Electromagnetic Field Energy

Our starting point is Maxwell's equations

$$\bar{\nabla}\cdot\bar{D} = \rho \qquad \bar{\nabla}\times\bar{H} = \bar{J} + \frac{\partial\bar{D}}{\partial t}$$
$$\bar{\nabla}\cdot\bar{B} = 0 \qquad \bar{\nabla}\times\bar{E} = -\frac{\partial\bar{B}}{\partial t} \tag{1.1}$$

Here, $\bar{E}$ and $\bar{H}$ are the vacuum electric and magnetic fields while $\bar{D}$ and $\bar{B}$, given by:

$$\bar{D} = \varepsilon_0\bar{E} + \bar{P} \quad ; \quad \bar{B} = \mu_0(\bar{H} + \bar{M}) \tag{1.2}$$

are the Electric and magnetic fields in materials. $\bar{P}$ and $\bar{M}$, meanwhile, are the polarization and magnetization respectively.

Rewriting Maxwell's equations in terms of the vacuum fields:

$$\bar{\nabla}\times\bar{H} = \bar{J} + \frac{\partial}{\partial t}(\varepsilon_0\bar{E} + \bar{P})$$
$$\bar{\nabla}\times\bar{E} = -\frac{\partial}{\partial t}\mu_0(\bar{H} + \bar{M}) \tag{1.3}$$

Our goal is to determine the energy density stored in the field. To do so, we first take the dot product of $\bar{\nabla}\times\bar{H}$ with $\bar{E}$ and $\bar{\nabla}\times\bar{E}$ with $\bar{H}$:

$$\bar{E}\cdot(\bar{\nabla}\times\bar{H}) = \bar{E}\cdot\bar{J} + \varepsilon_0\bar{E}\cdot\frac{\partial\bar{E}}{\partial t} + \bar{E}\cdot\frac{\partial\bar{P}}{\partial t}$$
$$\bar{H}\cdot(\bar{\nabla}\times\bar{E}) = -\mu_0\bar{H}\cdot\frac{\partial\bar{H}}{\partial t} - \mu_0\bar{H}\cdot\frac{\partial\bar{M}}{\partial t}$$

Notice that we can rewrite the terms:

$$\varepsilon_0\bar{E}\cdot\frac{\partial\bar{E}}{\partial t} = \frac{\varepsilon_0}{2}\frac{\partial}{\partial t}(\bar{E}\cdot\bar{E}) = \frac{\varepsilon_0}{2}\frac{\partial}{\partial t}E^2$$
$$\mu_0\bar{H}\cdot\frac{\partial\bar{H}}{\partial t} = \frac{\mu_0}{2}\frac{\partial}{\partial t}H^2$$

In order to obtain a meaningful expression, we make use of the vector calculus rule

$$\bar{\nabla}\cdot(\bar{E}\times\bar{H}) = \bar{H}\cdot(\bar{\nabla}\times\bar{E}) - \bar{E}\cdot(\bar{\nabla}\times\bar{H})$$

Thus

$$-\bar{\nabla}\cdot(\bar{E}\times\bar{H}) = \bar{E}\cdot\bar{J} + \frac{\varepsilon_0}{2}\frac{\partial}{\partial t}E^2 + \bar{E}\cdot\frac{\partial\bar{P}}{\partial t} + \frac{\mu_0}{2}\frac{\partial}{\partial t}H^2 + \mu_0\bar{H}\cdot\frac{\partial\bar{M}}{\partial t}$$

Grouping terms yields <u>Poynting's Theorem</u>:

⚠ NOTE: This assumes that $\bar{E}, \bar{H}, \bar{J}, \bar{P}, \bar{M}$ are PURE REAL

$$-\bar{\nabla}\cdot(\bar{E}\times\bar{H}) = \bar{E}\cdot\bar{J} + \frac{\partial}{\partial t}\left(\frac{\varepsilon_0}{2}E^2 + \frac{\mu_0}{2}H^2\right) + \bar{E}\cdot\frac{\partial\bar{P}}{\partial t} + \mu_0\bar{H}\cdot\frac{\partial\bar{M}}{\partial t} \quad (1.5)$$

The quantity $\bar{E}\times\bar{H}$ is known as the Poynting vector $\bar{S}$. Notice that in the RHS, $\frac{\varepsilon_0}{2}E^2 + \frac{\mu_0}{2}H^2$ has units of energy. Thus the RHS is the rate that the electric and magnetic field energy is changing. We can thus interpret the LHS as the Flux of energy out of (in to) a small volume. 'Poynting's Theorem' is thus a continuity equation for the electromagnetic field energy.

This idea is made more evident by applying Gauss' Theorem:

$$-\int_\Omega dV\,(\bar{\nabla}\cdot\bar{E}\times\bar{H}) = -\int_\sigma d\bar{a}\cdot\bar{E}\times\bar{H}$$

Energy stored in Vacuum $\bar{E}$

$$= \int_\Omega dV\left(\bar{E}\cdot\bar{J} + \frac{\partial}{\partial t}\left(\frac{\varepsilon_0}{2}E^2\right) + \frac{\partial}{\partial t}\left(\frac{\mu_0}{2}H^2\right) + \cdots\right)$$

Most often, $\bar{P}$ is assumed to be proportional to $\bar{E}$, ie

$$\bar{P} = \varepsilon_0\chi\bar{E}$$

Which we can use to write the power in the electric field as:

$$\dot{W}_E = \frac{\partial}{\partial t}\left(\frac{\varepsilon_0}{2}E^2\right) + \bar{E}\cdot\frac{\partial\bar{P}}{\partial t} = \frac{\partial}{\partial t}\left(\frac{\varepsilon_0}{2}E^2\right) + \varepsilon_0\chi\bar{E}\cdot\frac{\partial\bar{E}}{\partial t}$$

$$\Rightarrow \quad \dot{W}_E = \frac{\partial}{\partial t}\left(\frac{\varepsilon_0\varepsilon_r}{2}E^2\right) \quad \text{where} \quad \varepsilon_r = 1+\chi$$

Integrating this expression in time yields an expression for the electric field at time t:

$$W_E = \int_0^t dt' \frac{\partial}{\partial t'}\left(\frac{\varepsilon_0 \varepsilon_r}{2} E^2\right) = \frac{\varepsilon_0 \varepsilon_r}{2}\int_0^t dt' \frac{\partial}{\partial t'}\left(E^2\right) = \underline{\underline{\frac{\varepsilon_0 \varepsilon_r}{2}|E|^2}} \tag{1.6}$$

This very common expression for the energy density of the electric field, however it is not technically correct for non-vacuum materials. This is because, we didn't adequately account for the fact that the electric field must be turned on, which corresponds to a broadband frequency response. Since materials are frequency dependent, the $\bar{E} \cdot \frac{dP}{dt}$ term in the energy density will change as a result.

In order to approximate this effect ($\sim$ 1st order) we model the electric field as having frequency components near ω_0. Generally, we may express the electric field in the time domain as a fourier transform:

$$E(t) = \int_{-\infty}^{\infty} E(\omega)\, e^{i\omega t}\, d\omega$$

In this case, we explicitly highlight the dominant frequency ω_0 by taking $\omega = \omega_0 + \alpha$:

$$E_0(t) = \int_{-\infty}^{\infty} E(\omega_0+\alpha)\, e^{i(\omega_0+\alpha)t}\, d\alpha = e^{i\omega_0 t}\int_{-\infty}^{\infty} d\alpha\, E(\omega_0+\alpha)\, e^{i\alpha t}\, d\alpha$$

Since $E(\omega_0+\alpha)$ is fairly narrow in the frequency domain, it must be broad in the time domain. As a result we say $E_0(t) = \int_{-\infty}^{\infty} d\alpha\, E(\omega_0+\alpha)\, e^{i\alpha t}$ is the "slowly varying envelope". The electric field can thus be written more concisely by:

$$E(t) = E_0(t)\, e^{i\omega_0 t}$$

Recall that the polarization in the frequency domain is given by

$$P(\omega) = \epsilon_0 \chi(\omega) E(\omega) \tag{1.7}$$

Because it depends linearly on the electric field, we expect $P(\omega)$ to have a similarly narrow frequency response centered around ω_0. As is such, we can approximate the time-domain polarization using a Fourier transform, integrating over $\omega = \omega_0 + \alpha$:

$$\begin{aligned} P(t) &= \epsilon_0 \int_{-\infty}^{\infty} d\omega\, \chi(\omega) E(\omega) \\ &= \epsilon_0 \int_{-\infty}^{\infty} d\alpha\, \chi(\omega_0+\alpha) E(\omega_0+\alpha)\, e^{i\alpha t} e^{i\omega_0 t} \end{aligned} \tag{1.8}$$

For the sake of achieving a reasonably simple approximation, we taylor expand $\chi(\omega)$ about ω_0:

$$P(t) = \epsilon_0 \int_{-\infty}^{\infty} d\alpha \left[\chi(\omega_0) + \alpha \left.\frac{\partial \chi}{\partial \omega_0}\right|_{\omega_0} \right] E(\omega_0+\alpha)\, e^{i\alpha t} e^{i\omega_0 t}$$

⚠ This result (supplied in the notes) does not appear to be correct. The correct series expansion would be $\chi(\omega_0) + \alpha \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0}$. This will modify the final result. From here on out, we will deviate from the notes and, later on, compare the "correct" results to the note's results.

