

VIII. NONLINEAR OPTICS -- QUANTUM PICTURE:⁴⁵

A QUANTUM MECHANICAL VIEW OF THE BASICS OF NONLINEAR OPTICS⁴⁶

In what follows we draw on the discussion of the density operator in Review of Basic Quantum Mechanics: Dynamic Behavior of Quantum Systems, Section II of the lecture set entitled *The Interaction of Radiation and Matter: Semiclassical Theory* (hereafter referred to as IRM:ST). The macroscopic polarization is given by

$$\langle \bar{\mathbf{P}} \rangle = \text{Tr} \left(\bar{\mathbf{P}} \right) \quad [\text{VIII-1}]$$

We take the total Hamiltonian of a particular system in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{random}} \quad [\text{VIII-2}]$$

where $\mathcal{H}_{\text{random}}$ is a Hamiltonian describing the random perturbations on the system by the thermal reservoir surrounding the system. Thus

$$\frac{d}{dt} = \frac{i}{\hbar} \left[\cdot, (\mathcal{H}_0 + \mathcal{H}_{\text{int}}) \right] + \frac{d}{dt} \Big|_{\text{relax}} \quad [\text{VIII-3}]$$

where

$$\frac{d}{dt} \Big|_{\text{relax}} = \frac{i}{\hbar} \left[\cdot, \mathcal{H}_{\text{random}} \right] \quad [\text{VIII-4}]$$

To find the nonlinear susceptibility, we make use of the following perturbation expansions:

$$= {}^{(0)} + {}^{(1)} + {}^{(2)} + \dots \quad [\text{VIII-5a}]$$

⁴⁵ See Nonlinear Optics -- Classical Picture which is Section VII in the lecture set entitled *On Classical Electromagnetic Fields* (OCEF).

⁴⁶ See, for example, Chapter 2 in Y. R. Shen's *Principles of Nonlinear Optics*, Wiley (1984).

$$\langle \bar{\mathbf{P}} \rangle = \langle \bar{\mathbf{P}}^{(0)} \rangle + \langle \bar{\mathbf{P}}^{(1)} \rangle + \langle \bar{\mathbf{P}}^{(2)} \rangle + \dots \quad [\text{VIII-5b}]$$

with
$$\langle \bar{\mathbf{P}}^{(\cdot)} \rangle = \text{Tr} \left(\rho^{(\cdot)} \bar{\mathbf{P}} \right) \quad [\text{VIII-5c}]$$

By substituting these expansions into Equation [VIII-3] and equating terms of like order in \mathcal{H}_{int} , we obtain the following hierarchy of equations:

$$\frac{d}{dt} \rho^{(0)} = \frac{i}{\hbar} \left[\rho^{(0)}, \mathcal{H}_0 \right] + \left. \frac{d}{dt} \rho^{(0)} \right|_{\text{relax}} \quad [\text{VIII-6a}]$$

$$\frac{d}{dt} \rho^{(1)} = \frac{i}{\hbar} \left\{ \left[\rho^{(1)}, \mathcal{H}_0 \right] + \left[\rho^{(0)}, \mathcal{H}_{\text{int}} \right] \right\} + \left. \frac{d}{dt} \rho^{(1)} \right|_{\text{relax}} \quad [\text{VIII-6b}]$$

$$\frac{d}{dt} \rho^{(2)} = \frac{i}{\hbar} \left\{ \left[\rho^{(2)}, \mathcal{H}_0 \right] + \left[\rho^{(1)}, \mathcal{H}_{\text{int}} \right] \right\} + \left. \frac{d}{dt} \rho^{(2)} \right|_{\text{relax}} \quad [\text{VIII-6c}]$$

$$\frac{d}{dt} \rho^{(3)} = \frac{i}{\hbar} \left\{ \left[\rho^{(3)}, \mathcal{H}_0 \right] + \left[\rho^{(2)}, \mathcal{H}_{\text{int}} \right] \right\} + \left. \frac{d}{dt} \rho^{(3)} \right|_{\text{relax}} \quad [\text{VIII-6d}]$$

.....

Following earlier considerations, it is reasonable to write

$$\left. \frac{d}{dt} \rho^{(n)} \right|_{\text{relax}} = - \gamma_{nn} \rho^{(n)} \quad [\text{VIII-7}]$$

Since the perturbing field is resolvable into an **appropriate** set of Fourier components (either discrete or continuous), we may write

$$\mathcal{H}_{\text{int}} = \mathcal{H}_{\text{int}}(k) \exp(-i k t) \quad [\text{VIII-8a}]$$

$$= \mathcal{H}_{\text{int}}(k) \exp(-i k t) \quad [\text{VIII-8b}]$$

and resolve Equations [VIII-6] into a hierarchy of algebraic equations. The first member of that hierarchy becomes⁴⁷

$$\begin{aligned} \langle n | \mathcal{H}_{\text{int}}(k) \{ i(\omega_{nn} - \omega_k) + \omega_{nn} \} | n \rangle &= \frac{i}{\hbar} \langle n | \{ \mathcal{H}_{\text{int}}(k) - \mathcal{H}_{\text{int}}(k) \} | n \rangle \\ &= \frac{i}{\hbar} \langle n | \mathcal{H}_{\text{int}}(k) | n \rangle \{ \omega_{nn} - \omega_{nn} \} \end{aligned} \quad [\text{VIII-9a}]$$

or⁴⁸

$$\langle n | \mathcal{H}_{\text{int}}(k) | n \rangle = \frac{i}{\hbar} \langle n | \mathcal{H}_{\text{int}}(k) | n \rangle \{ \omega_{nn} - \omega_{nn} \} \mathcal{D}(\omega_{nn} - \omega_k; \omega_{nn}) . \quad [\text{VIII-9b}]$$

