omega_{mg} - \omega_p)} \]
\[ + \frac{\mu^j_{gv} \mu^i_{vn} \mu^h_{nm} \mu^k_{mg}}{(\omega_{vg} + \omega_r)(\omega_{ng} + \omega_r + \omega_q + \omega_p)} \]
As in the case of the second-order susceptibility, the expression for $\chi^{(3)}$ can be written very compactly for the case of highly nonresonant excitation such that the imaginary parts of the resonance frequencies (recall that $\omega_{lg} = (E_l - E_g)/\hbar - i\Gamma_l/2$) can be ignored. In this case, the expression for $\chi^{(3)}$ can be written as

$$\chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_F \sum_{mnv} \frac{\mu_g^k \mu_v^j \mu_n^i \mu_m^h}{(\omega_{vg} - \omega_\sigma)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)}$$

$$\omega_\sigma = \omega_p + \omega_q + \omega_r$$
As an example of the use of \( \chi^{(3)} \) we next calculate the nonlinear optical susceptibility describing third-harmonic generation in a vapor of sodium atoms. We assume that the incident radiation is linearly polarized in the \( z \) direction. Consequently, the nonlinear polarization will have only a \( z \) component, and we can suppress the tensor nature of the nonlinear interaction. If we represent the applied field as:

\[
\tilde{E}(r, t) = E_1(r)e^{-i\omega t} + \text{c.c.}
\]

we find that the nonlinear polarization can be represented as:

\[
\tilde{P}(r, t) = P_3(r)e^{-i3\omega t} + \text{c.c.}
\]

\[
P_3(r) = \varepsilon_0 \chi^{(3)}(3\omega) E_1^3
\]

\( \chi^{(3)}(3\omega = \omega + \omega + \omega) \).
\[
\chi^{(3)}(3\omega) = \frac{N}{\varepsilon_0 \hbar^3} \sum_{mnv} \mu_{gv} \mu_{vn} \mu_{nm} \mu_{mg} \times \begin{bmatrix}
\frac{1}{(\omega_{vg} - 3\omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} \\
\frac{1}{(\omega_{vg} + \omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} \\
\frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} - \omega)} \\
\frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} + 3\omega)}
\end{bmatrix}
\]
Energy-level diagram of the sodium atom.

The third-harmonic generation process.
\[ \chi^{(3)}(3\omega) = \frac{N}{\varepsilon_0 \hbar^3} \sum_{mnv} \mu_{gm} \mu_{vn} \mu_{nm} \mu_{mg} \]

\[
\times \left[ \frac{1}{(\omega_{vg} - 3\omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} 
+ \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} - 2\omega)(\omega_{mg} - \omega)} 
+ \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} - \omega)} 
+ \frac{1}{(\omega_{vg} + \omega)(\omega_{ng} + 2\omega)(\omega_{mg} + 3\omega)} \right].
\]

can become fully resonant. This term becomes fully resonant when \(\omega\) is nearly equal to \(\omega_{mg}\), \(2\omega\) is nearly equal to \(\omega_{ng}\), and \(3\omega\) is nearly equal to \(\omega_{vg}\).

According to the selection rule:

\[ \Delta l = \pm 1 \]

\&

since the ground state is an s-state.
Figure 3.2.6 The nonlinear susceptibility describing third-harmonic generation in atomic sodium vapor plotted versus the vacuum wavelength of the fundamental radiation (after Miles and Harris, 1973).
Density Matrix Formulation of Quantum Mechanics

We use this formalism because it is capable of treating effects, such as collisional broadening of the atomic resonances, that cannot be treated by the simple theoretical formalism based on the atomic wave function. We need to be able to treat such effects for a number of related reasons.
Let us begin by reviewing how the density matrix formalism follows from the basic laws of quantum mechanics:

\[ i\hbar \frac{\partial \psi_s({\bf r}, t)}{\partial t} = \hat{H} \psi_s({\bf r}, t) \]

We can hence represent the wavefunction of states as

\[ \psi_s({\bf r}, t) = \sum_n C^s_n(t) u_n({\bf r}) \]

the time-dependent Schrödinger equation

the time-independent Schrödinger equation

\[ \hat{H}_0 u_n({\bf r}) = E_n u_n({\bf r}) \]

which are assumed to be orthonormal in that they obey the relation

\[ \int u^*_m({\bf r}) u_n({\bf r}) \, d^3r = \delta_{mn} \]
\[ i\hbar \frac{\partial \psi_s(r, t)}{\partial t} = \hat{H}\psi_s(r, t) \]

\[ \psi_s(r, t) = \sum_n C_n^s(t)u_n(r) \]

\[ i\hbar \sum_n \frac{dC_n^s(t)}{dt} u_n(r) = \sum_n C_n^s(t) \hat{H}u_n(r) \]

\[ \int u_n^*(r)u_n(r) \, d^3r = \delta_{mn} \]

\[ H_{mn} = \int u_m^*(r) \hat{H}u_n(r) \, d^3r \]

\[ i\hbar \frac{d}{dt} C_m^s(t) = \sum_n H_{mn} C_n^s(t) \]
The expectation value \( \langle A \rangle \) can be expressed in terms of the probability amplitudes \( C_n^s(t) \) by:

\[
\langle A \rangle = \sum_{mn} C_m^s \overline{C}_n^s A_{mn}
\]

where

\[
A_{mn} = \langle u_m | \hat{A} | u_n \rangle = \int u_m^* \hat{A} u_n \, d^3r
\]

We will back to \( \langle A \rangle \) by the density matrix.
Under such circumstances, where the precise state of the system is unknown, the density matrix formalism can be used to describe the system in a statistical sense. Let us denote by \( p(s) \) the probability that the system is in the state \( s \).

In terms of \( p(s) \), we define the elements of the density matrix of the system by:

\[
\rho_{nm} = \sum_s p(s) C^s_m C^s_n
\]

This relation can also be written symbolically as:

\[
\rho_{nm} = \langle C_m^* C_n \rangle
\]

denotes an ensemble average, that is, an average over all of the possible states of the system.

The elements of the density matrix have the following physical interpretation: The diagonal elements \( \rho_{nn} \) give the probability that the system is in energy eigenstate \( n \).

The off-diagonal elements have a somewhat more abstract interpretation: \( \rho_{nm} \) gives the “coherence” between levels \( n \) and \( m \), in the sense that \( \rho_{nm} \) will be nonzero only if the system is in a coherent superposition of energy eigenstate \( n \) and \( m \).
the expectation value for the case in which the exact state of the system is not known is obtained by averaging \( \langle A \rangle \) over all possible states of the system, to yield:

\[
\langle A \rangle = \sum_{m} \sum_{n} C^{s^*}_m C^s_n A_{mn}
\]

\[
\langle A \rangle = \sum_{s} \sum_{n\text{m}} \rho_{nm} A_{mn}
\]

\[
\sum_{nm} \rho_{nm} A_{mn} = \sum_n \left( \sum_m \rho_{nm} A_{mn} \right) = \sum_n (\hat{\rho} A)_{nn} \equiv \text{tr}(\hat{\rho} A)
\]

\[
\langle A \rangle = \text{tr}(\hat{\rho} A)
\]
In order to determine how any expectation value evolves in time, it is thus necessary only to determine how the density matrix itself evolves in time. By direct time differentiation of:

\[ \rho_{nm} = \sum_s p(s) C_m^s C_n^s \]

we find that:

\[ \dot{\rho}_{nm} = \sum_s \frac{dp(s)}{dt} C_m^s C_n^s + \sum_s p(s) \left( C_m^s \frac{dC_n^s}{dt} + \frac{dC_m^s}{dt} C_n^s \right) \]

**Assume that** \( p(s) \) **does not vary in time**

\[ C_m^s \frac{dC_n^s}{dt} = -\frac{i}{\hbar} C_m^s \sum_v H_{nv} C_v^s, \]

\[ C_n^s \frac{dC_m^s}{dt} = \frac{i}{\hbar} C_n^s \sum_v H_{vm}^* C_v^{s*} = \frac{i}{\hbar} C_n^s \sum_v H_{vm} C_v^{s*} \]
describes how the density matrix evolves in time as the result of interactions that are included in the Hamiltonian. However, there are certain interactions (such as those resulting from collisions between atoms) that cannot conveniently be included in a Hamiltonian description. Such interactions can lead to a change in the state of the system, and hence to a nonvanishing value of $dp(s)/dt$. 

\[
\dot{\rho}_{nm} = \sum_s p(s) \frac{i}{\hbar} \sum_v (C_n^s C_v^{s*} H_{vm} - C_m^{s*} C_v^s H_{nv})
\]

\[
\rho_{nm} = \sum_s p(s) C_m^{s*} C_n^s
\]

\[
\dot{\rho}_{nm} = \frac{i}{\hbar} \sum_v (\rho_{nv} H_{vm} - H_{nv} \rho_{vm})
\]

\[
\dot{\rho}_{nm} = \frac{i}{\hbar} (\hat{\rho} \hat{H} - \hat{H} \hat{\rho})_{nm} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]_{nm}
\]
We include such effects in the formalism by adding phenomenological damping terms to

\[
\dot{\rho}_{nm} = \frac{i}{\hbar} (\hat{\rho} \hat{H} - \hat{H} \hat{\rho})_{nm} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]_{nm}
\]

There is more than one way to model such decay processes. We shall often model such processes by taking the density matrix equations to have the form:

\[
\dot{\rho}_{nm} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm} (\rho_{nm} - \rho_{nm}^{(eq)})
\]

a phenomenological damping term, which indicates that \(\rho_{nm}\) relaxes to its equilibrium value \(\rho_{nm}^{(eq)}\) at rate \(\gamma_{nm}\). Since \(\gamma_{nm}\) is a decay rate, we assume that \(\gamma_{nm} = \gamma_{mn}\). In addition, we make the physical assumption that:

\[
\rho_{nm}^{(eq)} = 0 \quad \text{for} \quad n \neq m
\]

\[
\dot{\rho}_{nm} = -i \hbar^{-1} [\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm} \rho_{nm}, \quad n \neq m,
\]

\[
\dot{\rho}_{nn} = -i \hbar^{-1} [\hat{H}, \hat{\rho}]_{nn} + \sum_{E_m > E_n} \Gamma_{nm} \rho_{mm} - \sum_{E_m < E_n} \Gamma_{mn} \rho_{nn}.
\]

the damping rate of the \(\rho_{nm}\) coherence

the rate per atom at which population decays from level \(m\) to level \(n\)
under quite general conditions the off-diagonal elements can be represented as:

\[ \gamma_{nm} = \frac{1}{2} (\Gamma_n + \Gamma_m) + \gamma_{nm}^{(col)} \]

the dipole dephasing rate due to processes (such as elastic collisions)

total decay rates of population out of levels \( n \) and \( m \)

\[ \Gamma_n = \sum_{n' \ (E_{n'} < E_n)} \Gamma_{n'n} \]