The correct expression for the polarization is:

$$P(t) = \epsilon_0 \int_{-\infty}^{\infty} d\alpha \left[\chi(\omega_0) + \alpha \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \right] E(\omega_0+\alpha)\, e^{i\alpha t} e^{i\omega_0 t}$$

Splitting up the integral into two parts yields:

$$P(t) \approx \epsilon_0 \chi(\omega_0) \int_{-\infty}^{\infty} d\alpha\, E(\omega_0+\alpha) e^{i\alpha t} e^{i\omega_0 t}$$

$$+ \epsilon_0 \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \int_{-\infty}^{\infty} d\alpha\, E(\omega_0+\alpha)\alpha e^{i\alpha t} e^{i\omega_0 t}$$

$$\approx \epsilon_0 \left[\chi(\omega_0) E_0(t) - i \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \frac{\partial E_0}{\partial t} \right]$$

Where we noticed that $\frac{\partial E_0}{\partial t} = \int_{-\infty}^{\infty} d\alpha\, E(\omega_0+\alpha) i\alpha e^{i\alpha t}$ to rewrite the second term. Recall that we are searching for an expression for $\bar{E} \cdot \frac{\partial \bar{P}}{\partial t}$. We thus need to compute $\frac{\partial \bar{P}}{\partial t}$:

$$\frac{\partial \bar{P}}{\partial t} \approx \epsilon_0 \left[\chi(\omega_0) \frac{\partial E_0}{\partial t} - i \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \frac{\partial^2 E_0}{\partial t^2} + i\omega_0 \chi(\omega_0) E_0(t) + \omega_0 \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \frac{\partial E_0}{\partial t} \right] e^{i\omega_0 t}$$

Recall that we assumed $E_0(t)$ represented a slowly varying envelope; under the "slowly varying envelope approximation" the second derivative $\partial^2 E_0/\partial t^2$ is comparitively smaller than the other terms. Eliminating this term, we have:

$$\frac{\partial \bar{P}}{\partial t} \approx \epsilon_0 \left[i\omega_0 \chi(\omega_0) E_0(t) + \omega_0 \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \frac{\partial E_0}{\partial t} + \chi_0(\omega_0) \frac{\partial E_0}{\partial t} \right] e^{i\omega_0 t}$$

Notice that

$$\omega_0 \left.\frac{\partial \chi}{\partial \alpha}\right|_{\omega_0} \frac{\partial E_0}{\partial t} + \chi(\omega_0) \frac{\partial E_0}{\partial t} = \left.\frac{\partial}{\partial \alpha}\left(\alpha \chi(\omega)\right)\right|_{\omega_0} \frac{\partial E_0}{\partial t}$$

Thus

$$\frac{\partial \bar{P}}{\partial t} \approx \epsilon_0 \left[i\omega_0 \chi(\omega_0) E_0(t) + \left.\frac{\partial}{\partial \alpha}(\alpha \chi)\right|_{\omega_0} \frac{\partial E_0}{\partial t} \right] e^{i\omega_0 t}$$

Recall that our expression for the Poynting theorem requires that all the fields be real. Thus in order to compute the energy density, we really need to find $\mathrm{Re}\{E\}\mathrm{Re}\{\frac{\partial P}{\partial t}\}$:

$$\mathrm{Re}\{E\}\mathrm{Re}\left\{\frac{\partial P}{\partial t}\right\} = \frac{1}{4}\left(E^* \frac{\partial P}{\partial t} + E \frac{\partial P}{\partial t}^*\right)$$

⚠ This expression neglects the term $\mathrm{Re}\{E\frac{dP}{dt}\}$ → WHY ???

Recall that $E(t) = E_0(t)e^{i\omega_0 t}$. Assuming E_0 is real, and that $\chi(\omega_0)$ is real (Note: Without an imaginary part, the Kramers-Kronig relationships tell us that χ cannot be dispersive. We get around this by noting that we assumed only a small spread of frequencies and by assuming that the loss is sufficiently small to be neglected in this calculation), we have:

$$\mathrm{Re}\left\{E\frac{\partial P}{\partial t}\right\} = \frac{\epsilon_0}{2}\frac{\partial}{\partial \alpha}(\alpha\chi)\Big|_{\omega_0} E_0 \frac{dE_0}{dt}$$

This is the contribution to the power density due to the polarization of the material. Integrating wrt time gives the Energy density:

$$\int_0^t dt\, \mathrm{Re}\left\{E\frac{dP}{dt}\right\} = \frac{\epsilon_0}{2}\frac{\partial}{\partial\alpha}(\alpha\chi)\Big|_{\omega_0}\int_0^t dt' E_0 \frac{dE_0}{dt'}$$

$$= \frac{\epsilon_0}{2}\frac{\partial}{\partial\alpha}(\alpha\chi)\Big|_{\omega_0}\int_{E(0)}^{E_0(t)} dE_0\, E_0 = \frac{\epsilon_0}{2}\frac{\partial}{\partial\alpha}(\alpha\chi)\Big|_{\omega_0} E_0^2(t)$$

$$= \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}(\alpha\chi)\Big|_{\omega_0} E^2$$

We finish by adding this to the vacuum Electric field energy

The total energy stored in the electric field is:

$$W_E \approx \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}(\alpha\chi)\Big|_{\omega_0} E^2 + \frac{\epsilon_0}{4}E^2$$

⚠ This is not the correct vacuum energy that we computed before → Where did the factor of $\frac{1}{2}$ come from?

$$\Rightarrow \boxed{W_E \approx \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}\left[\alpha(1+\chi)\right]_{\omega_0} E^2} \quad \text{where } \chi = \chi(\omega_0+\alpha) \qquad (1.9)$$

This is an approximate form for the dispersively-correct Electric field energy density. There are a few interesting things to notice about this expression. First, notice that $1+\chi$ is, by definition, the relative dielectric constant. The E Field energy density can thus be written:

$$W_E \approx \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}(\alpha\epsilon_r)\Big|_{\omega_0} E^2$$

Next, we could have applied an identical analysis to the magnetic field + Magnetization. In this case, we would obtain the result

$$W_H \approx \frac{\mu_0}{4}\frac{\partial}{\partial\beta}(\beta\mu_r)\Big|_{\omega_0} H^2$$

It follows that in the absence of a free current $\bar{J}$, the total energy stored in the electromagnetic fields is:

$$W_{tot} \approx \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}(\alpha\epsilon_r)\Big|_{\omega_0}\bar{E}\cdot\bar{E}^* + \frac{\mu_0}{4}\frac{\partial}{\partial\beta}(\beta\mu_r)\Big|_{\omega_0}\bar{H}\cdot\bar{H}^*$$

⚠ Now let us contrast this expression to what is found in our notes / Landau & Lifshitz:

$$W_{tot} \approx \frac{\epsilon_0}{4}\frac{\partial}{\partial\omega_0}(\omega_0\epsilon_r)\bar{E}\cdot\bar{E}^* + \frac{\mu_0}{4}\frac{\partial}{\partial\omega_0}(\omega_0\mu_r)\bar{H}\cdot\bar{H}^* \qquad (1.10)$$

Notice the key difference in the derivative. This problem needs resolution. It does not make sense (to me) to take a derivative with respect to the center dominant frequency ω_0 since it is a constant that will not vary in the system.

⚠ Furthermore, this expression does not appear to reduce to the correct form for the energy density if we assume the material is non dispersive. In this case, the electric field energy density reduces to:

$$W_E = \frac{\epsilon_0}{4}\frac{\partial}{\partial\alpha}(\alpha\epsilon_r)\Big|_{\omega_0} E^2 = \frac{\epsilon_0\epsilon_r}{4}E^2$$

⚠ According to Landau & Lifshitz this is the time average, accounting for the factor of 2.

which differs by a factor of 2 from what we determined by assuming no dispersion from the very beginning. These expressions should thus be used with great care.

⚠ Landau & Lifshitz go about the derivation a bit differently which accounts for all of the differences and appears to be correct.

Group Velocity

In this section, we are going to derive the phase velocity and from the corresponding $\omega(k)$ relationship, we will find the group velocity. Our starting point is Maxwell's equations. Recall:

$$\bar{\nabla}\times\bar{E} = -\frac{\partial\bar{B}}{\partial t} \quad \text{and} \quad \bar{\nabla}\times\bar{H} = \frac{\partial\bar{D}}{\partial t}$$

We assume:

$$\bar{\nabla}\cdot\bar{E}=0 \;;\quad \bar{J}=0 \;;\quad \bar{\nabla}\cdot\bar{B}=0$$

i.e. there are no sources or free charge present. Recall how the vacuum and material Fields are related:

$$\bar{D} = \epsilon_0 \bar{E} + \bar{P} = \epsilon_0 \epsilon_r \bar{E} = \epsilon \bar{E}$$

$$\bar{B} = \mu_0 (\bar{H} + \bar{M}) = \mu_0 \mu_r \bar{H} = \mu \bar{H}$$

Maxwell's Equation become:

$$\bar{\nabla} \times \bar{E} = -\mu \frac{\partial \bar{H}}{\partial t} \quad \text{and} \quad \bar{\nabla} \times \bar{H} = \epsilon \frac{\partial \bar{E}}{\partial t}$$

Taking the curl of the 1st equation and substituting into the second yields the vector wave equation:

$$\bar{\nabla} \times \bar{\nabla} \times \bar{E} = -\mu\epsilon \frac{\partial^2 \bar{E}}{\partial t^2} \qquad (2.1)$$

Finally, we apply the vector identity $\bar{\nabla} \times \bar{\nabla} \times \bar{E} = \bar{\nabla}(\bar{\nabla} \cdot \bar{E}) - \bar{\nabla}^2 \bar{E}$:

$$\bar{\nabla}(\underbrace{\bar{\nabla} \cdot \bar{E}}_{=0}) - \nabla^2 \bar{E} = -\mu\epsilon \frac{\partial^2 \bar{E}}{\partial t^2}$$

$$\Rightarrow \quad \nabla^2 E = \mu\epsilon \frac{\partial^2 E}{\partial t^2} \qquad (2.2)$$

Let us assume a plane wave solution $\bar{E} \propto e^{i\bar{k}\cdot\bar{r} - i\omega t}$. Note that plane waves form an orthogonal basis and can thus be added together to represent just about any propagating field. Solving for the velocity of a plane wave is thus useful in a broad range of situations.

Substituting for $\bar{E}$:

$$-k^2 \bar{E} = -\mu\epsilon\omega^2 \bar{E} \Rightarrow [-k^2 + \epsilon\mu\omega^2] \bar{E} = 0$$

This equality holds if:

$$\frac{\omega}{k} = \frac{1}{\sqrt{\epsilon\mu}} = \frac{1/\sqrt{\epsilon_0 \mu_0}}{\sqrt{\epsilon_r \mu_r}} = \frac{c}{n} \qquad (2.3)$$

This is the phase velocity of the wave

$$\boxed{v_{ph} = \frac{\omega}{k} = \frac{c}{n}} \qquad (2.4)$$

which corresponds to the velocity of information carried by the wave if the medium through which it travels is non-dispersive.

In dispersive media, the phase velocity is a bit misleading. In most cases, the rate of information transfer is given by the group velocity. The group velocity is given by:

$$v_g = \frac{d\omega}{dk} = \frac{1}{dk/d\omega} \qquad (2.5)$$

Consider

$$\frac{dk}{d\omega} = \frac{d}{d\omega}\left(\frac{\omega n}{c}\right) = \frac{1}{c}\frac{d}{d\omega}(\omega n) = \frac{1}{c}\left(n + \omega\frac{dn}{d\omega}\right)$$

Thus the group velocity is:

$$\boxed{v_g = \frac{c}{\frac{d}{d\omega}(\omega n)} = \frac{c}{n + \omega\frac{dn}{d\omega}}} \qquad (2.6)$$

Kramers-Kronig Relations

The Kramers-Kronig relations impose a strict relationship between the real and imaginary parts of the linear susceptibility. The implications of these relations are significant and will be discussed later on.