The second member of the hierarchy becomes

$$\langle n | \mathcal{H}_{\text{int}}(k) \{ i(\omega_{nn} - \omega_k) + \omega_{nn} \} | n \rangle = \frac{i}{\hbar} \langle n | \left[\mathcal{H}_{\text{int}}(k), \mathcal{H}_{\text{int}}(k - k) \right] | n \rangle \quad [\text{VIII-10a}]$$

or

$$\begin{aligned} \langle n | \mathcal{H}_{\text{int}}(k) \{ i(\omega_{nn} - \omega_k) + \omega_{nn} \} | n \rangle &= \frac{i}{\hbar} \mathcal{D}(\omega_{nn} - \omega_k; \omega_{nn}) \left\{ \langle n | \mathcal{H}_{\text{int}}(k - k) | n \rangle \right. \\ &\quad \left. - \langle n | \mathcal{H}_{\text{int}}(k - k) | n \rangle \omega_{nn} \right\} \end{aligned} \quad [\text{VIII-10b}]$$

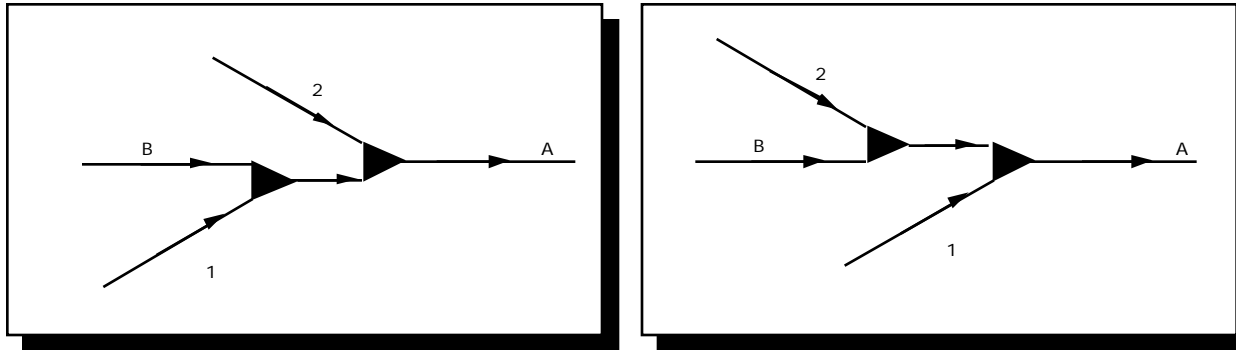
⁴⁷ we presume in this development that \mathcal{H}_{int} is a Hermitian operator.

⁴⁸ Recall that $\mathcal{D}(u - v; w) = [i(u - v) + w]^{-1}$ is the so called complex Lorentzian denominator.

Thus, we see that this expansion yields results akin to those embodied in Equations [VII-8] through [VIII-13] in OCEF.

TWO-PHOTON ABSORPTION

Let us consider two-photon absorption by a single atom (or by a set of paired \vec{k} -states in a semiconductor as discussed Section 7 of IRM:ST).



Two-Photon Absorption Process

From earlier discussions, the appropriate interaction Hamiltonian is given by

$$\mathcal{H}_{2p} = -e \vec{r} \cdot \vec{E}^{(+)}(\vec{R}, t) = -e \vec{r} \cdot [\vec{E}_1^{(+)}(\vec{R}, t) + \vec{E}_2^{(+)}(\vec{R}, t)] \quad [VIII-11]$$

In the appendix to this section we establish -- viz., in Equation [VIIIA-12] -- that the second approximation to the transition rate is given by

$$\frac{1}{(2)} \frac{d}{dt} P_{i \rightarrow f}^{(2)}(t, t_0) = \frac{2}{\hbar^2} \left| \langle f | \mathcal{H}_{int} | i \rangle + \frac{1}{\hbar} \sum_m \frac{\langle f | \mathcal{H}_{int} | m \rangle \langle m | \mathcal{H}_{int} | i \rangle}{\omega_{im}} \right|^2 \quad (i \rightarrow f)$$

Thus for the two-photon process

$$\frac{1}{(2)} \frac{2 e^4}{\hbar^4} \left| \sum_m \frac{\langle f | \vec{r} \cdot \vec{E}^{(+)} | m \rangle \langle m | \vec{r} \cdot \vec{E}^{(+)} | i \rangle}{i - m} \right|^2 \quad (i - f) \quad [\text{VIII-12}]$$

For two beam, two-photon processes

$$\frac{1}{(2)} \frac{2 e^4}{\hbar^4} \left| \sum_m \frac{\langle f | \vec{r} \cdot \vec{E}_2^{(+)} | m \rangle \langle m | \vec{r} \cdot \vec{E}_1^{(+)} | i \rangle}{i - m} + \frac{\langle f | \vec{r} \cdot \vec{E}_1^{(+)} | m \rangle \langle m | \vec{r} \cdot \vec{E}_2^{(+)} | i \rangle}{i - m} \right|^2 \quad (i - f) \quad [\text{VIII-13a}]$$

and **for one beam, two-photon processes**

$$\frac{1}{(2)} \frac{2 e^4}{\hbar^4} \left| \sum_m \frac{\langle f | \vec{r} \cdot \vec{E}^{(+)} | m \rangle \langle m | \vec{r} \cdot \vec{E}^{(+)} | i \rangle}{i - m} \right|^2 \quad (2_{\text{beam}} - f) \quad [\text{VIII-13b}]$$

If we use once again the factorization used in Section VI of this lecture set -- viz. we write the initial state as $| i \rangle = | i = \{ i, i \} \rangle = | A(i) \rangle | F(i) \rangle$ where $| A(i) \rangle$ and $| F(i) \rangle$ are, respectively, the initial electronic (atomic) and field (photon) states.