Let's see why \( \gamma_{nm} \) depends upon the population decay rates in the manner indicated?

note that if level \( n \) has life time \( \tau_n = \frac{1}{\Gamma_n} \), the probability to be in level \( n \) must decay as:

\[ |C_n(t)|^2 = |C_n(0)|^2 e^{-\Gamma_n t} \]

Thus, the coherence between the two levels must vary as

\[ C_n^*(t)C_m(t) = C_n^*(0)C_m(0)e^{-i\omega_{nm}t}e^{-(\Gamma_n+\Gamma_m)t/2} \]

But since the ensemble average of \( C_n^*C_m \) is just \( \rho_{nm} \), whose damping rate is denoted \( \gamma_{nm} \), it follows that:

\[ \gamma_{mn} = \frac{1}{2} (\Gamma_n + \Gamma_m) \]
Example: Two-Level Atom

The matrix representation of the dipole moment operator is:

\[
\hat{\mu} \Rightarrow \begin{bmatrix}
0 & \mu_{ab} \\
\mu_{ba} & 0
\end{bmatrix}
\]

\[
\hat{\rho} \hat{\mu} \Rightarrow \begin{bmatrix}
\rho_{aa} & \rho_{ab} \\
\rho_{ba} & \rho_{bb}
\end{bmatrix} \begin{bmatrix}
0 & \mu_{ab} \\
\mu_{ba} & 0
\end{bmatrix} = \begin{bmatrix}
\rho_{ab} \mu_{ba} & \rho_{aa} \mu_{ab} \\
\rho_{bb} \mu_{ba} & \rho_{ba} \mu_{ab}
\end{bmatrix}
\]

where

\[
\mu_{ij} = \mu_{ji}^* = -e \langle i | \hat{z} | j \rangle
\]

\[
\langle \hat{\mu} \rangle = \text{tr}(\hat{\rho} \hat{\mu}) = \rho_{ab} \mu_{ba} + \rho_{ba} \mu_{ab}
\]
Perturbation Solution of the Density Matrix Equation of Motion

\[ \dot{\rho}_{nm} = -\frac{i}{\hbar} \left[ \hat{H}, \rho \right]_{nm} - \gamma_{nm} \left( \rho_{nm} - \rho_{nm}^{(eq)} \right) \]

In general, this equation cannot be solved exactly for physical systems of interest, and for this reason it is useful to develop a perturbative technique for solving it.

\[ \hat{H} = \hat{H}_0 + \hat{V}(t) \]
\[ \hat{V} = -\hat{\mu} \cdot \tilde{E}(t) \]
\[ \hat{\mu} = -e\hat{r} \]

We assume that the states \( n \) represent the energy eigenfunctions \( u_n \) of the unperturbed Hamiltonian \( \hat{H}_0 \) and thus satisfy the equation

\[ \hat{H}_0 u_n = E_n u_n \]

As a consequence, the matrix representation of \( \hat{H}_0 \) is diagonal that is:

\[ H_{0,nm} = E_n \delta_{nm} \]

The commutator can thus be expanded as
we replace $V_{ij}$ in by $\lambda V_{ij}$, where $\lambda$ is a parameter ranging between zero and one that characterizes the strength of the perturbation. The value $\lambda=1$ is taken to represent the actual physical situation. We now seek a solution to in the form of a power series in $\lambda$ that is:

$$\rho_{nm} = \rho^{(0)}_{nm} + \lambda \rho^{(1)}_{nm} + \lambda^2 \rho^{(2)}_{nm} + \cdots$$
We take the steady-state solution to this equation to be

\[ \rho_{nm}^{(0)} = \rho_{nm}^{(eq)} \]

where \( \rho_{nm}^{(eq)} = 0 \) for \( n \neq m \).

Now that \( \rho_{nm}^{(0)} \) is known, can be integrated. To do so, we make a change of variables by representing \( \rho_{nm}^{(1)} \) as:

\[ \rho_{nm}(t) = S_{nm}^{(1)}(t)e^{-(i\omega_{nm} + \gamma_{nm})t} \]

\[ \frac{\rho_{nm}^{(1)}}{\rho_{nm}(t)} = -(i\omega_{nm} + \gamma_{nm})S_{nm}^{(1)}e^{-(i\omega_{nm} + \gamma_{nm})t} + \frac{\dot{S}_{nm}^{(1)}}{S_{nm}}e^{-(i\omega_{nm} + \gamma_{nm})t} \]
This equation can be integrated to give

\[ \dot{S}_{nm}^{(1)} = \frac{-i}{\hbar} \left[ \hat{V}, \hat{\rho}^{(0)} \right]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t} \]

\[ S_{nm}^{(1)} = \int_{-\infty}^{t} \frac{-i}{\hbar} \left[ \hat{V}(t'), \hat{\rho}^{(0)} \right]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} dt' \]

\[ \rho_{nm}^{(1)}(t) = S_{nm}^{(1)}(t) e^{-(i\omega_{nm} + \gamma_{nm})t} \]

\[ \rho_{nm}^{(1)}(t) = \int_{-\infty}^{t} \frac{-i}{\hbar} \left[ \hat{V}(t'), \hat{\rho}^{(0)} \right]_{nm} e^{(i\omega_{nm} + \gamma_{nm})(t' - t)} dt' \]
Density Matrix Calculation of the Linear Susceptibility

\[ \rho_{nm}^{(1)}(t) = e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^{t} dt' \frac{-i}{\hbar} [\hat{V}(t'), \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} \]

Remember that:

\[ \hat{V}(t') = -\hat{\mu} \cdot \tilde{E}(t') \]

\[ \rho_{nm}^{(0)} = 0 \text{ for } n \neq m \]

We represent the applied field as

\[ \tilde{E}(t) = \sum_{p} \mathbf{E}(\omega_p) e^{-i\omega_p t} \]

\[ [\hat{V}(t), \hat{\rho}^{(0)}]_{nm} = \sum_{\nu} [\hat{V}(t)_{n\nu} \rho_{\nu m}^{(0)} - \rho_{n\nu}^{(0)} \hat{V}(t)_{\nu m}] \]

\[ = -\sum_{\nu} [\mathbf{\mu}_{n\nu} \rho_{\nu m}^{(0)} - \rho_{n\nu}^{(0)} \mathbf{\mu}_{\nu m}] \cdot \tilde{E}(t) \]

\[ = - (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \mathbf{\mu}_{nm} \cdot \tilde{E}(t) \]
By replacing $\star$ in:

$$\rho_{nm}^{(1)}(t) = e^{-(i\omega_{nm}+\gamma_{nm})t} \int_{-\infty}^{t} dt' \frac{-i}{\hbar} [\hat{V}(t'), \hat{\rho}^{(0)}]_{nm} e^{(i\omega_{nm}+\gamma_{nm})t'}$$

$$\rho_{nm}^{(1)}(t) = \frac{i}{\hbar} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \mu_{nm} \cdot e^{-(i\omega_{nm}+\gamma_{nm})t} \int_{-\infty}^{t} \tilde{E}(t') e^{(i\omega_{nm}+\gamma_{nm})t'} dt'$$

$$\tilde{E}(t) = \sum_{p} E(\omega_p) e^{-i\omega_p t}$$

$$\rho_{nm}^{(1)}(t) = \frac{i}{\hbar} (\rho_{mm}^{(0)} - \rho_{nn}^{(0)}) \mu_{nm} \cdot \sum_{p} E(\omega_p) \times e^{-(i\omega_{nm}+\gamma_{nm})t} \int_{-\infty}^{t} e^{[i(\omega_{nm}-\omega_p)+\gamma_{nm}]t'} dt'$$

can be evaluated explicitly as:
We next use this result to calculate the expectation value of the induced dipole moment:

\[
\langle \tilde{\mu}(t) \rangle = \text{tr} \left( \hat{\rho}^{(1)} \hat{\mu} \right) = \sum_{nm} \rho_{nm}^{(1)} \mu_{mn} \\
= \sum_{nm} \hbar^{-1} \left( \rho_{mm}^{(0)} - \rho_{nn}^{(0)} \right) \sum_p \frac{\mu_{mn} \cdot \mathbf{E}(\omega_p) e^{-i\omega_p t}}{\left(\omega_{nm} - \omega_p - i\gamma_{nm}\right)}
\]

Decompose \( \langle \tilde{\mu}(t) \rangle \) into its frequency components according to

\[
\langle \tilde{\mu}(t) \rangle = \sum_p \langle \mu(\omega_p) \rangle e^{-i\omega_p t}
\]
\[ P(\omega_p) = N\langle \mu(\omega_p) \rangle = \epsilon_0 \chi^{(1)}(\omega_p) \cdot E(\omega_p) \]

\[ \langle \tilde{\mu}(t) \rangle = \text{tr} \left( \hat{\rho}^{(1)} \hat{\mu} \right) = \sum_{nm} \rho^{(1)}_{nm} \mu_{mn} \]

\[ = \sum_{nm} \hbar^{-1} \left( \rho^{(0)}_{mm} - \rho^{(0)}_{nn} \right) \sum_p \frac{\mu_{mn} [\mu_{nm} \cdot E(\omega_p)] e^{-i\omega_p t}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} \]

\[ \chi^{(1)}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} \left( \rho^{(0)}_{mm} - \rho^{(0)}_{nn} \right) \frac{\mu_{mn} \mu_{nm}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} \]

\[ P_i(\omega_p) = N\langle \mu_i(\omega_p) \rangle = \sum_j \epsilon_0 \chi^{(1)}_{ij}(\omega_p) E_j(\omega_p) \]

\[ \chi^{(1)}_{ij}(\omega_p) = \frac{N}{\epsilon_0 \hbar} \sum_{nm} \left( \rho^{(0)}_{mm} - \rho^{(0)}_{nn} \right) \frac{\mu^i_{mn} \mu^j_{nm}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} \]
Interchange the dummy indices $n$ and $m$ in the second summation so that the two summations can be recombined as:

\[
\chi_{ij}^{(1)}(\omega_p) = \frac{N}{\varepsilon_0 \hbar} \sum_{nm} \left[ \rho_{mm}^{(0)} - \rho_{nn}^{(0)} \right] \frac{\mu_{mn}^i \mu_{nm}^j}{(\omega_{nm} - \omega_p) - i\gamma_{nm}}
\]

use the fact that $\omega_{mn} = -\omega_{nm}$ and $\gamma_{nm} = \gamma_{mn}$
\[ \chi^{(1)}_{ij}(\omega_p) = \frac{N}{\varepsilon_0 \hbar} \sum_{nm} \rho^{(0)}_{mm} \left[ \frac{\mu^i_{mn} \mu^j_{nm}}{(\omega_{nm} - \omega_p) - i\gamma_{nm}} + \frac{\mu^j_{nm} \mu^i_{mn}}{(\omega_{nm} + \omega_p) + i\gamma_{nm}} \right] \]