We will not derive the relations here, however we will motivate them (see Yariv, Boyd, etc for derivation).

We begin by remembering/realizing that the time-dependent polarization is equal to the convolution of the linear susceptibility and electric field:

$$\bar{P}(t) = \int_{-\infty}^{t} dt' \, \chi(t-t') \bar{E}(t') \qquad (3.1)$$

The limits of integration demonstrate the importance of <u>causality</u> — the polarization depends only on events before up to the current time t. For times $t' > t$, $\chi = 0$. As long as we are careful to remember this, we can safely rewrite the polarization as:

$$P(t) = \int_{-\infty}^{\infty} dt' \, \chi(t-t') E(t')$$

Next, take the Fourier transform of $\bar{P}(t)$:

$$P(\omega) = \int_{-\infty}^{\infty} dt \, P(t) e^{i\omega t} = \int_{-\infty}^{\infty} dt e^{i\omega t} \int_{-\infty}^{\infty} dt' \, \chi(t-t') E(t')$$

$$= \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt \, \chi(t-t') E(t') e^{i\omega t} \quad \text{let } t'' = t - t' \Rightarrow dt = dt''$$

$$= \underbrace{\int_{-\infty}^{\infty} dt' \, E(t') e^{i\omega t}}_{E(\omega)} \underbrace{\int_{-\infty}^{\infty} dt'' \, \chi(t'') e^{i\omega t''}}_{\chi(\omega)}$$

Thus,

$$\boxed{P(\omega) = \chi(\omega) E(\omega)} \qquad (3.2)$$

This result is exactly what we would expect since the fourier transform of the convolution of two functions is equal to the product of the Fourier transform of the two functions.

The Kramers-Kronig relations are concerned with the frequency-dependent susceptibility $\chi(\omega)$. Specifically, $\chi(\omega)$, in general, can be complex ie

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$$

It turns out that given either the real or imaginary parts of the susceptibility, the other part can be uniquely determined. This relationship can be determined by evaluting the expression

$$\oint d\omega' \frac{\chi(\omega')}{\omega - \omega'} = 0 \qquad (3.3)$$

where $\oint d\omega'$ is a contour integral in the complex ω' plane (the various physical properties ensure that this expression is valid). Splitting up the contour integral into easily evaluatable pieces yields the famous <u>Kramers-Kronig relations:</u>

$$\begin{cases} \chi'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\chi''(\omega')}{\omega - \omega'} \\ \chi''(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\chi'(\omega')}{\omega - \omega'} \end{cases} \qquad (3.4)$$

Here $P\int_{-\infty}^{\infty} d\omega'$ denotes the "principle part" of the integral.

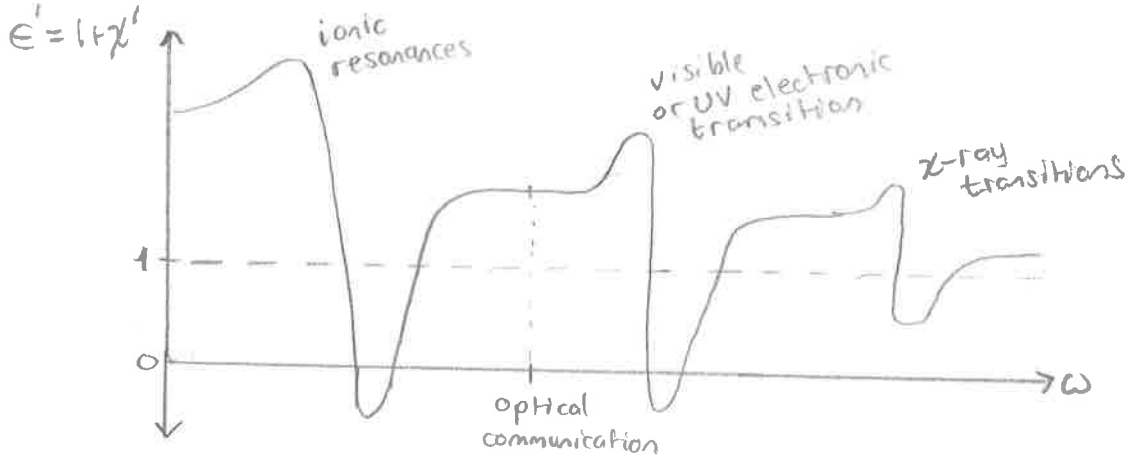
Notice a few important implications of these expressions:

(1) if $\chi'(\omega) = 0 \Rightarrow \chi''(\omega) = 0$ and vice versa $\rightarrow$ All dielectrics have loss!

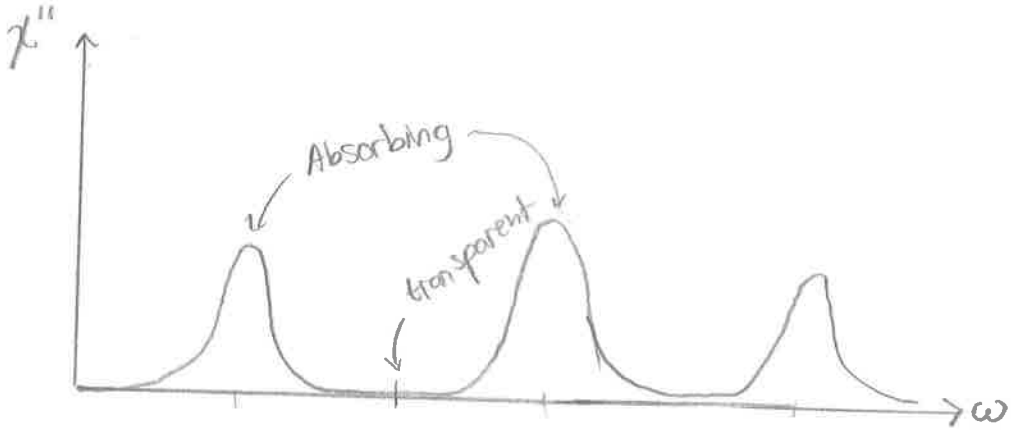
(2) knowing χ' (χ'') means you also know χ'' (χ')

(3) This result applies to any linear response function

As a consequence of the Kramers – Kronig relations, we observe material responses which look like:



(F3.1)



(F3.2)

<u>Side Note</u>: Ideal operating frequency (wavelength) for communications.

Notice in the figures above that there is a region where the imaginary χ'' is very small. This region corresponds to low loss propagation through the media. We might ask what is the ideal operating frequency?

We essentially have two options. The most obvious choice is the frequency which has the lowest loss. In glass, for example, this corresponds to $\lambda = 1.55\ \mu m$.

However, an alternative choice is the frequency at which dispersion is minimized. This is important if high bandwidths over long distances are desired. A bit of information is encoded as a pulse of light; in the presence of dispersion, a short pulse will spread out in time, limiting bandwidth.

To determine which frequency minimizes this effect, we need to minimize the derivative of group velocity with respect to frequency.

We do this by noticing that the group velocity is constant where

$$\frac{d}{d\omega}(\omega n(\omega)) = \text{constant} \qquad (3.5)$$

Taking another derivative yields an expression which when solved yields the frequency for which dispersion is minimal:

$$\frac{d^2}{d\omega^2}\left[\omega n(\omega)\right] = 0 \qquad (3.6)$$

Notice that dispersion is still present since $n(\omega) \neq 0$.
In the case of glass, dispersion is minimized for $\omega = 1.3\ \mu m$

Lorentz-Lorenz Model for Dielectric Constant

In order to estimate the dielectric constant of a material, we will attempt to treat it as a sum of many oscillating electrons whose oscillations are excited by an incident electric field. We will then add them together to get the polarization and, from that, determine the refractive index.

We begin w/ the equation of motion for a harmonic oscillator w/ an electric field driving force:

$$\text{Force} = q\bar{E} = \underset{\substack{\uparrow \\ \text{acceleration}}}{m\ddot{\bar{x}}} + \underset{\substack{\uparrow \\ \text{damping}}}{\frac{m}{\tau}\dot{\bar{x}}} + \underset{\substack{\uparrow \\ \text{restoring force} \\ \text{e.g. spring } F=-kx=-m\omega_0^2 x}}{m\omega_0^2\bar{x}} \qquad (4.1)$$

Assuming harmonic time dependence in x an E, that is

$$x = x_0 e^{i\omega t} \quad \text{and} \quad E = E_0 e^{i\omega t}$$

And dropping the vector notation, we have

$$\frac{qE_0}{m} = -\omega^2 x + i\frac{\omega}{\tau}x + \omega_0^2 x = \left[(\omega_0^2-\omega^2) + i\frac{\omega}{\tau}\right]x$$

Solving for x yields the distance from equilibrium of an electron oscillating in the applied electric field:

$$x(\omega) = \frac{qE_0/m}{(\omega_0^2-\omega^2) + i\,\omega/\tau} \qquad (4.2)$$

As the electron is displaced, it forms an oscillating dipole moment, which is given by $p = qx(\omega)$:

$$p = \frac{q^2E_0/m}{(\omega_0^2-\omega^2) + i\,\omega/\tau}$$

Finally, adding up N dipoles per unit volume gives a rough expression for the Polarization of a material:

$$P \simeq \frac{Nq^2/m}{(\omega_0^2-\omega^2) + i\,\omega/\tau}E_0 \qquad (4.3)$$

Next, recall that for a linear material, the linear electric susceptibility is given by $P = \epsilon_0 \chi E$. Comparing this to Equation (4.3) we see that

$$\epsilon_0 \chi \approx \frac{Nq^2/m}{\omega_0^2 - \omega^2 + i\frac{\omega}{\tau}} \qquad (4.4)$$

Recall that the permitivity ϵ is given by $\epsilon = \epsilon_0(1+\chi)$. Substituting $\epsilon_0\chi$ for Equation (4.4) yields the <u>complex permitivity</u>:

$$\epsilon = \epsilon_0 \underbrace{\epsilon_r}_{\text{relative } \epsilon_r} = \epsilon_0 + \frac{Nq^2/m}{\omega_0^2 - \omega^2 + i\,\omega/\tau} \qquad (4.5)$$

From here on out, it will be convenient to consider the real and imaginary parts of of ϵ seperately. First consider the real part:

$$\epsilon' = \epsilon_0\epsilon_r' = \epsilon_0 + \epsilon_0\chi' = \epsilon_0 + \frac{(Nq^2/m)(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2 + \omega^2/\tau^2} \qquad (4.6)$$