Using closure on the intermediate photon states, we find **for two beam, two-photon processes**

$$\frac{1}{(2)} \frac{2 e^4}{\hbar^4} | \mathcal{M}(1,2) |^2 \quad (i - f) \quad [\text{VIII-14a}]$$

$$\times \text{Tr} \left[\mathbf{E}_1^{(-)} \mathbf{E}_2^{(-)} \mathbf{E}_2^{(+)} \mathbf{E}_1^{(+)} \right]$$

where

$$\mathcal{M}_{(1,2)} = \frac{\langle A(f) | \vec{r} | A(m) \rangle \hat{\omega}_1 \hat{\omega}_2 \langle A(m) | \vec{r} | A(i) \rangle}{\omega_1 - m} + \frac{\langle A(f) | \vec{r} | A(m) \rangle \hat{\omega}_2 \hat{\omega}_1 \langle A(m) | \vec{r} | A(i) \rangle}{\omega_2 - m} \quad [\text{VIII-15a}]$$

and for **one beam, two-photon processes**

$$\frac{1}{(2)} \frac{2 e^4}{\hbar^4} | \mathcal{M}_{(1,1)} |^2 (2 \omega_1 - \omega_f) \times \text{Tr} [\mathbf{E}_1^{(-)} \mathbf{E}_1^{(-)} \mathbf{E}_1^{(+)} \mathbf{E}_1^{(+)}] \quad [\text{VIII-14b}]$$

where

$$\mathcal{M}_{(1,1)} = \frac{\langle A(f) | \vec{r} | A(m) \rangle \hat{\omega}_1 \hat{\omega}_1 \langle A(m) | \vec{r} | A(i) \rangle}{\omega_1 - m} \quad [\text{VIII-15b}]$$

FOUR WAVE MIXING:

Four Wave Mixing Spectroscopy:

We explore here a particular set of four wave interactions. To that end, we consider an input field which consists of two plane waves

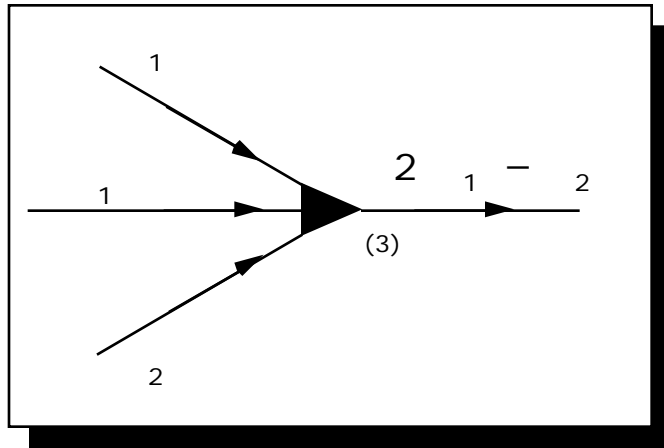
$$\mathbf{E}(\vec{r}, t) = \mathbf{E} \bar{\mathbf{k}}_1 \exp [i (\bar{\mathbf{k}}_1 \cdot \vec{r} - \omega_1 t)] + \mathbf{E} \bar{\mathbf{k}}_2 \exp [i (\bar{\mathbf{k}}_2 \cdot \vec{r} - \omega_2 t)] + \text{c.c.} \quad [\text{VIII-16}]$$

where frequencies ω_1 and ω_2 lie in the visible part of the spectrum. As Equation [VIII-3] of OCEF informs us, this input incident on a third-order nonlinear material, will **directly generate** a component of nonlinear polarization at a frequency $2 \omega_1 - \omega_2$ -- viz.

$$^{(3)}\mathbf{P}^{(NL)}(\bar{\mathbf{r}}, t) = 3 \quad ^{(3)} \left(\begin{matrix} 1; & 1; & - & 2 \end{matrix} \right) \mathbf{E} \bar{\mathbf{k}}_1, \quad \mathbf{E} \bar{\mathbf{k}}_1, \quad \mathbf{E} \bar{\mathbf{k}}_2, \quad \mathbf{E} \bar{\mathbf{k}}_2 \quad [\text{VIII-17}]$$

$$\times \exp \left[i \left(2\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2 \right) \cdot \bar{\mathbf{r}} \right] \exp \left[-i \left(2\omega_1 - \omega_2 \right) t \right]$$

which may be associated with the destruction of two photons at ω_1 and the creation of photons at ω_2 and $2\omega_1 - \omega_2$.



Four wave mixing - direct process

If, however, the material lacks a center of symmetry there is also an alternate path to obtain $2\omega_1 - \omega_2$ radiation. In a second-order material [VIII-3] of OCEF informs us we can also have a nonlinear polarization at $2\omega_1 - \omega_2$

$$^{(2)}\mathbf{P}^{(NL)}(\bar{\mathbf{r}}, t) = \left\{ 2 \quad ^{(2)} \left(\begin{matrix} 1 - & 2; & 1 \end{matrix} \right) \mathbf{E} \bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2, \quad \mathbf{E} \bar{\mathbf{k}}_1, \quad \mathbf{E} \bar{\mathbf{k}}_1 \right.$$

$$\left. + \quad ^{(2)} \left(\begin{matrix} 2 & 1; & - & 2 \end{matrix} \right) \mathbf{E} \quad 2\bar{\mathbf{k}}_1, \quad 2\omega_1 \quad \mathbf{E} \bar{\mathbf{k}}_2, \quad \mathbf{E} \bar{\mathbf{k}}_2 \right\} \quad [\text{VIII-18}]$$