First make the simplifying assumption that all of the population is in one level (typically the ground state), which we denote as level \( a \). Mathematically, this assumption can be stated as:

\[ \rho^{(0)}_{aa} = 1, \quad \rho^{(0)}_{mm} = 0 \quad \text{for} \quad m \neq a. \]

\[ \chi^{(1)}_{ij}(\omega_p) = \frac{N}{\varepsilon_0 \hbar} \sum_n \left[ \frac{\mu^i_{an} \mu^j_{na}}{(\omega_{na} - \omega_p) - i\gamma_{na}} + \frac{\mu^j_{na} \mu^i_{an}}{(\omega_{na} + \omega_p) + i\gamma_{na}} \right] \]

We see that for positive frequencies (i.e., \( \omega_p > 0 \)), only the first term can become resonant. The second term is known as the antiresonant or counter-rotating term. We can often drop the second term, especially when \( \omega_p \) is close to one of the resonance frequencies of the atom. Let us assume that \( \omega_p \) is nearly resonant with the transition frequency \( \omega_{na} \). Then to good approximation the linear susceptibility is given by

\[ \chi^{(1)}_{ij}(\omega_p) = \frac{N}{\varepsilon_0 \hbar} \frac{\mu^i_{an} \mu^j_{na}}{(\omega_{na} - \omega_p) - i\gamma_{na}} = \frac{N}{\varepsilon_0 \hbar} \frac{\mu^i_{an} \mu^j_{na}}{(\omega_{na} - \omega_p)^2 + \gamma_{na}^2} \]
Lorentzian line shape with a linewidth (full width at half maximum) equal to $2\gamma_{na}$
Linear Response Theory

\[ \chi^{(1)}(\omega) = \frac{N}{\varepsilon_0 \hbar} \sum_n \frac{1}{3} |\mu_{na}|^2 \left[ \frac{1}{(\omega_{na} - \omega) - i \gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i \gamma_{na}} \right] \]

The summation over \( n \) includes all of the magnetic sublevels of the atomic excited states. However, on average only one-third of the \( a \rightarrow n \) transitions will have their dipole transition moments parallel to the polarization vector of the incident field, and hence only one-third of these transitions contribute effectively to the susceptibility.

Let's define oscillator strength of the \( a \rightarrow n \) transition:

\[ 0 \leq f_{na} \leq 1 \]

\[ f_{na} = \frac{2 m \omega_{na} |\mu_{na}|^2}{3 \hbar e^2} \]

\[ \sum_n f_{na} = 1 \]

\[ \chi^{(1)}(\omega) = \sum_n \frac{N f_{na} e^2}{2 \varepsilon_0 m \omega_{na}} \left[ \frac{1}{(\omega_{na} - \omega) - i \gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i \gamma_{na}} \right] \]

\[ \sim \sum_n f_{na} \left[ \frac{N e^2 / \varepsilon_0 m}{\omega_{na}^2 - \omega^2 - 2i \omega_{na} \gamma_{na}} \right]. \]
Let us next see how to calculate the refractive index and absorption coefficient.

\[ n(\omega) = \sqrt{\varepsilon^{(1)}(\omega)} = \sqrt{1 + \chi^{(1)}(\omega)} \simeq 1 + \frac{1}{2} \chi^{(1)}(\omega) \]

linear dielectric constant
linear susceptibility
If assumed \( \chi^{(1)} \ll 1 \)

The significance of the refractive index \( n(\omega) \) is that the propagation of a plane wave through the material system is described by:

\[ k = n(\omega)\omega/c. \]

\[ \tilde{E}(z, t) = E_0 e^{i(kz - \omega t)} + \text{c.c.} \]

Hence, the intensity \( I = nc\varepsilon_0 (\tilde{E}(z, t)^2) \) of this wave varies with position in the medium according to:

\[ I(z) = I_0 e^{-\alpha z} \]

\[ \alpha = 2n'\omega/c \]

\[ n(\omega) = n' + in'' \]

\[ \chi^{(1)}(\omega) = \chi^{(1)'} + i\chi^{(1)''} \]
\[ \chi^{(1)}(\omega) = \sum_n \frac{N f_{na} e^2}{2\varepsilon_0 m \omega_{na}} \left[ \frac{1}{(\omega_{na} - \omega) - i\gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i\gamma_{na}} \right] \]

\[ \approx \sum_n f_{na} \left[ \frac{N e^2 / \varepsilon_0 m}{\omega_{na}^2 - \omega^2 - 2i\omega_{na}\gamma_{na}} \right] \]

\[ \alpha \approx \sum_n \frac{f_{na} N e^2}{2m\varepsilon_0 c \gamma_{na}} \left[ \frac{\gamma_{na}^2}{(\omega_{na} - \omega)^2 + \gamma_{na}^2} \right] \]
We define the atomic polarizability $\gamma^{(1)}(\omega)$ as the coefficient relating the induced dipole moment $\langle \mu(\omega) \rangle$ and the applied field $E(\omega)$:

$$\langle \mu(\omega) \rangle = \gamma^{(1)}(\omega) E(\omega)$$

The susceptibility and polarizability are related (when local-field corrections can be ignored) through:

$$\chi^{(1)}(\omega) = N \gamma^{(1)}(\omega)$$

$$\chi^{(1)}(\omega) = \frac{N}{\varepsilon_0 \hbar} \sum_n \frac{1}{3} |\mu_{na}|^2 \left[ \frac{1}{(\omega_{na} - \omega) - i \gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i \gamma_{na}} \right]$$

$$\gamma^{(1)}(\omega) = \frac{1}{\varepsilon_0 \hbar} \sum_n \frac{1}{3} |\mu_{na}|^2 \left[ \frac{1}{(\omega_{na} - \omega) - i \gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i \gamma_{na}} \right]$$
the absorption cross section $\sigma$

Remember:

$$\alpha = \chi^{(1)''} \omega / c$$

$$\chi^{(1)}(\omega) = N \gamma^{(1)}(\omega)$$

$$\chi^{(1)}(\omega) = \chi^{(1)'} + i \chi^{(1)''}$$

$$\gamma^{(1)} = \gamma^{(1)'} + i \gamma^{(1)''}$$

$$\sigma = \gamma^{(1)''} \omega / c$$

Remember from slide 40:

$$\gamma_{nm} = \frac{1}{2} (\Gamma_n + \Gamma_m) + \gamma^{(\text{col})}_{nm}$$

Next we calculate the maximum values that the polarizability and absorption cross section can attain. We consider the case of resonant excitation ($\omega = \omega_{na}$) of some excited level $n$. We find, through use of $\star$ and dropping the nonresonant contribution, that the polarizability is purely imaginary and is given by:
1/3 no longer appears because we are now considering a particular state of the upper level and are no longer summing over n.

\[ \gamma^{(1)}(\omega) = \frac{1}{\varepsilon_0 \hbar} \sum_n \frac{1}{3} |\mu_{na}|^2 \left[ \frac{1}{(\omega_{na} - \omega) - i\gamma_{na}} + \frac{1}{(\omega_{na} + \omega) + i\gamma_{na}} \right] \]

\[ \gamma_{\text{res}}^{(1)} = \frac{i |\mu_{n'a}|^2}{\varepsilon_0 \hbar \gamma_{n'a}} \]

When it is min
when \( \gamma_{n'a}^{\text{(col)}} = 0 \)

\[ \gamma_{n'a} = \frac{1}{2} \Gamma_{n'} \]

\[ \Gamma_{n'} = \frac{\omega_{na}^3 |\mu_{n'a}|^2}{3\pi \varepsilon_0 \hbar c^3} \]

\[ \gamma^{(1)}_{\text{max}} = i6\pi \left( \frac{\lambda}{2\pi} \right)^3 \]
\[ \sigma = \gamma^{(1)''} \omega / c \]

\[ \sigma_{\text{max}} = \frac{3\lambda^2}{2\pi} \]

These results show that under resonant excitation an atomic system possesses an effective linear dimension approximately equal to an optical wavelength.