We can simplify this expression quite a bit by assuming that the damping is very weak and thus $\omega^2/\tau^2 \to 0$:

$$\epsilon' \simeq \epsilon_0 + \frac{Nq^2/m}{\omega_0^2 - \omega^2} \qquad (4.7)$$

It should be noted that we can only hope for this expression to be a reasonable approximation off resonance, ie $\omega \ll \omega_0$ or $\omega \gg \omega_0$ since ϵ' blows up as $\omega \to \omega_0$, which does not happen in the original expression. In the limit that $\omega \to 0$ and $\omega \to \infty$, the simplified expression (4.7) yields the same behavior as 4.6

Namely,

$$\lim_{\omega \to 0} \epsilon'(\omega) \simeq \epsilon_0 + \frac{Nq^2/m}{\omega_0^2} \qquad (4.8)$$

And

$$\lim_{\omega \to \infty} \epsilon'(\omega) \simeq \epsilon_0$$

Notice that the value of ϵ' is reduced by an amount $\Delta\epsilon \simeq Nq^2/m\omega_0^2$ when moving across the resonance. Next, we can rewrite $(\omega_0^2 - \omega^2) = (\omega_0 + \omega)(\omega_0 - \omega)$. Near resance, $\omega \approx \omega_0$ and so we can write $\omega_0 + \omega \simeq 2\omega_0$. If damping is negligable, the ϵ' near resonance can be approximated by:

$$\epsilon' \simeq \epsilon_0 + \frac{Nq^2/2m\omega_0}{\omega_0 - \omega} \quad \text{if } \omega \approx \omega_0 \qquad (4.9)$$

Our understanding of the dielectric constant is not complete without considering the imaginary part. Taking the imaginary part of Equation (4.6) yields

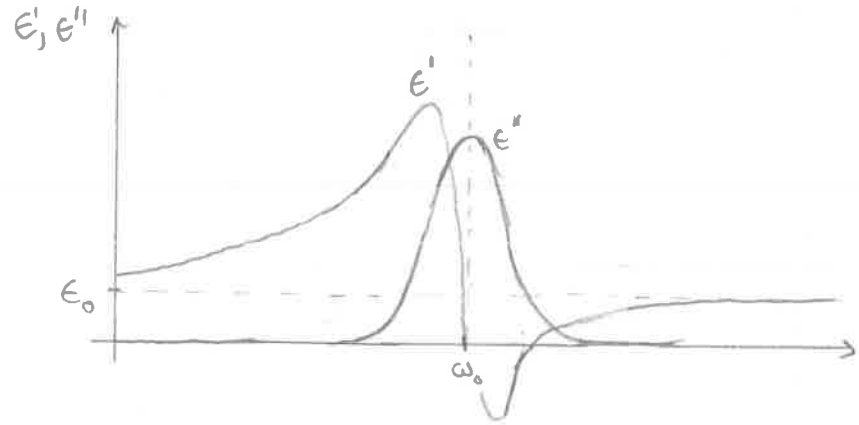
$$\epsilon'' = \frac{(Nq^2/m)(\omega/\tau)}{(\omega_0^2 - \omega^2)^2 + \omega^2/\tau} \qquad (4.10)$$

Notice that in the limit that $\omega \to 0$ and $\omega \to +\infty$, $\epsilon'' \to 0$. Near resonance, $\omega \approx \omega_0$, Equation (4.10) simplifies slightly:

$$\epsilon'' \simeq \frac{(Nq^2/m)(\omega_0/\tau)}{4\omega_0^2(\omega_0^2 - \omega^2) + \omega_0^2/\tau} \simeq \frac{(Nq^2/m)(1/4\omega_0^2\tau)}{(\omega - \omega_0)^2 + (1/2\tau)^2} \qquad (4.11)$$

Notice that the imaginary part of ϵ takes on the familiar Lorentzian line shape while the real part has a more complex shape.

Graphically, ϵ' and ϵ'' looking like:



(F4.1)

The behavior depicted above demonstrates the importance of the Kramers-Kronig relations: In order to get a high ϵ', you must also be willing to accept a high ϵ''.

In the model we just worked through, we assumed that a material consisted of a homogenous collection of identical oscillators. In reality, materials have multiple resonances and consist of many different oscillators. In order to capture this behavior, we can try rewriting the linear susceptibility as a weighted sum of different oscillators:

$$\epsilon_0 \chi(\omega) = \sum_i \frac{Nq^2/m \times S_i}{(\omega_i^2 - \omega^2) - i\frac{\omega}{\tau}} \qquad (4.12)$$

If we add ϵ_0 and calculate the real part to find ϵ' as we did before, we see that the "step-down", that is $\chi(\omega \to 0) - \chi(\omega \to \infty)$ is:

$$\frac{\Delta \epsilon'}{\epsilon_0} = \frac{Nq^2}{m\omega_0^2 \epsilon_0} \times S_i \qquad (4.13)$$

Equation (4.13) is unitless and we call it the "Oscillator strength".

A side note: Since we are dealing with a weighted sum, we impose the constraint that all of the s_i add to 1:

$$\sum_i s_i = 1.$$

This requirement is useful when evaluating an expression for the absorption coefficient. By definition, the absorption coefficient is given by:

$$\underset{[W/cm^3]}{\frac{\text{Power Absorbed}}{\text{Volume}}} = \underset{[1/cm]}{\alpha(\omega)} \times \underset{[W/cm^2]}{\text{Intensity}}$$

The intensity of a traveling wave is given either by the time-averaged Poynting vector or by multiplying the energy density of the wave by its velocity:

2 becaus of magnetic contribution

$$I = \frac{2}{4}\epsilon_0 \epsilon_r |E|^2 \times \frac{c}{\sqrt{\epsilon_r}} = \frac{1}{2} c \epsilon_0 \sqrt{\epsilon_r} |E|^2 \quad (4.14)$$

Recall that we derived this expression assuming E was real, thus the real part must be taken before computing $|E|^2$.

The dissipated power, meanwhile can be shown to be:

$$\frac{\text{Power dis.}}{\text{Vol}} = \frac{\epsilon_0}{2} \omega \chi'' |E|^2 \quad (4.15)$$

Equating the power to the intensity $\times\, \alpha(\omega)$:

$$\alpha(\omega) \times \cancel{\tfrac{c}{2}}\, \cancel{\epsilon_0} \sqrt{\epsilon_r}\, \cancel{|E|^2} = \frac{\epsilon_0}{\cancel{2}}\, \omega\, \chi''(\omega)\, \cancel{|E|^2}$$

$$\Rightarrow \quad \alpha(\omega) = \frac{1}{\sqrt{\epsilon_r}} \frac{\omega}{c} \chi''(\omega) \qquad (4.16)$$

Equation (4.16) gives the frequency dependent absorption coefficient.

An important-ish relation can be obtained by substituting our oscillator model for $\chi''(\omega)$ in (4.16) and then integrating over frequency:

$$\int_0^\infty \alpha(\omega)\, d\omega = \frac{1}{\sqrt{\epsilon_r}} \int_0^\infty \frac{\omega}{c} \chi''(\omega)\, d\omega$$

If the resonances are sufficiently narrow:

$$\int_0^\infty \alpha(\omega)\, d\omega \simeq \frac{1}{\sqrt{\epsilon_r}} \sum_i \frac{\omega_i}{c} \int_0^\infty \chi''(\omega; \omega_i)\, d\omega$$

$$= \frac{2\pi^2}{\sqrt{\epsilon_r}} \frac{N q^2}{4\pi\epsilon_0 m c} \sum_i S_i \qquad \text{Math}$$

Recall that we required that $\sum_i S_i = 1$. It follows that:

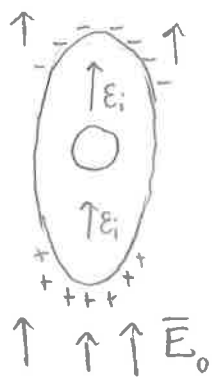
$$\int_0^\infty \alpha(\omega)\, d\omega = \frac{2\pi}{\sqrt{\epsilon_r}} \frac{N q^2}{4\pi\epsilon_0 m c} \qquad (4.17)$$

This expression called the <u>Oscillator strength sum rule.</u>

Despite all of the work we just did, if you actually try to calculate the permitivity of a medium using our harmonic oscillator model, you will get a wrong answer. This becaus the harmonic oscillator model has two major issues:

1) In our calculation of the oscillator stregth sum rule, we factored out $\sqrt{\varepsilon_r}$ from the integral. This is not really allowed since it contains an explicit frequency dependence.
   Furthermore, we used the non-dispersive energy density. Instead, we should have used the dispersive energy density given by equation (1.10).

2) We did not take into account the local fields of



the constituent atoms. The field seen by a given atom is influenced by the surrounding dipoles. If the atom is ~ a spherical hole, then the actual electric field is

$$E_i = E_0 + \frac{P}{3\epsilon_0}$$

Extra due to surrounding dipole moments

This modifies the polarization: $P = \epsilon_0 \chi E_i = \epsilon_0 N \gamma E_i$

Polarization of one atom

Plasmas

A final interesting result can be obtained from our harmonic oscillator model. In some materials such as metals, a large number of electrons are effectively free, acting like an electron gas. In this case

there is no restoring force and thus $\omega_0 = 0$. In this case the permittivity becomes

$$\epsilon = \epsilon_0 - \frac{Nq^2/m}{\omega^2 + i\omega/\tau} \qquad (4.18)$$

Taking the real part:

$$\epsilon' = \epsilon_0 - \frac{Nq^2/m}{\omega^2 + 1/\tau^2}$$

Notice that if damping is small, then ϵ' will become negative when

$$\omega^2 < \frac{Nq^2}{\epsilon_0 m} \qquad (4.19)$$

The frequency $\omega_p^2 = Nq^2/\epsilon_0 m$ is called the plasma frequency. Notice that waves with frequencies $\omega < \omega_p$ will be unable to propogate through the medium — they will instead decay exponentially.

This phenomenon can also occur is materials with a non-zero restoring force and will happen near resonances. As we will see later on, waves which exist around this forbidden band are called polaritons.