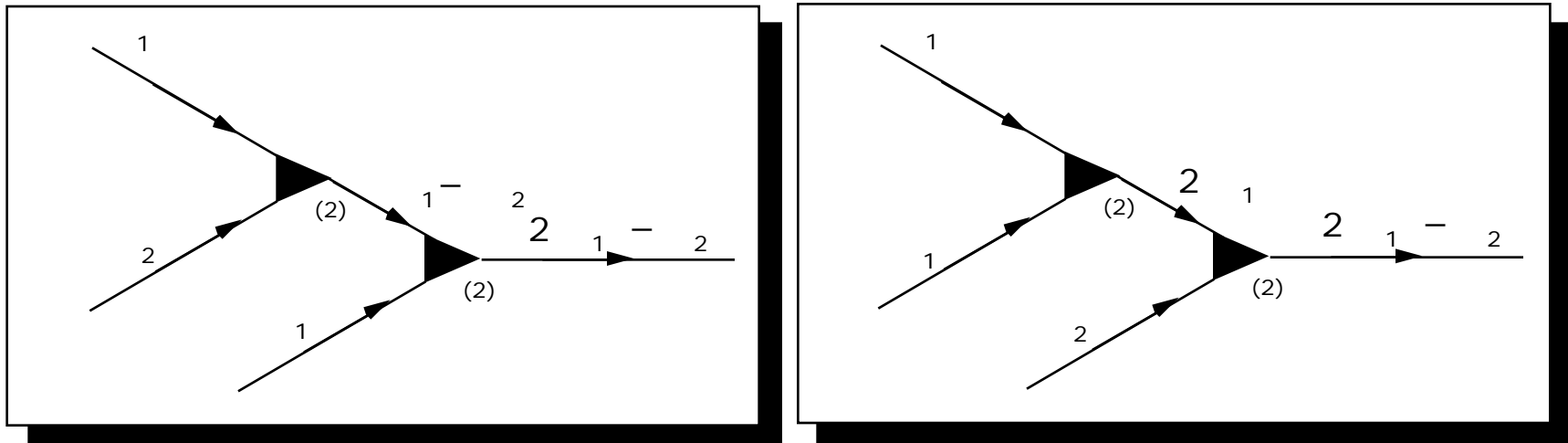
$$\times \exp \left[i \left(2\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2 \right) \cdot \bar{\mathbf{r}} \right] \exp \left[-i \left(2\omega_1 - \omega_2 \right) t \right]$$

if we have driving fields $\mathbf{E}(\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2, \omega_1 - \omega_2)$ and $\mathbf{E}(2\bar{\mathbf{k}}_1, 2\omega_1)$. Such fields are, in fact, generated by the input field through the nonlinear polarization components

$${}^{(2)}\mathbf{P}^{(NL)}(\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2, \omega_1 - \omega_2) = 2 \chi^{(2)}(\omega_1; -\omega_2) \mathbf{E}(\bar{\mathbf{k}}_1, \omega_1) \mathbf{E}(\bar{\mathbf{k}}_2, \omega_2) \quad [\text{VIII-19a}]$$

and

$${}^{(2)}\mathbf{P}^{(NL)}(2\bar{\mathbf{k}}_1, 2\omega_1) = 2 \chi^{(2)}(\omega_1; \omega_1) \mathbf{E}(\bar{\mathbf{k}}_1, \omega_1) \mathbf{E}(\bar{\mathbf{k}}_1, \omega_1) \quad [\text{VIII-19b}]$$



Four wave mixing - indirect processes

We may solve for $\mathbf{E}(\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2, \omega_1 - \omega_2)$ and $\mathbf{E}(2\bar{\mathbf{k}}_1, 2\omega_1)$ from Equation [VIII-23] in OCEF -- viz.

$$|\bar{\mathbf{Q}}|^2 - \mathbf{Q} \mathbf{Q} - \left(\frac{2}{c^2} \omega_0 \right) \chi^{(2)}(\omega_1; -\omega_2) \mathbf{E}(\bar{\mathbf{Q}}, \omega_1) = \mu_0 \chi^{(2)}(\omega_1; \omega_1) \mathbf{P}^{(NL)}(\bar{\mathbf{Q}}, \omega_1) \quad [\text{VIII-20a}]$$

or using the operator $\bar{\mathbf{K}}(\bar{\mathbf{k}}) = (\bar{\mathbf{k}} \bar{\mathbf{k}}) \bar{\mathbf{1}} - \bar{\mathbf{k}} \bar{\mathbf{k}} = |k|^2 \{ \bar{\mathbf{1}} - \bar{\mathbf{k}} \bar{\mathbf{k}} \}$ defined in OCEF

$$\left\{ \omega_0^{-1} \left(\bar{\mathbf{Q}} \right) - \left(\frac{2}{c^2} \omega_0 \right) \chi^{(2)}(\omega_1; -\omega_2) \right\} \mathbf{E}(\bar{\mathbf{Q}}, \omega_1) = \left(\frac{2}{c^2} \omega_0 \right)^{-1} \chi^{(2)}(\omega_1; \omega_1) \mathbf{P}^{(NL)}(\bar{\mathbf{Q}}, \omega_1) \quad [\text{VIII-20b}]$$

If we define

$$\mathcal{G}(\bar{\mathbf{Q}}; \omega) = \left\{ \epsilon_0^{-1}(\omega) - \left(\bar{\mathbf{Q}} - \left(\frac{\omega}{c^2} \right) \right) \right\} \quad [\text{VIII-21}]$$

we can, *in principle*, write

$$\mathbf{E}(\bar{\mathbf{Q}}) = \left[\frac{\omega}{c^2} \right] \mathcal{G}^{-1}(\bar{\mathbf{Q}}; \omega) \mathbf{P}^{(\text{NL})}(\bar{\mathbf{Q}}) \quad [\text{VIII-22}]$$

Therefore, for a material lacking a center of symmetry, the complete nonlinear polarization may be written

$$\begin{aligned} \mathbf{P}^{(\text{NL})}(\bar{\mathbf{r}}, t) = & 3 \exp \left[i \left(2 \bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2 \right) \cdot \bar{\mathbf{r}} \right] \exp \left[-i \left(2 \omega_1 - \omega_2 \right) t \right] \mathbf{E}(\bar{\mathbf{k}}_1) \cdot \mathbf{E}(\bar{\mathbf{k}}_1) \cdot \mathbf{E}(\bar{\mathbf{k}}_2) \\ & \times \left\{ \epsilon^{(3)}(\omega_1; \omega_1; -\omega_2) \right. \\ & + \frac{4}{3} \left[\frac{\omega}{c^2} \right] \epsilon^{(2)}(\omega_1 - \omega_2; \omega_1) \mathcal{G}^{-1}(\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2, \omega_1 - \omega_2) \epsilon^{-1}(\omega_1 - \omega_2) \epsilon^{(2)}(\omega_1; -\omega_2) \\ & \left. + \frac{2}{3} \left[\frac{\omega}{c^2} \right] \epsilon^{(2)}(2\omega_1; -\omega_2) \mathcal{G}^{-1}(2\bar{\mathbf{k}}_1, 2\omega_1) \epsilon^{-1}(2\omega_1) \epsilon^{(2)}(\omega_1; \omega_1) \right\} \end{aligned} \quad [\text{VIII-23}]$$