Recall that the treatment given in this subsection assumes the case of a \( J = 0 \) lower level and a \( J = 1 \) upper level. More generally, when \( J_a \) is the total angular momentum quantum number of the lower level and \( J_b \) is that of the upper level, the maximum on-resonance cross section can be shown to have the form

\[ g_b = 2J_b + 1 \]

\[ \sigma_{\text{max}} = \frac{g_b}{g_a} \frac{\lambda^2}{2\pi} \]

\[ g_a = 2J_a + 1 \]
Density Matrix Calculation of the Second-Order Susceptibility

\[ \rho_{nm}^{(2)} = e^{-i(\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^{t} \frac{-i}{\hbar} [\hat{V}, \hat{\rho}^{(1)}]_{nm} e^{i(\omega_{nm} + \gamma_{nm})t'} dt' \]

\[ [\hat{V}, \hat{\rho}^{(1)}]_{nm} = - \sum_{\nu} (\mu_{\nu \nu} \rho_{\nu \nu}^{(1)} - \rho_{\nu \nu}^{(1)} \mu_{\nu \nu}) \cdot \tilde{E}(t) \]

\[ \rho_{vm}^{(1)} = \hbar^{-1} (\rho_{mm}^{(0)} - \rho_{\nu \nu}^{(0)}) \sum_{p} \frac{\mu_{\nu \nu} \cdot E(\omega_{p})}{(\omega_{\nu \nu} - \omega_{p} - i\gamma_{\nu \nu})} e^{-i\omega_{p}t} \]

\[ \rho_{nv}^{(1)} = \hbar^{-1} (\rho_{\nu \nu}^{(0)} - \rho_{nn}^{(0)}) \sum_{p} \frac{\mu_{\nu \nu} \cdot E(\omega_{p})}{(\omega_{\nu \nu} - \omega_{p} - i\gamma_{\nu \nu})} e^{-i\omega_{p}t} \]

The applied optical field is expressed as:

\[ \tilde{E}(t) = \sum_{q} E(\omega_{q}) e^{-i\omega_{q}t} \]
\[
[\hat{V}, \hat{\rho}^{(1)}]_{nm} = -\hbar^{-1} \sum_{\nu} \left( \rho_{mn}^{(0)} - \rho_{\nu\nu}^{(0)} \right) \\
\times \sum_{pq} \frac{[\mu_{np} \cdot \mathbf{E}(\omega_q)] [\mu_{pm} \cdot \mathbf{E}(\omega_p)]}{(\omega_{pm} - \omega_q) - i\gamma_{pm}} e^{-i(\omega_p + \omega_q)t} \\
+ \hbar^{-1} \sum_{\nu} \left( \rho_{\nu\nu}^{(0)} - \rho_{nn}^{(0)} \right) \\
\times \sum_{pq} \frac{[\mu_{np} \cdot \mathbf{E}(\omega_p)] [\mu_{pm} \cdot \mathbf{E}(\omega_q)]}{(\omega_{np} - \omega_p) - i\gamma_{np}} e^{-i(\omega_p + \omega_q)t}
\]
\[ \rho_{nm}^{(2)} = \sum_{\nu} \sum_{pq} e^{-i(\omega_p + \omega_q)t} \times \left\{ \frac{\rho_{mm}^{(0)} - \rho_{vv}^{(0)}}{\hbar^2} \frac{[\mu_{nv} \cdot \mathbf{E}(\omega_q)][\mu_{vm} \cdot \mathbf{E}(\omega_p)]}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right\} \]

\[ = \sum_{\nu} \sum_{pq} K_{nm\nu} e^{-i(\omega_p + \omega_q)t}. \]

We have given the complicated expression in curly braces the label \( K_{nm\nu} \) because it appears in many subsequent equations.
We next calculate the expectation value of the atomic dipole moment:

\[ \langle \hat{\mu} \rangle = \sum_{nm} \rho_{nm} \mu_{mn} \]

\[ \langle \hat{\mu} \rangle = \sum_r \langle \mu(\omega_r) \rangle e^{-i\omega_r t} \]

\[ \langle \mu(\omega_p + \omega_q) \rangle = \sum_{nmv} \sum_{(pq)} K_{nmv} \mu_{mn} \]

**polarization oscillating:**

\[ P^{(2)}(\omega_p + \omega_q) = N \langle \mu(\omega_p + \omega_q) \rangle = N \sum_{nmv} \sum_{(pq)} K_{nmv} \mu_{mn} \]

We define the nonlinear susceptibility through the equation:

\[ P_i^{(2)}(\omega_p + \omega_q) = \varepsilon_0 \sum_{jk} \sum_{(pq)} \chi^{(2)}_{ijk}(\omega_p + \omega_q, \omega_q, \omega_p) E_j(\omega_q) E_k(\omega_p) \]
\[ \chi_{ijk}^{(2)'}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^2} \times \sum_{mnv} \left\{ \left( \rho^{(0)}_{mm} - \rho^{(0)}_{vv} \right) \frac{\mu^i_{mn} \mu^j_{nv} \mu^k_{vm}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right. \\
- \left( \rho^{(0)}_{vv} - \rho^{(0)}_{nn} \right) \frac{\mu^i_{mn} \mu^j_{vm} \mu^k_{nv}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{nv} - \omega_p) - i\gamma_{nv}]} \right\} . \]
\[
\chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{2\epsilon_0 \hbar^2} \times \sum_{mnv} \left\{ \left( \rho_{mm}^{(0)} - \rho_{vv}^{(0)} \right) \left[ \frac{\mu_i^{\mu_m} \mu_j^{\mu_n} \mu_k^{\mu_v}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][\omega_{vm} - \omega_p - i\gamma_{vm}]} \right] \right\}.
\]

\[\begin{align*}
&+ \frac{\mu_i^{\mu_m} \mu_j^{\mu_n} \mu_k^{\mu_v}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][\omega_{vm} - \omega_q - i\gamma_{vm}]} \\
&- \left( \rho_{vv}^{(0)} - \rho_{nn}^{(0)} \right) \left[ \frac{\mu_i^{\mu_m} \mu_j^{\mu_n} \mu_k^{\mu_v}}{[(\omega_{vm} - \omega_p - \omega_q) - i\gamma_{nm}][\omega_{nv} - \omega_p - i\gamma_{nv}]} \right] \\
&+ \frac{\mu_i^{\mu_m} \mu_j^{\mu_n} \mu_k^{\mu_v}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][\omega_{nv} - \omega_q - i\gamma_{nv}]} \right\}.
\end{align*}\]
\[
\chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{2\varepsilon_0 \hbar^2} \sum_{mnv} \left( \rho^{(0)}_{mm} - \rho^{(0)}_{vv} \right) \times \left\{ \begin{array}{c}
\frac{\mu^i_{mn} \mu^j_{nv} \mu^k_{vm}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \\
\frac{\mu^i_{mn} \mu^k_{nv} \mu^j_{vm}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_q) - i\gamma_{vm}]} \\
- \frac{\mu^i_{nv} \mu^j_{mn} \mu^k_{vm}}{[(\omega_{vn} - \omega_p - \omega_q) - i\gamma_{vn}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \\
- \frac{\mu^i_{nv} \mu^k_{mn} \mu^j_{vm}}{[(\omega_{vn} - \omega_p - \omega_q) - i\gamma_{vn}][(\omega_{vm} - \omega_q) - i\gamma_{vm}]} \end{array} \right\} \right.
\]
\[
\chi^{(2)}_{ijk}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{2} \varepsilon_0 \hbar^2 \sum_{lmn} \left( \rho^{(0)}_{ll} - \rho^{(0)}_{mm} \right) \\
\times \left\{ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{\left[ (\omega_{nl} - \omega_p - \omega_q) - i \gamma_{nl} \right] \left[ (\omega_{ml} - \omega_p) - i \gamma_{ml} \right]} \right\} (a_1) \\
+ \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{\left[ (\omega_{nl} - \omega_p - \omega_q) - i \gamma_{nl} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \\
+ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{ml} - \omega_p) - i \gamma_{ml} \right]} \\
+ \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \right\}. (a_2) \\
+ \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{\left[ (\omega_{nl} - \omega_p - \omega_q) - i \gamma_{nl} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \\
+ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{ml} - \omega_p) - i \gamma_{ml} \right]} \\
+ \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \right\}. (b_1) \\
+ \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{\left[ (\omega_{nl} - \omega_p - \omega_q) - i \gamma_{nl} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \\
+ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{ml} - \omega_p) - i \gamma_{ml} \right]} \\
+ \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{nl} - \omega_q) - i \gamma_{ml} \right]} \right\}. (b_2)
\]
\[
\left\{ \frac{\mu^i_{mn} \mu^j_{nv} \mu^k_{vm}}{[(\omega_{nm} - \omega_p - \omega_q) - i\gamma_{nm}][(\omega_{vm} - \omega_p) - i\gamma_{vm}]} \right\}
\]
\[
\frac{\mu_n^i \mu_m^k \mu_{vn}^j}{[(\omega_{vn} - \omega_p - \omega_q) - i \gamma_{vn}][(\omega_{vm} - \omega_q) - i \gamma_{vm}]} \}
\]
دانشگاه تربیت معلم
If we now perform the summation over the dummy indices $l$, $m$, and $n$ and retain only those terms in which both factors in the denominator are resonant, we find that the nonlinear susceptibility is given by:

\[
\chi_{ijk}^{(2)}(\omega_3, \omega_2, \omega_1) = \frac{N}{2\varepsilon_0 \hbar^2} \left\{ \left( \rho_{aa}^{(0)} - \rho_{bb}^{(0)} \right) \left[ \frac{\mu_{ac}^{i} \mu_{cb}^{j} \mu_{ba}^{k}}{[(\omega_{ca} - \omega_3) - i\gamma_{ca}][(\omega_{ba} - \omega_1) - i\gamma_{ba}]} \right] + \left( \rho_{cc}^{(0)} - \rho_{bb}^{(0)} \right) \left[ \frac{\mu_{ac}^{i} \mu_{cb}^{j} \mu_{ba}^{k}}{[(\omega_{ca} - \omega_3) - i\gamma_{ca}][(\omega_{cb} - \omega_2) - i\gamma_{cb}]} \right] \right\}.
\]
\[ X_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) \]
\[
N \frac{2}{\varepsilon_0 \hbar^2} \sum_{lnm} \rho_{ll}^{(0)} \left\{ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][[(\omega_{ml} - \omega_p) - i\gamma_{ml}]} + \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][[(\omega_{ml} - \omega_q) - i\gamma_{ml}]} + \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][[(\omega_{nl} + \omega_p) + i\gamma_{nl}]} + \frac{\mu^j_{ln} \mu^i_{nm} \mu^k_{ml}}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][[(\omega_{nl} + \omega_q) + i\gamma_{nl}]} + \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][[(\omega_{ml} - \omega_p) - i\gamma_{ml}]} + \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][[(\omega_{ml} - \omega_q) - i\gamma_{ml}]} + \frac{\mu^k_{ln} \mu^j_{nm} \mu^i_{ml}}{[(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][[(\omega_{nl} + \omega_p) + i\gamma_{nl}]} + \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{[(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][[(\omega_{nl} + \omega_q) + i\gamma_{nl}]} \right\}. \]
\[
\left\{ \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right. \\
(a_1)
\]
\[
+ \frac{\mu^i_{ln} \mu^k_{nm} \mu^j_{ml}}{[(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \tag{a_2}
\]
\[ \left( a_1' \right) \]
\[ + \frac{\mu^i_{ln} \mu^j_{nm} \mu^k_{ml}}{\left[ (\omega_{mn} - \omega_p - \omega_q) - i \gamma_{mn} \right] \left[ (\omega_{nl} + \omega_p) + i \gamma_{nl} \right]} \]