Nonlinear Optics: Anharmonic Oscillator

In our previous models, we assumed that electrons responded linearly to incident electromagnetic fields. In reality, electrons always exhibit some degree of non-linearity. One explanation is the fact that electrons in atoms feel a non-parabolic potential which leads to higher order forces beyond the $-kx$ restoring force. In order to better understand the nonlinear response of materials, we look to the <u>anharmonic oscillator model</u>:

$$\ddot{x} + \frac{\dot{x}}{\tau} + \omega_0^2 x = \frac{q}{m} E + D x^2 + F x^3 \qquad (5.1)$$

Here, Dx^2 and Fx^3 correspond to higher order responses. In order to solve for the electron position, we assume higher order terms are progressively weaker and apply perturbation theory. Let us assume the displacement is given by:

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} \qquad (5.2)$$

Here $x^{(1)}$ is the 1st order response, $x^{(2)}$ is the 2nd order response and so on. λ is a parameter such that $0 < \lambda < 1$ which allows us to "turn on" the higher order responses. Substituting x into (5.1) yields:

$$\left(\lambda \ddot{x}^{(1)} + \lambda^2 \ddot{x}^{(2)} + \lambda^3 \ddot{x}^{(3)}\right) + \frac{1}{\tau}\left(\lambda \dot{x}^{(1)} + \lambda^2 \dot{x}^{(2)} + \lambda^3 \dot{x}^{(3)}\right) + \omega_0^2\left(\lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)}\right)$$
$$= \frac{q}{m} E + D\left(\lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)}\right)^2 + F\left(\lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)}\right)^3$$

Next, we match orders of λ which yields an equation for each order of x:

$$\begin{cases} ① \ \ddot{x}^{(1)} + \frac{1}{\tau}\dot{x}^{(1)} + \omega_0^2 x^{(1)} = \frac{q}{m}E \\ ② \ \ddot{x}^{(2)} + \frac{1}{\tau}\dot{x}^{(2)} + \omega_0^2 x^{(2)} = D(x^{(1)})^2 \\ ③ \ \ddot{x}^{(3)} + \frac{1}{\tau}\dot{x}^{(3)} + \omega_0^2 x^{(3)} = 2D x^{(1)} x^{(2)} + F(x^{(1)})^3 \end{cases} \qquad (5.3)$$

Note: For this process to work, we must also assume that $E = \lambda E^{(1)}$.

To solve the equations, we assume both $x^{(1)}$ and E have the same harmonic time depence (if E does, x must). For the most general solution, we assume E & x are a sum of three different frequencies:

$$E = E_1 e^{i\omega_1 t} + E_2 e^{i\omega_2 t} + E_3 e^{i\omega_3 t}$$

$$x = x_1 e^{i\omega_1 t} + x_2 e^{i\omega_2 t} + x_3 e^{i\omega_3 t}$$

substituting these expressions into ① of (5.3):

$$\left(\omega_0^2 - \omega_i^2 + i\frac{\omega_i}{\tau}\right) x_i^{(1)} = \frac{q}{m} E_i$$

So,

$$x^{(1)} = \sum_i^3 \frac{qE_i/m}{\omega_0^2 - \omega_i^2 + i\,\omega_i/\tau} e^{i\omega_i t} \qquad (5.4)$$

This is the 1st order or <u>linear response</u>. The corresponding susceptibility was found in the previous section. The second order response is found by substituting (5.4) into (5.3) ②:

$$x^{(2)} = \sum_i^3 \sum_j^3 \frac{D q E_i E_j/m}{D(\omega_i+\omega_j) D(\omega_i) D(\omega_j)} e^{i(\omega_i+\omega_j)t} \qquad (5.5)$$

Where

$$D(\omega) = \omega_0^2 - \omega^2 + i\frac{\omega}{\tau}$$

Finally, substituting (5.4) and (5.5) into (5.3) yields the third order response:

$$\chi^{(3)} = \sum_i \sum_j \sum_k \left\{ \frac{2D^2}{D(\omega_i+\omega_j+\omega_k)\,D(\omega_i+\omega_j)\,D(\omega_i)\,D(\omega_j)\,D(\omega_k)} \right. \qquad (5.6)$$

$$\left. + \frac{F}{D(\omega_i+\omega_j+\omega_k)\,D(\omega_i)\,D(\omega_j)\,D(\omega_j)} \right\} E_i E_j E_k e^{i(\omega_i+\omega_j+\omega_k)t}$$

Using these solutions, it would be straight forward to write the Polarization:

$$P = Nq\left\{ x_0^{(1)} + x_0^{(2)} + x_0^{(3)} + \cdots \right\}$$

Or explicitely in terms of susceptibilities:

$$P = \epsilon_0 \left\{ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots \right\} \qquad (5.7)$$

Here $\chi^{(2)}$ and $\chi^{(3)}$ are the non-linear susceptibilities. As a rule of thumb, the size of the linear susceptibilities is as large as the linear susceptibility when E is on the order of the strength of the electric field in an atom:

$$E_{atomic} \simeq \frac{2 \text{ Volts}}{0.1 \text{ nm}} \approx 2\times10^8 \text{ V/cm}$$

Miller's Rule

An interesting relationship exist between the higher order susceptibilities and the linear susceptibility $\chi^{(1)}$. For example, consider $\chi^{(2)}$ for a monochromatic incident field:

$$\chi^{(2)} = \frac{Dm\epsilon_0^2}{N^2q^3} \left\{ \underbrace{\frac{Nq^2/m\epsilon_0}{\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}}}_{\chi^{(1)}} \right\}^3$$

The expression in braces is the expression for $\chi^{(1)}$ given a monochromatic field. From this we make the observation that

$$\chi^{(2)} \propto \left(\chi^{(1)}\right)^3$$

Which we may write more explicitly as <u>Miller's Rule</u>:

$$\frac{\chi^{(2)}}{\left(\chi^{(1)}\right)^3} = \frac{Dm\,\varepsilon_0^2}{N^2 q^3} = \text{const} \qquad (5.8)$$

From this observation we can make two very important conclusions about how to achieve strong nonlinearities:

(1) Find materials with large permittivities ($\epsilon_r = 1 + \chi^{(1)}$ and higher order χ's go as $\left(\chi^{(1)}\right)^n$).

(2) Operate at the material's resonance $\rightarrow$ loss is also high at resonance!!

Next, notice from equation (5.5) that the 2nd order susceptibility is a function of two frequencies ω_i and ω_j and their corresponding field amplitudes E_i & E_j. As we sum through the possible i's & j's, notice that we will eventually get a term where i & j are swapped thus leading to a double counting. Often, we will normalize the susceptibility to account for this. We define:

$$\chi^{(2)}(-\omega_1-\omega_2, \omega_1, \omega_2) = \frac{2}{2^n}\chi^{(2)} \qquad (5.9)$$

For the $\chi^{(2)}$, n is equal to 2 and the normalization factor is $1/2$.

When using this notation, the frequency arguments must add up to zero, hence the two negative frequency arguments.
One explanation for the use of negatives is that $\chi^{(2)}$ more than just an electric field susceptibility: it is a contribution to the free energy (See page 23-24 of the notes for an explanation).

Alternatively, we can view $\chi^{(2)}(-\omega_1, -\omega_2, \omega_1, \omega_2)$ as the 2nd. order susceptibility that results in a wave whose frequency is the sum of $\omega_1 + \omega_2$. This is easily seen if we consider an incident electric field consisting of 2 frequencies which is real valued:

$$E = \frac{E_1}{2} e^{i\omega_1 t} + \frac{E_1}{2} e^{-i\omega_1 t} + \frac{E_2}{2} e^{i\omega_2 t} + \frac{E_2}{2} e^{-i\omega_2 t}$$

The second order polarization is:

$$P^{(2)} = \varepsilon_0 \chi^{(2)} E^2$$

Substituting for E yields:

$$P^{(2)} = \varepsilon_0 \chi^{(2)} \frac{E_1 E_2}{4} \left\{ e^{i(\omega_1 + \omega_2)t} + e^{-i(\omega_1 + \omega_2)t} \right\} + \text{other terms}$$

Thus we have two terms proportional to $E_1 E_2$. One has a phase factor w/ $\omega_1 + \omega_2$ and the other has the negative of the same phase factor (ensuring a real result). The notation above encompasses this result.
Notice that we could have started w/ the signs on ω_1 & ω_2 reversed (ie both negative) and we would have gotten the same result. The frequencies in the parentheses

can thus be permuted. E.g.:

$$\chi^{(2)}(\omega_3, \omega_1, \omega_2) = \chi^{(2)}(\omega_1, \omega_2, \omega_3) \quad \text{etc}$$

This notation is useful for describing a variety of effects. In our first example, ω_1 & ω_2 ared added together — This is sum frequency generation. There are many others:

(1) Sum frequency generation: $\chi^{(2)}(-\omega_1 - \omega_2, \omega_1, \omega_2)$

(2) Difference frequency generation: $\chi^{(2)}(-\omega_1 + \omega_2, \omega_1, -\omega_2)$

(3) 2nd harmonic generation: $\chi^{(2)}(-2\omega, \omega, \omega)$

(4) electro-optic Effect: $\chi^{(2)}(-\omega, \omega, 0)$

↳ "Pockel's Effect" → Electric field induced refractive index change; $\chi_{optical} = \chi^{(1)}(-\omega, \omega) + \chi^{(2)}(-\omega, \omega, 0) E_{dc}$

(5) Optical rectification: $\chi^{(2)}(0, \omega, -\omega)$

↳ "optically induced dc field"

6.1 Tensor Properties

Up until now, we have only considered scalar susceptibilities which relate polarization magnitudes to Electric field magnitudes. In general, the polarization is a vector, each of whom's components can be influenced by different components of the electric field. The "constant" of

proportionality of these two vectors must be a tensor. The susceptibilities are thus rank 2 and higher tensors. Consider 1st the linear susceptibility & polarization:

$$P_i^{(1)} = \varepsilon_0 \sum_j \chi_{ij}^{(1)} E_j \qquad (6.1)$$

The linear susceptibility χ_{ij} is thus a rank 2 tensor. For example, χ_{ij} might have the form:

$$\chi_{ij}^{(1)} = \begin{bmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{bmatrix} \qquad (6.2)$$

Next consider the 2nd order susceptibility $\chi^{(2)}$. Since two different electric fields are involved, 3 indices in $\chi^{(2)}$ are needed. $\chi^{(2)}$ is thus a rank 3 tensor. The 2nd order polarization is given by

$$P_i^{(2)} = \varepsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k \qquad (6.3)$$

At 1st glance, we see that here are 27 possible elements in this rank 3 tensor, so it would seem as if we need to specify these 27 values. This number can be somewhat reduced, however, by noticing that $E_j E_k = E_k E_j$ and thus $\chi_{ijk}^{(2)} = \chi_{ikj}^{(2)}$. Taking this into account, we can express our rank 3 tensors using rank 2 matrices by defining indices as follows:

$$xx = 1 \; ; \; yy = 2 \; ; \; zz = 3$$
$$yz = zy = 4 \; ; \; xz = zx = 5 \; ; \; xy = yx = 6 \qquad (6.4)$$

The second order polarization can then be written:

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} & \chi_{14} & \chi_{15} & \chi_{16} \\ \chi_{21} & \chi_{22} & \chi_{23} & \chi_{24} & \chi_{25} & \chi_{26} \\ \chi_{31} & \chi_{32} & \chi_{33} & \chi_{34} & \chi_{35} & \chi_{36} \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_zE_y \\ 2E_zE_x \\ 2E_xE_y \end{pmatrix} \qquad (6.5)$$

This is further simplified for a large class of materials (most!) which are <u>centro-symmetric</u>. Such materials exhibit <u>inversion symmetry</u>. Inversion symmetry means that as we move from $x \to -x$, $y \to -y$, and/or $z \to -z$ (ie we invert the material) its properties remain unchanged. Consider for example taking $x \to -x$. The material remains unchanged so $\chi^{(2)}_{xyz} = \chi^{(2)}_{-xyz}$. The polarization, however, does have its sign flipped, so:

$$P_{-x} = \varepsilon_0 \chi^{(2)}_{-xyz} E_y E_z = -P_x = -\varepsilon_0 \chi_{xyz} E_y E_z$$

Which leaves us w/ the condition:

$$\chi^{(2)}_{-xyz} = -\chi^{(2)}_{xyz} \qquad (6.6)$$

We have already asserted that $\chi^{(2)}_{xyz} = \chi^{(2)}_{-xyz}$, thus expression (6.6) is only true if $\chi^{(2)}_{xyz} = 0$. Applying this to the other tensor elements demonstrates that centro-symmetric materials do not have a $\chi^{(2)}$, which is true of most materials.