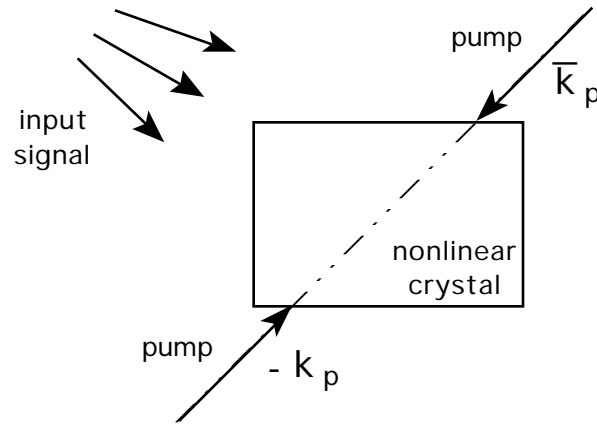
Notice the “resonance” in the second term when $|\bar{\mathbf{k}}_1 - \bar{\mathbf{k}}_2|$ and $\omega_1 - \omega_2$ are “tuned” to the wave number and frequency of coupled electromagnetic excitations or normal modes such as plasmons, polaritons and magnons.

Degenerate Four Wave Mixing (DFWM) - Phase Conjugation:

Consider now the reflected waves generated by the direct process -- *i.e.*, Equation [VIII-17] -- when the input field is the sum of two counter propagating “pump” fields, with $[\bar{\mathbf{k}}_p, \omega_p]$ and $[-\bar{\mathbf{k}}_p, \omega_p]$, plus a complex wave $\bar{\mathbf{E}}_{in}(\bar{\mathbf{r}}, t)$ represented a range of wave numbers components $\left\{ \bar{\mathbf{k}}_\ell \right\}$, -- *viz.*

$$\begin{aligned} \mathbf{E}(\bar{\mathbf{r}}, t) = & \mathbf{E}^{(+)} \exp[i(\bar{\mathbf{k}}_p \bar{\mathbf{r}} - t)] + \mathbf{E}^{(-)} \exp[i(-\bar{\mathbf{k}}_p \bar{\mathbf{r}} - t)] \\ & + \sum_{\ell} \mathbf{E}^{(\ell)} \exp[i(\bar{\mathbf{k}}_{\ell} \bar{\mathbf{r}} - t)] \exp[-i t] + \text{c.c.} \end{aligned} \quad [\text{VIII-24}]$$

as shown below

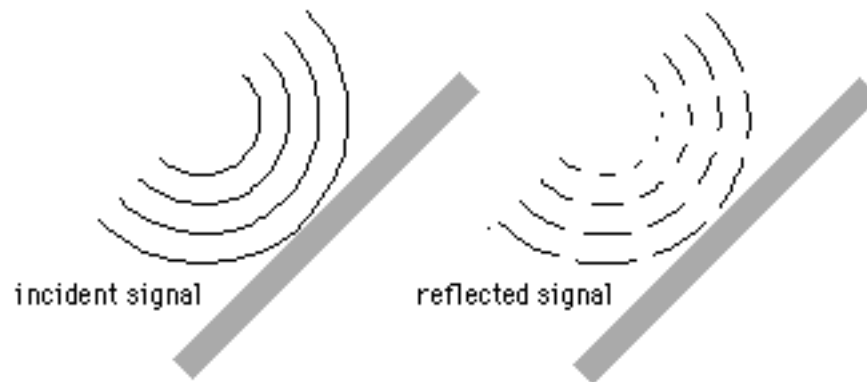


According to Equation [VIII-17], reflected waves are generated by nonlinear polarizations components with $[\{\bar{\mathbf{k}}_{\ell}\}, 3]$, $[\{2\bar{\mathbf{k}}_p + \bar{\mathbf{k}}_{\ell}\}, -]$, $[\{2\bar{\mathbf{k}}_p - \bar{\mathbf{k}}_{\ell}\}, -]$, and $[\{\bar{\mathbf{k}}_{\ell}\}, -]$. The latter component is the so-called **phase conjugate term** and may be written

$$\begin{aligned} {}^{(3)}\mathbf{P}^{(\text{NL})}(\bar{\mathbf{r}}, t) = & 3 \sum_{\ell} (\chi^{(3)}; \bar{\mathbf{k}}_{\ell}) \mathbf{E}^{(-)} \mathbf{E}^{(+)} \bar{\mathbf{k}}_{p, -1} \exp[-i(t + t)] \\ & \sum_{\ell} \mathbf{E}^{(\ell)*} \exp[-i(\bar{\mathbf{k}}_{\ell} \bar{\mathbf{r}} - t)] \exp[-i t] + \text{c.c.} \end{aligned} \quad [\text{VIII-25}]$$

which may be interpreted as the **time reversed image** of $\bar{\mathbf{E}}_{in}(\bar{\mathbf{r}}, t)$.