\[ \left( b_2 \right) \]
\[ + \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{\left[ (\omega_{nm} + \omega_p + \omega_q) + i \gamma_{nm} \right] \left[ (\omega_{ml} - \omega_q) - i \gamma_{ml} \right]} \]
\[ a'_2 \]
\[ + \frac{\mu^j_{ln} \mu^i_{nm} \mu^k_{ml}}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][(\omega_{nl} + \omega_q) + i\gamma_{nl}]} \]

\[ b_1 \]
\[ + \frac{\mu^j_{ln} \mu^i_{nm} \mu^k_{ml}}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \]
\[ (b'_1) \]

\[ + \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{[(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][(\omega_{nl} + \omega_p) + i\gamma_{nl}]} \]
\[
+ \frac{\mu_i^j \mu_{kn}^k \mu_{ml}^i}{[(\omega_{ml} + \omega_p + \omega_q) + i \gamma_{ml}][(\omega_{nl} + \omega_q) + i \gamma_{nl}]} \right] \right) \right] 
\]
\[
\begin{align*}
\text{(a)}: \quad & \rho_{ll}^{(0)} \rightarrow \rho_{ml}^{(1)} \rightarrow \rho_{nl}^{(2)},
\end{align*}
\]
\[+(\frac{\mu_{ln}^k \mu_{nm}^i \mu_{ml}^j}{(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}})[(\omega_{nl} + \omega_p) + i\gamma_{nl}]\]

\[+(\frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}})[(\omega_{nl} + \omega_q) + i\gamma_{nl}]\]

(a'):
\[\rho_{ll}^{(0)} \rightarrow \rho_{ln}^{(1)} \rightarrow \rho_{mn}^{(2)}\]

Double-sided Feynman diagrams.
\[ + \frac{\mu_l^i \mu_m^i \mu_n^j}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \]  

\[ + \frac{\mu_k^i \mu_m^i \mu_n^j}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \] 

\[(b): \quad \rho_{ll}^{(0)} \rightarrow \rho_{ml}^{(1)} \rightarrow \rho_{mn}^{(2)}\] 

Double-sided Feynman diagrams.
\[ (b') \]: \[ \rho^{(0)}_{ll} \rightarrow \rho^{(1)}_{ln} \rightarrow \rho^{(2)}_{lm} \]
We represent the density operator as

\[ \hat{\rho} = |\psi\rangle\langle\psi| \]

\[ \rho_{nm} = \langle n | \hat{\rho} | m \rangle. \]
In the numerators of terms \((a'_2)\) and \((b_1)\) are identical and that their denominators can be combined as follows:

\[
\chi^{(2)} \text{ in the Limit of Nonresonant Excitation}
\]

\[
(a'_2) + \frac{\mu^j_{in}\mu^i_{nm}\mu^k_{ml}}{[\omega_{mn} - \omega_p - \omega_q - i\gamma_{mn}][\omega_{nl} + \omega_q + i\gamma_{nl}]} + \frac{\mu^j_{in}\mu^i_{nm}\mu^k_{ml}}{[\omega_{nm} + \omega_p + \omega_q + i\gamma_{nm}][\omega_{ml} - \omega_p - i\gamma_{ml}]}
\]

\[
(b_1)
\]

\[
\frac{1}{(\omega_{mn} - \omega_p - \omega_q)(\omega_{nl} + \omega_q)} + \frac{1}{(-\omega_{mn} + \omega_p + \omega_q)(\omega_{ml} - \omega_p)}
\]

\[
= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[ \frac{1}{\omega_{nl} + \omega_q} - \frac{1}{\omega_{ml} - \omega_p} \right]
\]

\[
= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[ \frac{\omega_{ml} - \omega_p - \omega_{nl} - \omega_q}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \right]
\]

\[
= \frac{1}{(\omega_{mn} - \omega_p - \omega_q)} \left[ \frac{\omega_{mn} - \omega_p - \omega_q}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \right]
\]

\[
= \frac{1}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)}
\]
The same procedure can be performed on terms

\[
\frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{[(\omega_{mn} - \omega_p - \omega_q) - i\gamma_{mn}][(\omega_{nl} + \omega_p) + i\gamma_{nl}]} \quad (a'_1)
\]

\[
+ \frac{\mu^k_{ln} \mu^i_{nm} \mu^j_{ml}}{[(\omega_{nm} + \omega_p + \omega_q) + i\gamma_{nm}][(\omega_{ml} - \omega_q) - i\gamma_{ml}]} \quad (b_2)
\]

\[
\frac{1}{(\omega_{nl} + \omega_p)(\omega_{ml} - \omega_q)}
\]
\[ \chi_{ijk}^{(2)}(\omega_p + \omega_q, \omega_q, \omega_p) = \frac{N}{2\epsilon_0 h^2} \sum_{lmn} \rho_{ll}^{(0)} \left\{ \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{(\omega_{nl} - \omega_p - \omega_q)(\omega_{ml} - \omega_p)} \right\} \]

(a1)

\[ + \frac{\mu_{ln}^i \mu_{nm}^j \mu_{ml}^k}{(\omega_{nl} - \omega_p - \omega_q)(\omega_{ml} - \omega_q)} \]

(a2)

\[ + \frac{\mu_{ln}^j \mu_{nm}^i \mu_{ml}^k}{(\omega_{nl} + \omega_q)(\omega_{ml} - \omega_p)} \]

(b1), (a2')

\[ + \frac{\mu_{ln}^k \mu_{nm}^j \mu_{ml}^i}{(\omega_{nl} + \omega_p)(\omega_{ml} - \omega_q)} \]

(b2), (a1')

\[ + \frac{\mu_{ln}^k \mu_{nm}^j \mu_{ml}^i}{(\omega_{ml} + \omega_p + \omega_q)(\omega_{nl} + \omega_p)} \]

(b2')

\[ + \frac{\mu_{ln}^j \mu_{nm}^k \mu_{ml}^i}{(\omega_{ml} + \omega_p + \omega_q)(\omega_{ml} + \omega_q)} \]

(b2')
Density Matrix Calculation of the Third-Order Susceptibility

\[
\rho_{nm}^{(3)} = e^{-(i\omega_{nm} + \gamma_{nm})t} \int_{-\infty}^{t} \frac{-i}{\hbar} [\hat{V}, \hat{\rho}^{(2)}]_{nm} e^{(i\omega_{nm} + \gamma_{nm})t'} dt',
\]

\[
[\hat{V}, \hat{\rho}^{(2)}]_{nm} = - \sum_{v} (\mu_{nv} \rho_{vm}^{(2)} - \rho_{nv}^{(2)} \mu_{vm}) \cdot \tilde{E}(t),
\]

\[
\rho_{vm}^{(2)} = \sum_{l} \sum_{pq} K_{vml} e^{-i(\omega_{p} + \omega_{q})t},
\]

We also represent the electric field as:

\[
\tilde{E}(t) = \sum_{r} E(\omega_{r}) e^{-i\omega_{r}t}
\]

\[
[\hat{V}, \hat{\rho}^{(2)}]_{nm} = - \sum_{vl} \sum_{pqr} [\mu_{nv} \cdot E(\omega_{r})] K_{vml} e^{-i(\omega_{p} + \omega_{q} + \omega_{r})t} + \sum_{vl} \sum_{pqr} [\mu_{vm} \cdot E(\omega_{r})] K_{nvl} e^{-i(\omega_{p} + \omega_{q} + \omega_{r})t}
\]
The nonlinear polarization oscillating at frequency $\omega_p + \omega_q + \omega_r$ is given by

$$\mathbf{P}(\omega_p + \omega_q + \omega_r) = N\langle \mathbf{\mu}(\omega_p + \omega_q + \omega_r) \rangle$$

$$\langle \tilde{\mathbf{\mu}} \rangle = \sum_{nm} \rho_{nm} \mathbf{\mu}_{mn} = \sum_s \langle \mathbf{\mu}(\omega_s) \rangle e^{-i\omega_s t}$$

$$P_k(\omega_p + \omega_q + \omega_r) = \epsilon_0 \sum_{hij} \sum_{pqr} \chi^{(3)}_{kijh}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) \times E_j(\omega_r)E_i(\omega_q)E_h(\omega_p).$$