Now that we are expressing $\chi^{(2)}$ as a tensor, we can extend our earlier syntax to include this:

$$\chi^{(2)}_{ijk} = \chi^{(2)}_{ijk}(\omega_3, \omega_1, \omega_2) \qquad (6.7)$$

Notice that given this syntax, the fields E_j & E_k correspond to frequencies ω_1 and ω_2 while the Polarization P_i corresponds to frequency $-\omega_3$. As a consequence of this, we are free to permute spatial indices as long as we permute the frequencies in the same way.

This can be taken a step further if we consider which are very far from resonances of the material. At such frequencies, the material may be relatively non dispersive, and thus its response will be independent of frequency. As a result, the indices of χ_{ijk} can be freely permuted w/o changing its value, ie $\chi_{ijk} = \chi_{ikj} = \chi_{jik}$ etc. This property is known as <u>Kleinman Symmetry</u>.

Notice that under Kleinman Symmetry, the number of independent parameters in the matrix in (6.5) is reduced from 18 to 10.

Even without Kleinman Symmetry, crystal symmetries can significantly reduce the number of independent tensor elements need to describe χ. Consider, for example, The 3rd order susceptibility $\chi^{(3)}_{ijkl}$. $\chi^{(3)}$ can have $3^4 = 81$ different elements! However, if we consider a material w/ cubic symmetry, we find that $\chi^{(3)}_{xxxx} = \chi^{(3)}_{yyyy} = \chi^{(3)}_{zzzz}$

and elements w/ an odd number of unique subscripts like $\chi^{(3)}_{xxxy} = 0$ as a result of inversion symmetry.

It turns out that, after taking into account all of the symmetries associated w/ a cubic crystal structure, the total number of tensor elements is equal to 2: the $\chi^{(3)}_{xxyy}$ and $\chi^{(3)}_{xxxx}$ elements.

In isotropic centro-symmetry materials, there is really only one independent element since $\chi^{(3)}_{xxxx} = \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyxy} + \chi^{(3)}_{xyyx}$ (e.g. glass). Note: <u>$\chi^{(3)}$ is NEVER zero</u>

Having discussed $\chi^{(3)}$, it is interesting to list some of the phenomena associated w/ <u>$\chi^{(3)}$ nonlinearities</u>:

(1) 3rd Harmonic Generation: $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$

(2) refractive index change: $\chi^{(3)}(-\omega, \omega, -\omega, \omega)$

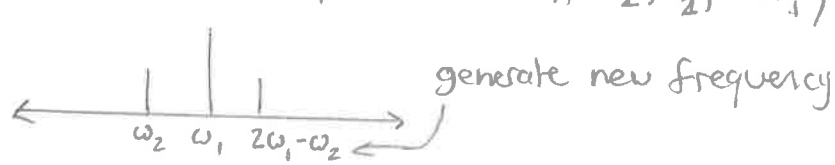
↳ $\chi^{(1)}_{effective} = \chi^{(1)}(-\omega, \omega) + \chi^{(3)}(-\omega, \omega, -\omega, \omega)|E(\omega)|^2$ ← Intensity dependent

(3) Refractive index change due to 2nd frequency: $\chi^{(3)}(-\omega_1, \omega_1, -\omega_2, \omega_2)$

(4) Raman gain/loss: $\mathrm{Im}\{\chi^{(3)}(-\omega_1, \omega_1, -\omega_2, \omega_2)\}$

↳ gain occurs if $\omega_2 > \omega_1$ and loss if $\omega_1 > \omega_2$

(5) Four wave mixing: $\chi^{(3)}(-2\omega_2 + \omega_1, \omega_2, \omega_2, -\omega_1)$



(6) Two Photon Absorption: $\mathrm{Im}\left\{\chi^{(3)}(-\omega_1, \omega_1, -\omega_2, \omega_2)\right\}$

(7) gain saturation or Absorption Saturation: $\mathrm{Im}\left\{\chi^{(3)}(-\omega_1, \omega_1, -\omega_1, \omega_1)\right\}$

6.2 Nonlinear Wave Equation

Up until now, we have discussed nonlinear optics in a relatively abstract way. Now we will actually attempt to establish a mathematical foundation for one of the nonlinear processes mentioned in the previous section.

Our starting point is the Nonlinear wave equation. This is easily obtained by including the Nonlinear polarization in Maxwell's equations and following the usual steps. The result is:

$$\nabla^2 \bar{E} - \mu_0 \epsilon \frac{\partial^2 \bar{E}}{\partial t^2} = \mu_0 \frac{\partial^2}{\partial t^2} \bar{P}_{NL} . \qquad (6.8)$$

Here $\bar{P}_{NL}$ could be $\bar{P}^{(2)} = \varepsilon_0 \bar{\bar{\chi}}^{(2)} |\bar{E}| \bar{E}$, $\bar{P}^{(3)} = \varepsilon_0 \bar{\bar{\bar{\chi}}}^{(3)} |\bar{E}|^2 \bar{E}$, etc.

In order to understand how light might propagate through a nonlinear material, let us consider an electric field consisting of three frequencies moving in the z-direction which are polarized in the $\hat{x}$ & $\hat{y}$ directions:

$$E_{1i}(z,t) = \mathrm{Re}\left\{E_{1i}(z) e^{ik_1 z - i\omega_1 t}\right\}$$
$$E_{2k}(z,t) = \mathrm{Re}\left\{E_{2k}(z) e^{ik_2 z - i\omega_2 t}\right\} \qquad (6.9)$$
$$E_{3j}(z,t) = \mathrm{Re}\left\{E_{3j}(z) e^{ik_3 z - i\omega_3 t}\right\}$$

since we will be investigating the 2nd order polarization, we will require that $\omega_3 = \omega_1 + \omega_2$. Furthermore, we will assume that E_{1i}, E_{2j}, E_{3k} are slowly varying envelopes.

With the Electric field defined, we can substitute it into the nonlinear wave equation (6.8). Since E is the sum of the three expressions, in (6.9), we can treat each of them separately. Let's begin by writing the wave equation for E_{1i}. Consider:

$$\nabla^2 E_{1i} = \left[-k_1^2 E_{1i} + 2ik\frac{\partial E_{1i}}{\partial z} + \frac{\partial^2 E_{1i}}{\partial z^2}\right] e^{i(k_1 z - \omega_1 t)}$$

Next, we invoke the <u>Slowly varying envelope approx</u> which says

$$k_1 \frac{dE_{1i}}{dz} \gg \frac{d^2 E_{1i}}{dz^2} \qquad (6.10)$$

Thus it follows that

$$\nabla^2 E_{1i} \approx \left[-k_1^2 E_{1i} + 2ik\frac{\partial E_{1i}}{\partial z}\right] e^{i(k_1 z - \omega_1 t)} \qquad (6.11).$$

Substituting this into the wave equation yields:

$$\left(-k_1^2 + \omega^2 \mu_0 \varepsilon\right) E_{1i} e^{i(k_1 z - \omega_1 t)} + 2ik_1 \frac{\partial E_{1i}}{\partial z} e^{i(k_1 z - \omega_1 t)} = \mu_0 \frac{\partial^2}{\partial t^2} P_{NL}$$

Since the phasors on each side of the equation must match, it is evident the term in P_{NL} that fits in the equation above is:

$$P_{NL}(\omega_1) = \epsilon_0 \chi^{(2)}_{ijk} \underbrace{E_{3j} E^*_{2k} e^{i[(k_3 - k_2)z - \overbrace{(\omega_3 - \omega_2)}^{\omega_1} t]}}_{= E_{3j}(z,t) E^*_{2k}(z,t)}$$

substituting this result for P_{NL} yields a wave equation describing the evolution of $E_{1i}(z)$:

$$e^{ik_1 z}\left(-k_1^2 + \omega_1^2 \mu_0 \varepsilon_1\right) E_{1i}(z) + 2ik_1 \frac{\partial E_{1i}}{\partial z} = \omega_1^2 \mu_0 \varepsilon_0 \chi^{(2)}_{ijk} E_{3j}(z) E^*_{2k}(z) e^{i(k_3-k_2)z}$$

Recall that when solving the linear wave equation, we found that $k^2 = \omega^2 \mu_0 \varepsilon$. From this, it follows that the change in the envelope of E_{1i} is given by:

$$ik_1 \frac{dE_{1i}}{dz} = -\frac{\omega_1^2}{2c^2} \chi^{(2)}_{ijk} E_{3j}(z) E^*_{2k}(z) e^{i[k_3-(k_2+k_1)]z}$$

Performing this same process w/ the other two waves results in expressions for how each wave's envelope changes as the waves propogate. These results are summarized as follows

⚠ Middle expression wrong in notes.

$$\frac{dE_{1i}}{dz} = \frac{i}{\sqrt{\epsilon_1}} \frac{\omega_1}{2c} \chi^{(2)}_{ijk} E_{3j}(z) E^*_{2k}(z) e^{i(k_3-k_2-k_1)z}$$

$$\frac{dE_{2k}}{dz} = \frac{i}{\sqrt{\epsilon_2}} \frac{\omega_2}{2c} \chi^{(2)}_{kij} E^*_{1i}(z) E_{3j}(z) e^{i(k_3-k_2-k_1)z} \qquad (6.11)$$

$$\frac{dE_{3j}}{dz} = \frac{i}{\sqrt{\epsilon_3}} \frac{\omega_3}{2c} \chi^{(2)}_{jik} E_{1i}(z) E_{2k} e^{-i(k_3-k_2-k_1)z}$$

Notice that the last equation corresponds to the wave which is generated as a result of the $\chi^{(2)}$ process. To understand how such a wave might develope, let's consider the case of 2nd harmonic generation: $\omega_1 = \omega_2 = \omega$ and $\omega_3 = 2\omega$.