TIME REVERSED IMAGING



THE RAMAN EFFECT

The Raman Nonlinearity:

In our discussion of the dielectric susceptibility thus far we have been implicitly assuming that the nuclei of system were clamped into fixed positions and have focused on the nonlinearities associate with electron dynamics. This is too limited a view. In general, we may expect that polarizability of, say, a molecule is a function of the nuclear positions and that the dipole moment can be expressed

$$\mathbf{p} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\}, \bar{\mathbf{E}} \right) = \mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) + a \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) \mathbf{E} + \dots \quad [\text{VIII-26}]$$

$\left\{ \bar{\mathbf{u}}^{(s)} \right\}$ denotes a collection of nuclear positions where $\bar{\mathbf{u}}^{(s)}$ is the displacement of the s nucleus from its nominal equilibrium position. Further, we may expand these terms in powers of the displacement -- *viz.*

$$\mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(i)} \right\} \right) = \mathbf{p}^{(0)} + \sum_{s=1}^N \frac{\partial \mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right)}{\partial \mathbf{u}^{(s)}} \bigg|_0 \mathbf{u}^{(s)} + \dots \quad [\text{VIII-27a}]$$

$$\mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(i)} \right\}, \bar{\mathbf{E}} \right) = a \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) \mathbf{E} = a^{(0)} \mathbf{E} + \sum_{s=1}^N a^{(R)} \mathbf{E} \mathbf{u}^{(s)} + \dots \quad [\text{VIII-27b}]$$

The second term in Equation [VIII-27b] is the so called **Raman nonlinearity**.

Since $\frac{1}{\mathbf{u}^{(s)}} p^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) \Big|_0$ has the dimensions of charge, Equation [VIII-27a] is

usually written

$$\mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) = \mathbf{p}^{(0)} + \sum_{s=1}^N e^{(s)} \mathbf{u}^{(s)} + \dots \quad [\text{VIII-27a'}]$$

where $e^{(s)}$ is the *dynamic effective charge tensor* associated with the s nucleus. The nuclear displacements are a linear combination of the normal modes of the system

$$\mathbf{u}^{(s)} = \sum_{=1}^{3N} (s;) q() \quad [\text{VIII-28}]$$

so that we may recast Equations [VIII-27a] and [VIII-27b] in the form

$$\mathbf{p}^{(0)} \left(\left\{ \bar{\mathbf{u}}^{(s)} \right\} \right) = p^{(0)} + \sum_{=1}^{3N} e () q() + \dots \quad [\text{VIII-29a}]$$

$$\mathbf{p}^{(R)} = \sum_{s=1}^N a^{(R)} \mathbf{E} \mathbf{u}^{(s)} = \sum_{=1}^{3N} a^{(R)} () \mathbf{E} q() \quad [\text{VIII-29b}]$$

where $e () = \sum_{s=1}^N e^{(s)} (s;)$ and $a^{(R)} () = \sum_{s=1}^N a^{(R)} (s;)$.

Quantum Theory of Raman Scattering

The Raman nonlinearity provides a coupling between the photon field described by the Hamiltonian

$$\mathcal{H}_{rad} = \sum_{\vec{k}} \hbar \omega_{\vec{k}} a_{\vec{k}}^{\dagger} a_{\vec{k}} + \frac{1}{2} \quad [VIII-30]$$

and the phonon field described by the Hamiltonian

$$\mathcal{H}_{vib} = \sum_{\vec{k}} \hbar \omega_{\vec{k}} b_{\vec{k}}^{\dagger} b_{\vec{k}} + \frac{1}{2} \quad [VIII-31]$$

where b^{\dagger} and b are, respectively, the phonon creation and destruction operators. In the electric dipole approximation, the interaction Hamiltonian can be written

$$\mathcal{H}_{int} = -\frac{1}{2} \sum_{\vec{k}} a^{(R)}(\vec{k}) \mathbf{E}(\vec{k}) \cdot \mathbf{q}(\vec{k}) \quad [VIII-32]$$

In earlier discussions we have shown that

$$\mathbf{q}(\vec{k}) = \frac{\hbar}{2M} \omega_{\vec{k}}^{1/2} (b_{\vec{k}}^{\dagger} + b_{\vec{k}}) \quad [VIII-33a]$$

and

$$\mathbf{E}(\vec{k}) = i \frac{2 \hbar \omega_{\vec{k}}}{V} \hat{\mathbf{e}}(\vec{k}) (a_{\vec{k}} - a_{\vec{k}}^{\dagger}) \quad [VIII-33b]$$

so that the complete interaction Hamiltonian may be expressed as

$$\mathcal{H}_{\text{int}} = \frac{1}{2} \frac{2}{V} \frac{\hbar}{\hbar} \sum_{\mathbf{k}} \frac{\hbar}{2M} a^{(R)}(\mathbf{k}) (b^\dagger + b) \times \sum_{\mathbf{k}} \frac{1}{\hbar} \hat{\mathbf{e}}(\mathbf{k}, \omega) (a_{\mathbf{k}} - a_{\mathbf{k}}^\dagger) \sum_{\mathbf{k}} \frac{1}{\hbar} \hat{\mathbf{e}}(\mathbf{k}, \omega) (a_{\mathbf{k}} - a_{\mathbf{k}}^\dagger) \quad [\text{VIII-34}]$$

To concentrate on the key issue, we write **scattering Hamiltonian** which is proportional to $a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$, and which describes the scattering of a photon from the $\{\mathbf{k}, \omega\}$ (initial) state to the $\{\mathbf{k}, \omega\}$ (final) state

$$\mathcal{H}_{\text{scat}} = \frac{2}{V} \frac{\hbar}{\hbar} \frac{\hbar}{2M} (\omega_i - \omega_f)^{1/2} a^{(R)}(I, F; \mathbf{k}) a_F^\dagger a_I (b^\dagger + b) \quad [\text{VIII-35}]$$

where $a^{(R)}(I, F; \mathbf{k}) = a^{(R)}(\mathbf{k}, \omega) \hat{\mathbf{e}}(I) \hat{\mathbf{e}}(F)$.