By combining through , we find that the third-order susceptibility is given by:
\[ \chi_{kji,h}^{(3)}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3 P_I} \sum_{nmvl} \left\{ \frac{(\rho_{nm}^{(0)} - \rho_{ll}^{(0)}) \mu_{mn}^{k} \mu_{nv}^{j} \mu_{vl}^{i} \mu_{lm}^{h}}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{vm} - \omega_p - \omega_q) - i\gamma_{vm}][(\omega_{lm} - \omega_p) - i\gamma_{lm}]} \right. \\
- \left[ (\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm} \right] \left[ (\omega_{vm} - \omega_p - \omega_q) - i\gamma_{vm} \right] \left[ (\omega_{vl} - \omega_p) - i\gamma_{vl} \right] \right. \\
\left. \frac{(\rho_{vl}^{(0)} - \rho_{vv}^{(0)}) \mu_{mn}^{k} \mu_{nv}^{j} \mu_{vl}^{i} \mu_{lm}^{h}}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv}][(\omega_{lv} - \omega_p) - i\gamma_{lv}]} \right. \\
- \left[ (\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm} \right] \left[ (\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv} \right] \left[ (\omega_{lv} - \omega_p) - i\gamma_{lv} \right] \right. \\
\left. \frac{(\rho_{nv}^{(0)} - \rho_{ll}^{(0)}) \mu_{mn}^{k} \mu_{vm}^{j} \mu_{nl}^{i} \mu_{lv}^{h}}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv}][(\omega_{nl} - \omega_p) - i\gamma_{nl}]} \right. \\
- \left[ (\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm} \right] \left[ (\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv} \right] \left[ (\omega_{nl} - \omega_p) - i\gamma_{nl} \right] \left\} \right. \\
+ \left. \frac{(\rho_{ll}^{(0)} - \rho_{nn}^{(0)}) \mu_{mn}^{k} \mu_{vm}^{j} \mu_{nl}^{i} \mu_{lv}^{h}}{[(\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm}][(\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv}][(\omega_{nl} - \omega_p) - i\gamma_{nl}]} \right. \\
- \left[ (\omega_{nm} - \omega_p - \omega_q - \omega_r) - i\gamma_{nm} \right] \left[ (\omega_{nv} - \omega_p - \omega_q) - i\gamma_{nv} \right] \left[ (\omega_{nl} - \omega_p) - i\gamma_{nl} \right] \right\}. \]
Here we have again made use of the intrinsic permutation operator $\mathcal{P}_I$, whose meaning is that everything to the right of it is to be averaged over all possible permutations of the input frequencies $\omega_p$, $\omega_q$, and $\omega_r$, with the cartesian indices $h, i, j$ permuted simultaneously. Next, we rewrite this equation as eight separate terms by changing the dummy indices so that $l$ is always the index of $\rho_{ii}^{(0)}$. We also require that only positive resonance frequencies appear if the energies are ordered so that $E_v > E_n > E_m > E_l$, and we arrange the matrix elements so that they appear in “natural” order, $l \rightarrow m \rightarrow n \rightarrow v$ (reading right to left). We obtain
\[
\chi_{k_jih}^{(3)}(\omega_p + \omega_q + \omega_r, \omega_r, \omega_q, \omega_p) = \sum_{v} \rho_{il}^{(0)} \left\{ \frac{\mu_k^l \mu_n^j \mu_m^i \mu_l^h}{[(\omega_{vL} - \omega_p - \omega_q - \omega_r) - i\gamma_{vl}][(\omega_{ml} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \right. \\
+ \frac{\mu_h^l \mu_v^k \mu_n^j \mu_m^i}{[(\omega_{nv} - \omega_p - \omega_q - \omega_r) - i\gamma_{nv}][(\omega_{mv} - \omega_p - \omega_q) - i\gamma_{mv}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \\
+ \frac{\mu_h^l \mu_v^k \mu_n^j \mu_m^i}{[(\omega_{mv} - \omega_p - \omega_q - \omega_r) - i\gamma_{mv}][(\omega_{ml} + \omega_p + \omega_q) + i\gamma_{ml}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \\
+ \frac{\mu_i^j \mu_n^k \mu_m^i \mu_l^h}{[(\omega_{vn} + \omega_p + \omega_q + \omega_r) + i\gamma_{vn}][(\omega_{nl} - \omega_p - \omega_q) - i\gamma_{nl}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \\
+ \frac{\mu_i^j \mu_n^k \mu_m^i \mu_l^h}{[(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i\gamma_{nm}][(\omega_{mv} + \omega_p + \omega_q) + i\gamma_{mv}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \\
+ \frac{\mu_i^j \mu_n^k \mu_m^i \mu_l^h}{[(\omega_{nm} + \omega_p + \omega_q + \omega_r) + i\gamma_{nm}][(\omega_{vm} + \omega_p + \omega_q) + i\gamma_{mv}][(\omega_{ml} - \omega_p) - i\gamma_{ml}]} \\
+ \frac{\mu_i^j \mu_n^k \mu_m^i \mu_l^h}{[(\omega_{ml} + \omega_p + \omega_q + \omega_r) + i\gamma_{ml}][(\omega_{nl} + \omega_p + \omega_q) + i\gamma_{nl}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \left\} 
\]
Double-sided Feynman diagrams
Double-sidered Feynman diagrams
\[
\frac{\mu_i \mu_k \mu_j \mu_h}{\mu_{1v}\mu_{1m}\mu_{1n}\mu_{1l}}\left[\left(\omega_{nv} - \omega_p - \omega_q - \omega_r\right) - i\gamma_{nv}\right]\left[\left(\omega_{vm} + \omega_p + \omega_q\right) + i\gamma_{vm}\right]\left[\left(\omega_{ml} - \omega_p\right) - i\gamma_{ml}\right]
\]

(b_1)

Double-sided Feynman diagrams
\[
\frac{\mu_{j}^{l} \mu_{v}^{k} \mu_{m}^{n} \mu_{i}^{p}}{[(\omega_{mn} - \omega_{p} - \omega_{q} - \omega_{r}) - i\gamma_{mn}][(\omega_{nl} + \omega_{p} + \omega_{q}) + i\gamma_{nl}][(\omega_{vl} + \omega_{p}) + i\gamma_{vl}]}
\]

(b_2)

Double-sided Feynman diagrams
\[ + \frac{\mu^j_{lv} \mu^k_{vn} \mu^{i}_{nm} \mu^h_{ml}}{(\omega_{vn} + \omega_p + \omega_q + \omega_r) + i \gamma_{vn}} \frac{1}{[(\omega_{nl} - \omega_p - \omega_q) - i \gamma_{nl}][\omega_{ml} - \omega_r - i \gamma_{ml}]} \]

(c_1)

**Double-sided Feynman diagrams**
Double-sided Feynman diagrams
Double-sided Feynman diagrams
\[
\frac{\mu^h_{lv}\mu^i_{vn}\mu^j_{nm}\mu^k_{ml}}{[(\omega_{ml} + \omega_p + \omega_q + \omega_r) + i\gamma_{ml}][(\omega_{nl} + \omega_p + \omega_q) + i\gamma_{nl}][(\omega_{vl} + \omega_p) + i\gamma_{vl}]} \right).
\]

(d_2)
Electromagnetically Induced Transparency

Typical situation for observing electromagnetically induced transparency (Fig. 3.8.1):

We thus first examine how linear absorption at frequency $\omega_4$ is modified by an intense saturating field of amplitude $E_s$ at frequency $\omega_s$, as illustrated in part (b) of Fig. 3.8.1. To treat this problem, we need to include states $a$, $d$, and $c$ in the atomic wavefunction. Common sense might suggest that we thus express the wavefunction as

$$\psi(\mathbf{r}, t) = C'_a(t)u_a(\mathbf{r})e^{-i\omega_a t} + C'_d(t)u_d(\mathbf{r})e^{-i\omega_d t} + C'_c(t)u_c(\mathbf{r})e^{-i\omega_c t}$$
It should be obey Schrödinger’s equation in the form:

\[ i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \quad \text{with} \quad \hat{H} = \hat{H}_0 + \hat{V} \]

where in the rotating-wave and electric-dipole approximations we can express the interaction energy as:

\[ \hat{V} = -\hat{\mu}(E_4 e^{-i\omega_4 t} + E^*_s e^{i\omega_s t}) \]

\[
\begin{align*}
&i\hbar \left[ \dot{C}_a u_a + \dot{C}_d u_de^{-i\omega_4 t} - i\omega_4 C_d u_de^{-i\omega_4 t} + \dot{C}_c u_c e^{-i(\omega_4 - \omega_s) t} \right] \\
&\quad - i(\omega_4 - \omega_s) C_c u_c e^{-i(\omega_4 - \omega_s) t} \\
&= C_a \hbar \omega_a u_a + C_d \hbar \omega_d u_de^{-i\omega_4 t} + C_c \hbar \omega_c u_c e^{-i(\omega_4 - \omega_s) t} \\
&+ \hat{V} \left[ C_a u_a + C_d u_de^{-i\omega_4 t} + C_c u_c e^{-i(\omega_4 - \omega_s) t} \right].
\end{align*}
\]

where \( \hbar \omega_j \) is the energy of level \( j \), and solve Schrödinger’s equation to determine the time evolution of the expansion coefficients \( C'_a(t) \), \( C'_d(t) \), and \( C'_c(t) \). But in fact the calculation proceeds much more simply if instead we work in the interaction picture and represent the wavefunction as: \[
\psi(\mathbf{r}, t) = C_a(t)u_a(\mathbf{r}) + C_d(t)u_d(\mathbf{r})e^{-i\omega_4 t} + C_c(t)u_c(\mathbf{r})e^{-i(\omega_4 - \omega_s) t}
\]
We turn this result into three separate equations by the usual procedure of multiplying successively by $u_a^*$, $u_d^*$, and $u_c^*$ and integrating the resulting equation over all space. Assuming the quantities $u_j$ to be orthonormal, we obtain:

\[
\begin{align*}
    i\hbar \dot{C}_a &= \hbar \omega_a C_a + V_{ad} C_d e^{-i\omega_4 t}, \\
    i\hbar \left[ \dot{C}_d e^{-i\omega_4 t} - i\omega_4 C_d e^{-i\omega_4 t} \right] &= \hbar \omega_d C_d e^{-i\omega_4 t} + V_{da} C_a + V_{dc} C_c e^{-i(\omega_4 - \omega_s) t}, \\
    i\hbar \left[ \dot{C}_e e^{-i(\omega_4 - \omega_s) t} - i(\omega_4 - \omega_s) C_e e^{-i(\omega_4 - \omega_s) t} \right] &= \hbar \omega_c C_c e^{-i(\omega_4 - \omega_s) t} + V_{cd} C_d e^{-i\omega_4 t}.
\end{align*}
\]

We next introduce the explicit forms of the matrix elements of $V$:

\[
V_{ad}^* = V_{da} = -\mu_{da} E_4 e^{-i\omega_4 t}, \\
V_{dc}^* = V_{cd} = -\mu_{cd} E_s^* e^{i\omega_s t}.
\]

Also, we measure energies relative to that of the ground state $a$ so that:

\[
\hbar \omega_a \rightarrow \hbar \omega_{aa} = 0, \quad \hbar \omega_d \rightarrow \hbar \omega_{da}, \quad \hbar \omega_c \rightarrow \hbar \omega_{ca}.
\]

In addition, we introduce the Rabi frequencies

\[
\Omega = \mu_{da} E_4 / \hbar \quad \text{and} \quad \Omega_s^* = \mu_{cd} E_s^* / \hbar.
\]