In this case, the last equation of (6.11) becomes:

$$\frac{dE_{3j}}{dz} = \frac{i\overset{=2\omega}{\omega_3}}{2c\sqrt{\varepsilon_3}} \chi^{(2)}_{jik} E_{1i} E_{2k} e^{i\Delta k z}$$

where we have chosen to write $k_3 - k_2 - k_1 = \Delta k$.
Next, we invoke the <u>parametric approximation</u> which says that the pump waves are sufficiently strong such that their amplitudes remain unchanged as the third wave develops. In this case, we regard $E_{1i} E_{2k}$ as constant, allowing us to easily solve for $E_{3j}(z)$:

$$E_{3j}(z) = \frac{i\omega_3}{2c\sqrt{\varepsilon_3}} \chi^{(2)}_{jik} E_{1i} E_{2k} \frac{e^{-i\Delta k L} - 1}{i\Delta k}$$

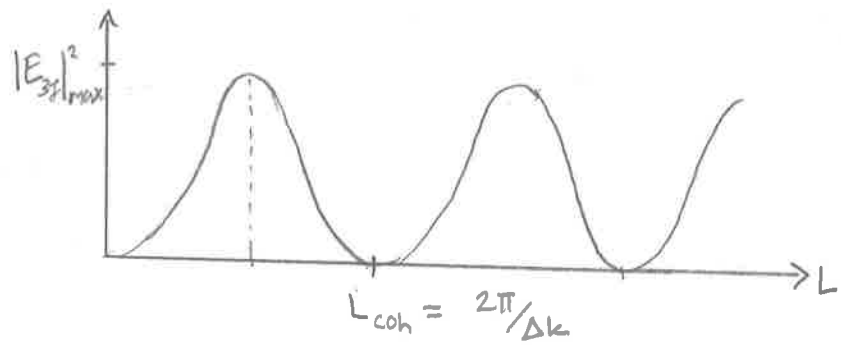
Often we care more about intensity, thus $|E_{3j}|^2$ is a bit more meaningful:

$$|E_{3j}(z)|^2 = \frac{\omega_3^2}{4c^2\varepsilon_3} |E_{1i}|^2 |E_{2k}|^2 \frac{\sin^2(\Delta k L/2)}{(\Delta k/2)^2} |\chi^{(2)}|^2 \quad (6.12)$$

This result demonstrates something very interesting (and potentially unfortunate) about the generated wave: Its intensity oscillates between zero and a maximum value given by:

$$|E_{3j}(z)|^2_{max} = \left| \frac{\omega_3}{c\sqrt{\varepsilon_3}} \frac{\chi^{(2)}}{\Delta k} E_{1i} E_{2k} \right|^2$$

Graphically, $|E_{3f}|^2$ looks like:



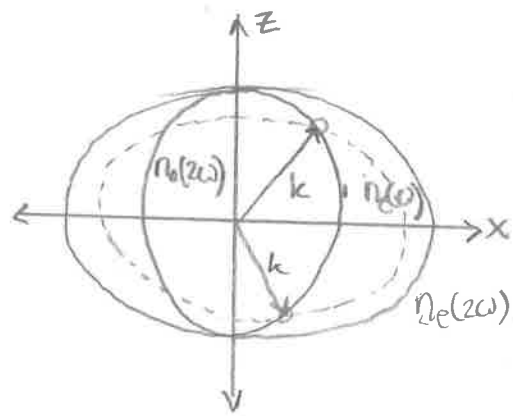
The coherence length L_{coh} is the length over which the generated field grows and decays back to zero.

In many situations, we would like for the third wave to grow to significant intensities. This is difficult there is a natural tendency for the third frequency to grow and decay periodically. There are a number of ways to get around this:

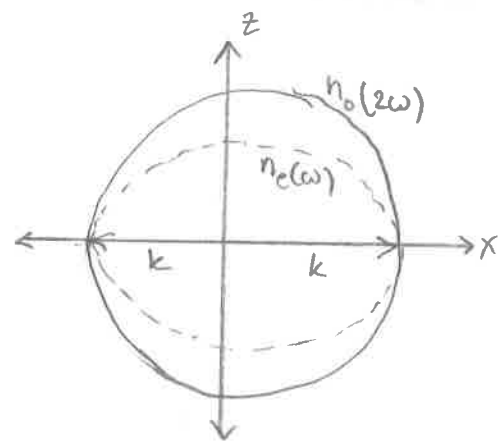
(1) <u>Phase matching</u>: certain materials make Δk very small or even zero. In a material where $\Delta k = 0$, $L_{coh} = \infty$ and the third frequency will grow until all of the energy ends up in it. (frequency conversion efficiency $\rightarrow 1$)

(2) <u>Crystal Poling</u>: Assemble multiple $\chi^{(2)}$ crystals of length L_{coh} front to back so that the third frequency grows sinusoidally in each section $\rightarrow$ common?

Minimizing phase mismatch is thus very important for 2nd harmonic generation where the coherence length $L_{coh} = \frac{2\pi}{k(2\omega) - 2k(\omega)} \approx 100\ \mu m$. Phase matching can be achieved more easily in materials which exhibit birefringence (anisotropy). In such crystals, there may be incidence angles at which the index ellipsoids of $n_e(2\omega)$ and $2n_o(\omega)$ overlap. At these incidence angles phase matching can be achieved



Phase matching in Birefringence



Ideal Birefringence For Phase matching

6.3 Manley-Rowe Relations

Though we may have illuded to it in the previous section, we have not explicitly treated the issue of conservation of energy. Demonstration of conservation of energy in non-linear media comes in the form of the so called "<u>Manley-Rowe" relations</u>.

Consider what happens when we multiply the three equations in (6.11) by E_{1i}^*, E_{2k}^*, and E_{3j}^* respectively:

$$E_{1i}^* \frac{dE_{1i}}{dz} = \frac{i}{\sqrt{\epsilon_1}} \frac{\omega_1}{2c} \chi^{(2)}_{ijk} E_{3j} E_{2k}^* E_{1i}^* e^{i\Delta k z}$$

$$E_{2k}^* \frac{dE_{2k}}{dz} = \frac{i}{\sqrt{\epsilon_2}} \frac{\omega_2}{2c} \chi^{(2)}_{kij} E_{3j} E_{2k}^* E_{1i}^* e^{i\Delta k z} \qquad (6.13)$$

$$E_{3j}^* \frac{dE_{3j}}{dz} = \frac{i}{\sqrt{\epsilon_3}} \frac{\omega_3}{2c} \chi^{(2)}_{jki} E_{3j}^* E_{2k} E_{1i} e^{-i\Delta k z}$$

Notice that the LHS of each equation is equal to $\frac{1}{2}\frac{d|E_{1i}|^2}{dz}$, etc. If we ignore dispersion such that $\epsilon_1 = \epsilon_2 = \epsilon_3$, then it follows that $\frac{1}{\omega_q} \times$ RHS is the same for all of the equations, and we find that:

$$\frac{1}{\omega_1}\frac{d|E_{1i}|^2}{dz} = \frac{1}{\omega_2}\frac{d|E_{2k}|^2}{dz} = -\frac{1}{\omega_3}\frac{d|E_{3j}|^2}{dz} \qquad (6.14)$$

These are the Manley-Rowe relations. Recall that $|E|^2 \propto$ energy and that the energy of an electric field can be expressed as $N\hbar\omega$, some multiple of photons. It follows that the Manley-Rowe relations take on an alternate form:

$$\frac{dN_1}{dz} = \frac{dN_2}{dz} = -\frac{dN_3}{dz} \qquad (6.15)$$

Next, we can write the change in total energy w/ distance as:

$$\frac{dW_E}{dz} \simeq \frac{dN_1}{dz}\hbar\omega_1 + \frac{dN_2}{dz}\hbar\omega_2 + \frac{dN_3}{dz}\hbar\omega_3$$

Applying the Manley-Rowe relations and recalling that $\omega_3 = \omega_1 + \omega_2$:

$$\frac{dW_E}{dz} = \frac{dN_1}{dz}\left(\hbar\omega_1 + \hbar\omega_2 - \overset{\hbar\omega_1 + \hbar\omega_2}{\hbar\omega_3}\right) = 0 \qquad (6.16)$$

Thus we see that <u>energy must be conserved</u> in the $\chi^{(2)}$ medium!

6.4 Nonlinear χ and the Propagation Vector

Notice that if ϵ is complex, the refractive index is also likely to be complex. We define:

$$n \equiv n' + in'' \qquad (6.17)$$

Such that

$$n^2 = \epsilon = \epsilon' + i\epsilon''$$

Where ϵ is the complex permitivitty. Working through som algebra, we can show that

$$\epsilon' = n'^2 - n''^2 \quad \text{and} \quad \epsilon'' = 2n'n'' \qquad (6.18)$$

How do we interpret the complex refractive index?
It leads to <u>attenuation</u>:

$$E(z) = E_0 \underbrace{e^{-n''\frac{\omega}{c}z}}_{\text{attenuation}} e^{in'\frac{\omega}{c}z}$$

It is important to distinguish attenuation from absorption. As we saw previously, fields can decay due to $\chi^{(2)}$ interactions w/o any energy actually being lost from the system.

We will define an attenuation constant

$$\alpha \equiv \frac{2n''\omega}{c} = \text{attenuation coeff} \qquad (6.19)$$

Recall that the power absorbed is given by $P_{abs} = -\frac{\epsilon_0}{2}\omega\chi''(\omega)|E(\omega)|^2$ and that $\epsilon = 1+\chi$ thus $\epsilon'' = \chi'' = 2n'n''$ per (6.18). It is apparent that we <u>need both a non-zero n' and n'' to get absorption.</u> Attenuation w/o absorption can happen if n is pure imaginary.

This is almost the case for some low-loss metals like silver where $n'' \simeq 0$ leading to a negative ϵ'. In such metals, $\epsilon'' \simeq 0 \rightarrow$ we say there is <u>strong reactive attenuation</u> w/ attenuation coefficient $\alpha = n''\omega/c$.