We may now use the **Fermi golden rule**⁴⁹ to calculate the transition rate per "molecule" for **inelastic Stokes scattering** events -- viz. for $\{n_I, n_F, n\} \rightarrow \{n_I - 1, n_F + 1, n + 1\}$

$$\begin{aligned} \frac{1}{(s)} &= \frac{2}{\hbar^2} \left| \langle f | \mathcal{H}_{\text{scat}} | i \rangle \right|^2 (\omega_i - \omega_f) \\ &= \frac{2}{\hbar^2} \frac{2}{V} \frac{\hbar^2}{2M} (\omega_i - \omega_f) \left| a^{(R)}(I, F; \mathbf{k}) \right|^2 \\ &\quad \times \left| \langle n_I - 1, n_F + 1, n + 1 | a_F^\dagger a_I b^\dagger | n_I, n_F, n \rangle \right|^2 (\omega_i - \omega_f) \end{aligned} \quad [\text{VIII-36a}]$$

$$\frac{1}{(s)} = \frac{8}{V^2} \frac{\hbar^3}{2M} (\omega_i - \omega_f) \left| a^{(R)}(I, F; \mathbf{k}) \right|^2 n_I (n_F + 1) (n + 1) (\omega_i - \omega_f) \quad [\text{VIII-36b}]$$

⁴⁹ See the appendix to this section for a recapitulation of the theory of transition rates.

and the transition rate per "molecule" for **inelastic anti-Stokes scattering** events -- viz. for $\{n_I, n_F, n\} \rightarrow \{n_I - 1, n_F + 1, n - 1\}$

$$\begin{aligned} \frac{1}{(AS)} &= \frac{2}{\hbar^2} \frac{2}{V} \frac{\hbar^2}{2M} \left(\begin{array}{c} I \\ F \end{array} \right) \left| a^{(R)}(I, F; \) \right|^2 \\ &\quad \times \left\langle n_I - 1, n_F + 1, n - 1 \left| a_F^\dagger a_I b \right| n_I, n_F, n \right\rangle^2 \left(\begin{array}{c} I + \\ - \\ F \end{array} \right) \quad [\text{VIII-36c}] \\ &= \frac{8}{V^2} \frac{\hbar^3}{2M} \left(\begin{array}{c} I \\ F \end{array} \right) \left| a^{(R)}(I, F; \) \right|^2 n_I (n_F + 1) n \left(\begin{array}{c} I + \\ - \\ F \end{array} \right) \end{aligned}$$

For a total number of "molecules" \mathcal{V}_{mol} we may write the total time rate of change of photons of frequency ν_F as

$$\begin{aligned} \left. \frac{d n_F}{d t} \right|_S &= \frac{8}{V} \mathcal{V}_{mol} \frac{\hbar^3}{2M} \left(\begin{array}{c} I \\ F \end{array} \right) \left| a^{(R)}(I, F; \) \right|^2 \\ &\quad \times n_I (n_F + 1) (n + 1) \left(\begin{array}{c} I - \\ - \\ F - \end{array} \right) \quad [\text{VIII-37a}] \end{aligned}$$

$$\begin{aligned} \left. \frac{d n_F}{d t} \right|_{AS} &= \frac{8}{V} \mathcal{V}_{mol} \frac{\hbar^3}{2M} \left(\begin{array}{c} I \\ F \end{array} \right) \left| a^{(R)}(I, F; \) \right|^2 \\ &\quad \times n_I (n_F + 1) n \left(\begin{array}{c} I + \\ - \\ F \end{array} \right) \quad [\text{VIII-37b}] \end{aligned}$$

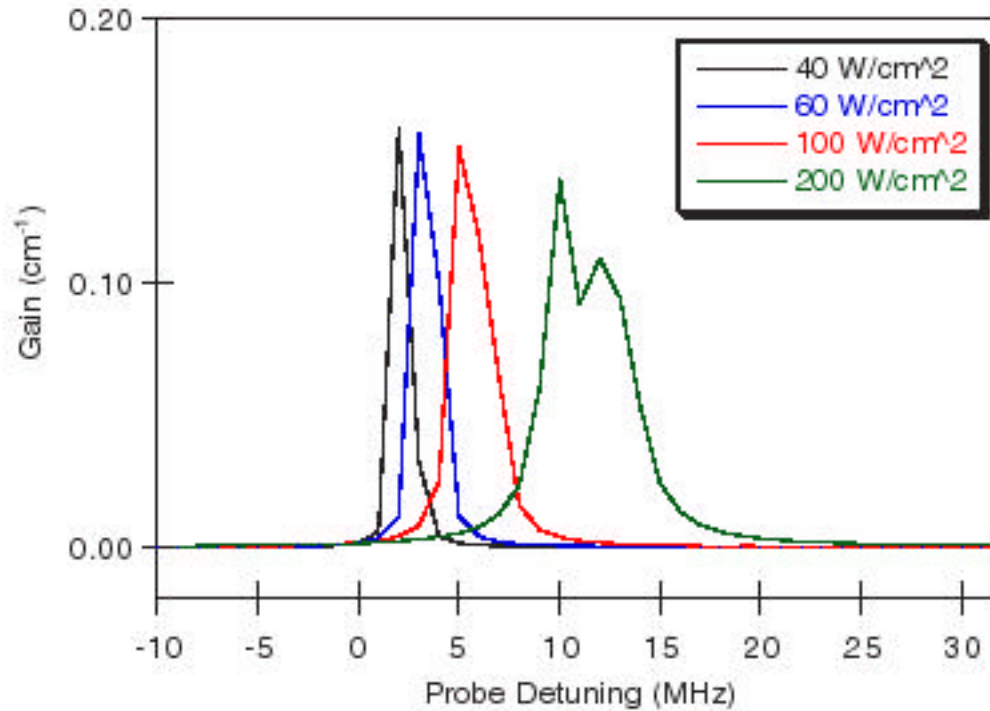
Stimulated Raman Effect: Simple model

Suppose that a high power laser at ν_I -- **the pump** -- propagates parallel to the z-axis and that the Raman medium occupies the half-space $z > 0$. The spatial rate of change of the *Stokes photons* at ν_F -- **the signal** -- may be written⁵⁰

$$\frac{d n_F(z)}{d z} = G_R n_I(z) [n_F(z) + 1] \quad [\text{VIII-38}]$$

⁵⁰ Assuming for the nonce that $n \gg 0$.