Equations thus become:
\[ \begin{align*}
\dot{C}_a &= iC_d \Omega^*, \\
\dot{C}_d - i\delta C_d &= iC_a \Omega + iC_c \Omega_s, \\
\dot{C}_c - i(\delta - \Delta)C_c &= iC_d \Omega_s^*,
\end{align*} \]

\[ \delta \equiv \omega_4 - \omega_{da} \quad \Delta \equiv \omega_s - \omega_{dc} \]

We want to solve these equations correct to all orders in \( \Omega_s \) and to lowest order in \( \Omega \). One might guess that one can do so by ignoring the first equation and replacing \( C_a \) by unity in the second equation. But to proceed more rigorously, we perform a formal perturbation expansion in the field amplitude \( \Omega \). We introduce a strength parameter \( \lambda \), which we assume to be real, and we replace \( \Omega \) by \( \lambda \Omega \). We also expand \( C_j \) as a power series in \( \lambda \) as

\[ C_j = C_j^{(0)} + \lambda C_j^{(1)} + \lambda^2 C_j^{(2)} + \cdots. \]

\[ \begin{align*}
\dot{C}_a^{(0)} + \lambda \dot{C}_a^{(1)} &= iC_d^{(0)} \lambda \Omega^* + iC_d^{(1)} \lambda^2 \Omega_s^*, \\
(\dot{C}_d^{(0)} - i\delta C_d^{(0)}) + \lambda(\dot{C}_d^{(1)} - i\delta C_d^{(1)}) &= iC_a^{(0)} \Omega \lambda + iC_a^{(1)} \Omega \lambda^2 + iC_c^{(0)} \Omega_s \lambda + iC_c^{(1)} \Omega_s \lambda^2, \\
[\dot{C}_c^{(0)} - i(\delta - \Delta)C_c^{(0)}] + \lambda[\dot{C}_c^{(1)} - i(\delta - \Delta)C_c^{(1)}] &= iC_d^{(0)} \lambda \Omega_s^* + iC_d^{(1)} \lambda^2 \Omega_s^*. \end{align*} \]
We next note that because these equations must be valid for arbitrary values of the parameter $\lambda$, the coefficients of each power of $\lambda$ must satisfy the equations separately. In particular, the portions of $\star$ that are independent of $\lambda$ are given by:

\[
\begin{align*}
\dot{C}_a^{(0)} &= 0, \\
\dot{C}_d^{(0)} - i\delta C_d^{(0)} &= iC_a^0\Omega + iC_c^{(0)}\Omega_s, \\
\dot{C}_c^{(0)} - i(\delta - \Delta)C_c^{(0)} &= iC_d^{(0)}\Omega_s^*. 
\end{align*}
\]

We take the solution to these equations to be the one corresponding to the assumed initial conditions that is,

\[
C_a^{(0)} = 1 \quad \text{and} \quad C_d^{(0)} = C_c^{(0)} = 0
\]

for all times. Next, we note that the portions of $\star$ that are linear in $\lambda$ are given by:

\[
\begin{align*}
\dot{C}_a^{(1)} &= 0, \\
\dot{C}_d^{(1)} - i\delta C_d^{(1)} &= i\Omega + iC_c^{(0)}\Omega_s, \\
\dot{C}_c^{(1)} - i(\delta - \Delta)C_c^{(1)} &= iC_d^{(0)}\Omega_s^*,
\end{align*}
\]

\[
\begin{align*}
\dot{C}_d - i\delta C_d &= i\Omega + i\Omega_s C_c, \\
\dot{C}_c - i(\delta - \Delta)C_c &= i\Omega_s^* C_d.
\end{align*}
\]
We can thus find the steady state solution to these equations by setting the time derivatives to zero:

\begin{align*}
0 &= \Omega + \delta C_d + \Omega_s C_c, \\
0 &= \Omega_s^2 C_d + (\delta - \Delta) C_c.
\end{align*}

We solve these equations algebraically to find that

\[ C_d = \frac{\Omega (\delta - \Delta)}{|\Omega_s|^2 - \delta (\delta - \Delta)}. \]

The physical quantity of primary interest is the induced dipole moment, which can be determined as follows:

\[ \vec{p} = \langle \psi | \hat{\mu} | \psi \rangle = \langle \psi^{(0)} | \hat{\mu} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{\mu} | \psi^{(0)} \rangle = \langle a | \hat{\mu} | d \rangle C_d e^{-i\omega_4 t} + \text{c.c.} = \mu_{ad} C_d e^{-i\omega_4 t} + \text{c.c.} \]

We thus find that the dipole moment amplitude is given by

\[ p = \frac{\mu_{ad} \Omega (\delta + \Delta)}{|\Omega_s|^2 - (\delta + \Delta)\delta} \]

and consequently that the polarization is given by

\[ P = Np \equiv \varepsilon_0 \chi^{(1)} E \]

\[ \chi^{(1)} = \frac{N |\mu_{da}|^2}{\varepsilon_0 \hbar} \frac{(\delta - \Delta)}{|\Omega_s|^2 - (\delta - \Delta)\delta} \]
by replacing $\delta$ by $\delta + i\gamma_d$ and $\Delta$ by $\Delta + i(\gamma_c - \gamma_d)$

$$p = \frac{\mu_{ad} \Omega (\delta - \Delta + i\gamma_c)}{|\Omega_s|^2 - (\delta + i\gamma_d)(\delta - \Delta + i\gamma_c)}$$

and that the general form for $\chi^{(1)}$ is given by

$$\chi^{(1)} = \frac{N}{\hbar} \frac{|\mu_{da}|^2 (\delta - \Delta + i\gamma_c)}{|\Omega_s|^2 - (\delta + i\gamma_d)(\delta - \Delta + i\gamma_c)}$$

Note that when both fields are turned to the exact resonance ($\delta = \Delta = 0$), the susceptibility becomes simply

$$\chi^{(1)} = \frac{N}{\hbar} \frac{|\mu_{da}|^2 i\gamma_c}{|\Omega_s|^2 + \gamma_c\gamma_d}$$

which is purely imaginary!
\[ \chi^{(1)} = \frac{N |\mu_{da}|^2 i\gamma_c}{\hbar |\Omega_s|^2 + \gamma_c \gamma_d} . \]

\( \Omega_s = 0 \) vs. \( \Omega_s = 5\gamma_d \)

\( \Omega_s = 0 \) vs. \( \Omega_s = 0.4\gamma_d \)

\[ \delta/\gamma_d = (\omega_4 - \omega_{da})/\gamma_d \]
We now calculate the response leading to sum-frequency generation. We express the wavefunction in the interaction picture as:

\[
\psi(r, t) = C_a(t)u_a(r) + C_b(t)u_b(r)e^{-i\omega t} + C_c(t)u_c(r)e^{-i2\omega t} + C_d(t)u_d(r)e^{-i(2\omega+\omega_s)t}
\]

\[
\hat{H} = \hat{H}_0 + \hat{V}
\]

\[
i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi
\]

We now separate this expression into four equations by the usual method of multiplying successively by \(u^*_a\), \(u^*_b\), \(u^*_c\), and \(u^*_d\) and integrating over all Space, we find that

\[
i\hbar \dot{C}_a = V_{ab} C_b e^{-i\omega t},
\]

\[
i\hbar (\dot{C}_b - i\omega C_b) e^{-i\omega t} = \hbar \omega_{ba} C_b e^{-i\omega t} + V_{ba} C_a + V_{bc} C_c e^{-i2\omega t},
\]

\[
i\hbar (\dot{C}_c - i2\omega C_c) e^{-i2\omega t} = \hbar \omega_{ca} C_c e^{-i2\omega t} + V_{cb} C_b e^{-i\omega t} + V_{cd} C_d e^{-i(2\omega+\omega_s)t},
\]

\[
i\hbar [\dot{C}_d - i(2\omega+\omega_s) C_d] e^{-(2\omega+\omega_s)t} = \hbar \omega_{da} C_d e^{-(2\omega+\omega_s)t} + V_{dc} C_c e^{-i2\omega t}.
\]
We next represent the matrix elements of the interaction Hamiltonian as

\[
V_{ba} = V_{ab}^* = -\mu_{ba} E e^{-i\omega t} = -\hbar \Omega_{ba} e^{-i\omega t}, \\
V_{cb} = V_{bc}^* = -\mu_{cb} E e^{-i\omega t} = -\hbar \Omega_{cb} e^{-i\omega t}, \\
V_{dc} = V_{cd}^* = -\mu_{dc} E e^{-i\omega s t} = -\hbar \Omega_{dc} e^{-i\omega s t},
\]

and introduce the detuning factors as

\[
\delta_1 = \omega - \omega_{ba}, \quad \delta_2 = 2\omega - \omega_{ca} \quad \text{and} \quad \Delta = \omega_s - \omega_{dc}.
\]

\[
\dot{C}_a = i C_b \Omega_{ba}^*, \\
\dot{C}_b - i C_b \delta_1 = i C_a \Omega_{ba} + i C_c \Omega_{cb}^*, \\
\dot{C}_c - i C_c \delta_2 = i C_b \Omega_{cb} + i C_d \Omega_{dc}^*, \\
\dot{C}_d - i C_d (\delta_2 + \Delta) = i C_c \Omega_{dc}.
\]

(3.8.32a) (3.8.32b) (3.8.32c) (3.8.32d)

We wish to solve these equations perturbatively in \(\Omega_{ba}\) and \(\Omega_{cb}\) but to all orders in \(\Omega_{dc}\). We first note that consistent with this assumption we can ignore Eq. (3.8.32a) altogether, as \(|C_b| \ll |C_a|\) and therefore \(C_a \approx 1\). In solving Eq. (3.8.32b), we can drop the last term because \(|C_c| \ll |C_b|\). Then setting \(C_a = 1\) and taking \(\dot{C}_b = 0\) for the steady-state solution, we find that

\[
C_b = -\Omega_{ba} / \delta_1
\]
We next need to find the simultaneous, steady-state solutions to Eqs. (3.8.32c) and (3.8.32d). We set the time derivatives to zero to obtain

\[
-C_c = \frac{C_b \Omega_{cb}}{\delta_2} + \frac{C_d \Omega_{dc}^*}{\delta_2},
\]

\[
C_d = \frac{-C_c \Omega_{dc}}{(\delta_2 + \Delta)}.
\]

\[
C_d = \frac{-\Omega_{ba} \Omega_{cb} \Omega_{dc}}{\delta_1 \delta_2 (\delta_2 + \Delta)} + C_d \frac{|\Omega_{dc}|^2}{(\delta_2 + \Delta) \delta_2}
\]

\[
C_d = -\frac{\Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 \delta_2 (\delta_2 + \Delta)} \left[ \frac{|\Omega_{dc}|^2}{\delta_2 (\delta_2 + \Delta)} \right]^{-1}
\]

\[
= -\frac{\Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]}.
\]
The induced dipole moment at the sum frequency is now calculated as

\[ \tilde{p} = \langle \psi | \hat{\mu} | \psi \rangle = \langle u_a | \hat{\mu} | C_d u_d \rangle + c.c. = \mu_{ad} C_d + c.c. \]

We thus find that the complex amplitude of the induced dipole moment is given by

\[ p = \frac{-\mu_{ad} \Omega_{dc} \Omega_{cb} \Omega_{ba}}{\delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]} = \frac{-\mu_{ad} \mu_{bc} \mu_{cb} \mu_{ba} E^2 E_s}{\hbar^3 \delta_1 [\delta_2 (\delta_2 + \Delta) - |\Omega_{dc}|^2]} \equiv \frac{3\epsilon_0 \chi^{(3)} E^2 E_c}{N}. \]

\[ \chi^{(3)} = \frac{-N \mu_{ad} \mu_{dc} \mu_{cb} \mu_{ba}}{3\epsilon_0 \hbar \delta_1 [(\delta_2 + i\gamma_c)(\delta_2 + \Delta + i\gamma_d) - |\Omega_{dc}|^2]}. \]
Local-Field Corrections to the Nonlinear Optical Susceptibility

- Local-Field Effects in Linear Optics:

we represent the dipole moment induced in a typical molecule as:

\[ \tilde{p} = \varepsilon_0 \alpha \mathbf{E}_{\text{loc}} \]

The local field that is, the effective electric field that acts on the molecule.

**FIGURE 3.9.1** Calculation of the Lorentz local field.
The field, which we identify as the Lorentz local field, is given by

$$\tilde{E}_{\text{loc}} = \tilde{E} + \frac{1}{3\varepsilon_0} \tilde{P}.$$ 

By definition, the polarization of the material is given by

$$\tilde{P} = N\tilde{P},$$

$$\tilde{P} = N\varepsilon_0\alpha \left( \tilde{E} + \frac{1}{3\varepsilon_0} \tilde{P} \right),$$

$$\tilde{P} = \varepsilon_0 \chi^{(1)} \tilde{E}.$$ 

$$\epsilon^{(1)} = 1 + \chi^{(1)}$$

$$\frac{\epsilon^{(1)} - 1}{\epsilon^{(1)} + 2} = \frac{1}{3} N\alpha$$

$$\frac{\epsilon^{(1)} + 2}{3} = \frac{1}{1 - \frac{1}{3} N\alpha}$$

$$\chi^{(1)} = \frac{N\alpha}{1 - \frac{1}{3} N\alpha}$$
\[ \chi^{(1)} = \frac{\epsilon^{(1)} + 2}{3} N\alpha. \]

This result shows that \( \chi^{(1)} \) is larger than \( N\alpha \) by the factor \( (\epsilon^{(1)} + 2)/3 \). The factor \( (\epsilon^{(1)} + 2)/3 \) can thus be interpreted as the local-field enhancement factor for the linear susceptibility.
Local-Field Effects in Nonlinear Optics:

the polarization now has both linear and nonlinear contributions:

\[ \tilde{P} = \tilde{P}^L + \tilde{P}^{NL} \]

We represent the linear contribution as

\[ \tilde{P}^L = N \epsilon_0 \gamma^{(1)} \tilde{E}_{loc} \]

Remember:

\[ \tilde{E}_{loc} = \tilde{E} + \frac{1}{3 \epsilon_0} \tilde{P} \]

\[ \tilde{P}^L = N \epsilon_0 \alpha \left( \tilde{E} + \frac{1}{3 \epsilon_0} \tilde{P}^L + \frac{1}{3 \epsilon_0} \tilde{P}^{NL} \right) \]

to express the factor \( N \alpha \) that appears in the resulting expression in terms of the linear dielectric constant. We thereby obtain

\[ \tilde{P}^L = \left[ \epsilon^{(1)} - 1 \right] \left( \epsilon_0 \tilde{E} + \frac{1}{3} \tilde{P}^{NL} \right) \]
Next we consider the displacement vector

\[ \tilde{D} = \varepsilon_0 \tilde{E} + \tilde{P} = \varepsilon_0 \tilde{E} + \tilde{P}^L + \tilde{P}^{NL} \]

By replacing \( \tilde{P}^L \) with

\[ \tilde{P}^L = [\varepsilon^{(1)} - 1](\varepsilon_0 \tilde{E} + \frac{1}{3} \tilde{P}^{NL}) \]

the nonlinear source polarization defined by

\[ \tilde{P}^{NLS} = \left( \frac{\varepsilon^{(1)} + 2}{3} \right) \tilde{P}^{NL} \]

\[ \tilde{D} = \varepsilon_0 \varepsilon^{(1)} \tilde{E} + \tilde{P}^{NLS} \]
When the derivation of the wave equation is carried out as in Section 2.1 using this expression for $\tilde{D}$, we obtain the result

$$\nabla \times \nabla \times \tilde{E} + \frac{\varepsilon^{(1)}}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \tilde{P}^{NLS}}{\partial t^2}$$

This result shows how local-field effects are incorporated into the wave equation.

by replacing $\tilde{P}$ by $\tilde{P}^L$ in

$$\tilde{E}_{loc} = \tilde{E} + \frac{1}{3 \varepsilon_0} \tilde{P}.$$  

$$\tilde{E}_{loc} = \tilde{E} + \frac{1}{3} \chi^{(1)} \tilde{E} = \left[1 + \frac{1}{3} (\varepsilon^{(1)} - 1)\right] \tilde{E},$$

$$\tilde{E}_{loc} = \left(\frac{\varepsilon^{(1)} + 2}{3}\right) \tilde{E}.$$  

We now apply the results given by $\star$ and $\star$ to the case of second-order nonlinear interactions. We define the nonlinear susceptibility by means of the equation
The nonlinear polarization (i.e., the second-order contribution to the dipole moment per unit volume) can be represented as

\[ P_{i\text{NLS}}^{\text{NLS}}(\omega_m + \omega_n) = \epsilon_0 \sum_{jk} \sum_{mn} \chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) E_j(\omega_m) E_k(\omega_n) \]

where

\[ P_{i\text{NL}}^{\text{NL}}(\omega_m + \omega_n) = \left( \frac{\epsilon^{(1)}(\omega_m + \omega_n) + 2}{3} \right) P_{i\text{NL}}^{\text{NL}}(\omega_m + \omega_n) \]

we find that the nonlinear susceptibility can be represented as

\[ P_{i\text{NL}}^{\text{NL}}(\omega_m + \omega_n) = N \epsilon_0 \sum_{jk} \sum_{mn} \beta_{ijk}(\omega_m + \omega_n, \omega_m, \omega_n) E_{j\text{loc}}^{\text{loc}}(\omega_m) E_{k\text{loc}}^{\text{loc}}(\omega_n) \]

\[ E_{j\text{loc}}^{\text{loc}}(\omega_m) = \left( \frac{\epsilon^{(1)}(\omega_m) + 2}{3} \right) E_j(\omega_m) \]
\[ \chi_{ijk}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) = \mathcal{L}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) N \beta_{ijk}(\omega_m + \omega_n, \omega_m, \omega_n) \]

where

\[ \mathcal{L}^{(2)}(\omega_m + \omega_n, \omega_m, \omega_n) = \left( \frac{\varepsilon^{(1)}(\omega_m + \omega_n) + 2}{3} \right) \left( \frac{\varepsilon^{(1)}(\omega_m) + 2}{3} \right) \left( \frac{\varepsilon^{(1)}(\omega_n) + 2}{3} \right) \]

gives the local-field enhancement factor for the second-order susceptibility.

This result is readily generalized to higher-order nonlinear interaction:

\[ \mathcal{L}^{(3)}(\omega_l + \omega_m + \omega_n, \omega_l, \omega_m, \omega_n) = \left( \frac{\varepsilon^{(1)}(\omega_l + \omega_m + \omega_n) + 2}{3} \right) \left( \frac{\varepsilon^{(1)}(\omega_l) + 2}{3} \right) \times \left( \frac{\varepsilon^{(1)}(\omega_m) + 2}{3} \right) \left( \frac{\varepsilon^{(1)}(\omega_n) + 2}{3} \right). \]
We assume that the total polarization (including both linear and nonlinear contributions) at the third-harmonic frequency is given by

\[ P(3\omega) = N\varepsilon_0 \alpha(3\omega) E_{loc}(3\omega) + N\varepsilon_0 \gamma(3\omega, \omega, \omega, \omega) E_{loc}^3(\omega) \]

Using:

\[ \tilde{E}_{loc} = \tilde{E} + \frac{1}{3\varepsilon_0} \tilde{P}. \]

\[ \tilde{E}_{loc} = \left( \frac{\varepsilon^{(1)} + 2}{3} \right) \tilde{E}. \]

This equation is now solved algebraically for \( P(3\omega) \) to obtain
We can identify the first and second terms of this expression as the linear and third-order polarizations, which we represent as

\[ P(3\omega) = \epsilon_0 \chi^{(1)}(3\omega) E(3\omega) + \epsilon_0 \chi^{(3)}(3\omega, \omega, \omega, \omega) E(\omega)^3 \]

where (in agreement with the unusual Lorentz Lorenz law) the linear susceptibility is given by:

\[ \chi^{(1)}(3\omega) = \frac{N \alpha(3\omega)}{1 - \frac{1}{3} N \alpha(3\omega)} \]

and where the third-order susceptibility is given by

\[ \chi^{(3)}(3\omega, \omega, \omega, \omega) = \left( \frac{\varepsilon^{(1)}(\omega) + 2}{3} \right)^3 \left( \frac{\varepsilon^{(1)}(3\omega) + 2}{3} \right) N \gamma(3\omega, \omega, \omega, \omega) \].