where
$$G_R = \frac{8^3}{cV} \frac{\hbar}{2M} \left| a^{(R)}(I, F;) \right|^2 \quad [VIII-39]$$



Raman Gain in rubidium vapor for different coupling laser intensities

The rate constant is included in this expression for gain to account for the broadening of a given vibrational state. Each Stokes event, of course, also depletes the incident beam so that

$$\frac{d n_I(z)}{d z} = -G_R n_I(z) [n_F(z) + 1] \quad [VIII-40]$$

which means that
$$n_F(z) + n_I(z) = n_I(0) . \quad [\text{VIII-41}]$$

Substituting this conservation condition into Equation [VIII-38] we see that

$$\frac{d n_F(z)}{d z} = G_R [n_I(0) - n_F(z)] [n_F(z) + 1] \quad [\text{VIII-42a}]$$

or that
$$\frac{d n_F(z)}{[n_F(z) + 1]} - \frac{d n_F(z)}{[n_F(z) - n_I(0)]} = G_R [1 + n_I(0)] d z \quad [\text{VIII-42b}]$$

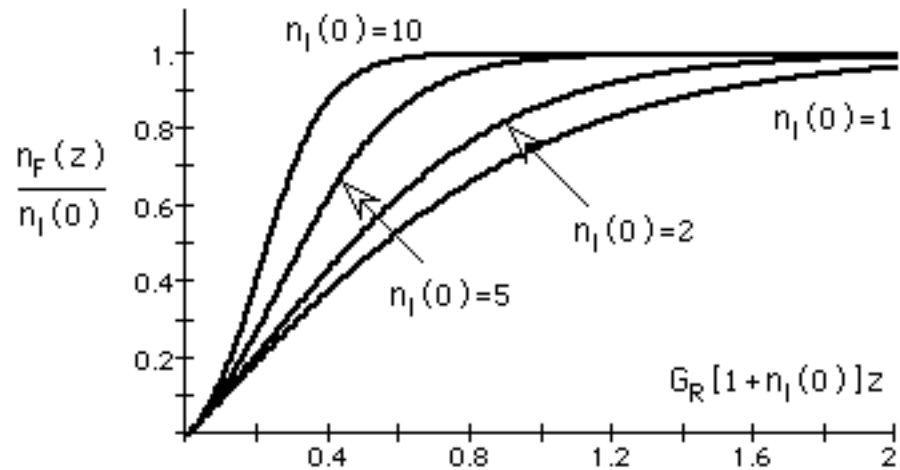
Therefore

$$n_F(z) = n_I(0) \frac{\exp \{ G_R [1 + n_I(0)] z \} - 1}{n_I(0) + \exp \{ G_R [1 + n_I(0)] z \}} \quad [\text{VIII-43}]$$

This simple model predicts that Stokes photons initially increase linearly with distance and that there complete conversion at distances large compared to $\{ G_R [1 + n_I(0)] \}^{-1}$ -- *i.e.*

$$\lim_{z \rightarrow 0} n_F(z) = G_R [1 + n_I(0)] z \quad [\text{VIII-44a}]$$

$$\lim_z n_F(z) = n_I(0) \quad [\text{VIII-44b}]$$



Coherent anti-Stokes Raman Spectroscopy (CARS):

There is an important four wave mixing process involving the Raman nonlinearity. We may see how this comes about by realizing that Equation [VIII-29] implies a potential energy contribution

$$\frac{1}{2} \sum_{s=1}^{3N} a^{(R)}(s) \mathbf{E} \cdot \mathbf{E} q(s) \quad [\text{VIII-45}]$$

so that inclusion of the Raman nonlinearity modifies the equation of motion for the vibrational normal modes -- viz.

$$\ddot{q}(t, s) + \omega_s^2 q(t, s) = \frac{1}{2M} a^{(R)}(s) \mathbf{E} \cdot \mathbf{E} \quad [\text{VIII-46}]$$

When the normal mode is driven by a two (visible) wave input (see discussion of four-wave processes above), its dominant response will be at the difference frequency $\omega_1 - \omega_2$ -- viz.

$$\ddot{q}(t, \omega) + \omega^2 q(t, \omega) = \frac{1}{M} a^{(R)}(\omega) \mathbf{E}(\omega_1) \mathbf{E}(\omega_2) \exp[-i(\omega_1 - \omega_2)t] + c.c. \quad [VIII-47]$$

so that

$$q(t, \omega) = \frac{1}{M} \frac{a^{(R)}(\omega) E(\omega_1) E(\omega_2) \exp[-i(\omega_1 - \omega_2)t]}{\omega^2 - (\omega_1 - \omega_2)^2} \quad [VIII-48]$$

From Equation [VIII-29b] we see that excitation of a vibrational mode, through the Raman nonlinearity, generates a nonlinear polarization

$$\mathbf{p}^{(R)} = \frac{1}{M} \frac{3N a^{(R)}(\omega) a^{(R)}(\omega) \mathbf{E}(\omega_1) \mathbf{E}(\omega_1) \mathbf{E}(\omega_2) \exp[-i(2\omega_1 - \omega_2)t]}{\omega^2 - (\omega_1 - \omega_2)^2} \quad [VIII-49]$$

at the four wave mixing frequency $2\omega_1 - \omega_2$. Thus, we see that the medium has an *effective third order susceptibility*

$$\left[\chi^{(3)}(2\omega_1 - \omega_2) \right]_{eff} = \chi^{(3)} + \frac{1}{3M} \frac{a^{(R)}(\omega) a^{(R)}(\omega)}{\omega^2 - (\omega_1 - \omega_2)^2} \quad [VIII-50]$$

which exhibits a resonance when $\omega_1 - \omega_2$ equals ω .