Lesson: Distinguish between reactive attenuation and absorption.

Next we consider a few assorted Effects:

Intensity-dependent refractive index

Consider what happens when a monochromatic wave passes through a $\chi^{(3)}$ media:

$$P = \epsilon_0 \left\{ \chi^{(1)} E + \chi^{(3)} E E^* E \right\} = \epsilon_0 \left\{ \chi^{(1)} E + \chi^{(3)} |E|^2 E \right\}$$

We thus see that the permittivity of the material is given by:

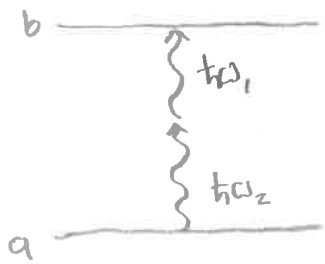
$$\epsilon = \epsilon_0 \left\{ 1 + \chi^{(1)} E + \chi^{(3)} |E|^2 E \right\}$$

The wave thus modifies the permittivity of the material,

$$\Delta \epsilon' = \mathrm{Re}\left\{ \epsilon_0 \chi^{(3)} |E|^2 \right\} \quad ; \quad \Delta \epsilon'' = \mathrm{Im}\left\{ \epsilon_0 \chi^{(3)} |E|^2 \right\} \qquad (6.20)$$

leading to a modification of the refractive index.

Two-Photon Absorption



As the name implies, two photon absorption requires the presence of 2 photons. Earlier, we listed that two-photon absorption results from the term:

$$\mathrm{Im}\left\{ \chi^{(3)}(-\omega_1, \omega_1, -\omega_2, \omega_2) \right\}$$

Applying equation (6.19), the attenuation coefficient (which in this case is an absorption / loss coefficient) is:

$$\alpha_{2ph}(\omega_1) = \frac{\omega_1}{n' c} \mathrm{Im}\left\{ \chi^{(3)} \right\} |E(\omega_2)|^2 \qquad (6.21)$$

where we have used the fact that $n'' = \dfrac{\epsilon''}{2n'}$.

We may compare this to single photon (ie normal) absorption:

$$\alpha_{1ph}(\omega_1) = \frac{\omega_1}{n'c} \, \mathrm{Im}\{\chi^{(1)}\} \qquad (6.22)$$

Most of the time these coefficients are negative leading to attenuation, however in some processes, they may be positive leading to exponential gain.

Detailed Balancing

Normally calculating susceptibilities and hence attenuation coefficients requires quantum mechanics, which can get pretty difficult. Instead, we look for a short cut. In turns out that we can link absorption to spontaneous emission using a fairly simple classical theory.

In thermal equilibrium, there is always black-body radiation. Since this radiation can be absorbed, it must be balanced by an equal emission of radiation, which we know to result from spontaneous emission.

To treat this situation, we will introduce the idea of "<u>absorption cross-section</u>" which relates the absorption coeff to the density of aborbing atoms/molecules/etc:

$$\alpha \equiv \sigma N \quad ; \quad \sigma \equiv \text{absorption cross-section} \qquad (6.23)$$

Next we introdue Brightness $B(\nu, T)$:

$$B(\nu, T) \equiv \frac{8\pi n^2 \nu^2 \Delta\nu}{c^2} \frac{1}{e^{h\nu/kT} - 1} \qquad (6.24)$$

Note: the units of brightness can be worked out to be

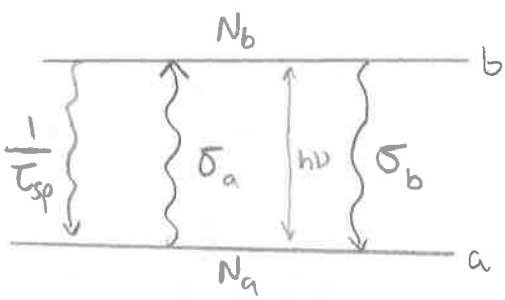
$$[B] = \text{Photons/area per unit bandwidth}$$
$$\cancel{\text{per unit time}}\ (?)$$
$$\text{per } 4\pi \text{ steradians}$$

And can be interpreted as the convential meaning of Brightness.

We can use the brightness to express the volumetric spontaneous emission rate:

$$B\sigma_a N_a - B\sigma_b N_b = \frac{N_b}{\tau_{sp}} \qquad (6.25)$$

where σ_a is the cross-section for absorption, σ_b is the cross-section for stimulated emission and τ_{sp} is the spontaneous emission lifetime. N_a & N_b correspond to the populations of two levels depicted below



(F6.1)

Substituting (6.24) for B in (6.25) and rearranging terms:

$$\frac{8\pi n^2 \nu^2 \Delta\nu}{c^2}\sigma_a\left(1 - \frac{\sigma_b}{\sigma_a}\frac{N_b}{N_a}\right) = \frac{N_b}{\tau_{sp} N_a}\left(e^{h\nu/kT} - 1\right) \qquad (6.26)$$

Recall that for a two level system $\frac{N_b}{N_a} = e^{-h\nu/kT}$ (in equilibrium)

Thus (6.26) becomes:

$$\frac{8\pi n^2 \nu^2 \Delta\nu}{c^2} \sigma_a \left(1 - \frac{\sigma_b}{\sigma_a} e^{-h\nu/kT}\right) = \frac{1}{\tau_{sp}}\left(1 - e^{-h\nu/kT}\right)$$

Notice that the two sides of this equation can only be equal if $\sigma_b = \sigma_a \neq 0$. Spontaneous emission must therefore exist!

Next, notice that the net absorption can be expressed as:

$$\alpha_{net} = \sigma_a N_a - \sigma_b N_b = \sigma_a (N_a - N_b) \qquad (6.27)$$

$$= \frac{c^2}{\tau_{sp} 8\pi n^2 \nu^2 \Delta\nu}$$

Notice that if $N_a > N_b$, $\alpha_{net} > 0$ and there is absorption. If $N_b > N_a$, however, $\alpha < 0$ leading to gain. This situation where $N_b > N_a$ is called a <u>Population inversion.</u>

Stimulated Raman Effect

(Coupled Wave Description)

We begin our discussion w/ the polarizability γ. that the polarization is given by:

$$P = \epsilon_0 \chi E = Np$$

Where p is the average dipole moment. The dipole

P, meanwhile is related to the electric field by the polarizability:

$$P = \epsilon_0 \gamma E$$

Thus the polarization is:

$$P = \epsilon_0 \chi E = N \epsilon_0 \gamma E \qquad (6.28)$$

From this it follows that

$$\epsilon_0 \chi = \epsilon_0 N \gamma \Rightarrow \epsilon_r = 1 + N\gamma \qquad (6.29)$$

We can use this this to write the electric field energy as a function of the polarizability:

$$U = \frac{1}{2} \epsilon_0 (1 + N\gamma) E^2$$

Now it turns out that that the polarizability γ is somewhat dependent on the molecular distortion distance Q:

$$\gamma \simeq \gamma_0 + \frac{d\gamma}{dQ} Q + \dots$$

We can now rewrite the energy in terms of this expansion:

$$U = \frac{1}{2} \epsilon_0 \left[1 + N\left(\gamma_0 + \frac{d\gamma}{dQ} Q + \dots \right) \right] E^2 \qquad (6.30)$$

Next, recall that the spatial derivative of an energy is a force, ie

$$\text{Force} = -\frac{dU}{dx}$$

In this case differentiating U w/ respect to Q represents force felt by the molecules in the material. doing so yields:

$$\text{Force} = -\frac{dU}{dQ} = -\frac{1}{2}\epsilon_0 N \frac{d\gamma}{dQ} E^2 = -\frac{1}{2}\epsilon_0 N \gamma' E^2 \qquad (6.31)$$

Consider, now, the situation where a single molecule is vibrating at some frequency ω_0. It would not be unreasonable to assume that the molecule follows our usual harmonic oscillator equations of motion:

$$\ddot{Q} + \frac{\dot{Q}}{\tau} + \omega_0^2 Q = \text{Force}/m$$

We have already computed the force in (6.31). Assuming that Q has harmonic time dependence, we can write a closed form expression:

$$Q \simeq \frac{\frac{1}{2}\epsilon_0 \gamma' |E|^2}{(\omega_0^2 - \omega^2) + i\omega/\tau} \qquad (6.32)$$

The vibration of the molecule can thus become significant when the frequency of the electric field (which is exciting the oscillation is close to ω_0.

Let us consider an incident wave composed of frequencies ω_1 and ω_2:

$$E = \frac{1}{2}E_1 e^{i\omega_1 t} + \frac{1}{2}E_2 e^{i\omega_2 t} + \text{c.c.}$$

Notice that there will be a term in E^2

$$E^2 = \frac{2}{4} E_2 E_1^* e^{i(\omega_2 - \omega_1)t} + \text{other terms} \qquad (6.33)$$

$\omega_2 - \omega_1$ can act as a driving force: for large oscillations if $\omega_2 - \omega_1$ is close to ω_0. Substituting for E^2 in (6.32) yields:

$$Q = \frac{(\epsilon_0 \gamma'/4m) E_2 E_1^* e^{i(\omega_2 - \omega_1)}}{\omega_0^2 - (\omega_2 - \omega_1)^2 + i\frac{(\omega_2 - \omega_1)}{\tau}} \qquad (6.33)$$

Recall that the polarization in (6.28) is a function of γ and thus a function of Q. Per equation (6.33), Q depends on E thus γ must contribute to a nonlinear polarization. It is easy to see that this nonlinear polarization has the form:

$$P^{NL} = \epsilon_0 N \gamma' Q E \qquad (6.34)$$

For whatever reason (not explained in the notes), we will consider a slightly different polarization:

$$P(\omega_1) = \epsilon_0 \gamma' Q^* E(\omega_2)$$

$$= \epsilon_0 N \gamma' \frac{(\epsilon_0 \gamma'/4m) E_2^* E_1 E_2 e^{i(\omega_1 - \cancel{\omega_2} + \cancel{\omega_2})t}}{\omega_0^2 - (\omega_2 - \omega_1)^2 - i(\omega_2 - \omega_1)/\tau}$$

Thus

$$P(\omega_1) = \frac{(\epsilon_0^2 N \gamma'^2/4m)|E_2|^2}{\omega_0^2 - (\omega_2 - \omega_1)^2 - i(\omega_2 - \omega_1)/\tau} E(\omega_1) \qquad (6.35)$$

Notice that the prefactor multiplying $E(\omega_1)$ is related to a nonlinear susceptibility:

$$P(\omega_1) = \epsilon_0 \chi^{NL}_{Raman} |E_2|^2 E_1 \qquad (6.36)$$

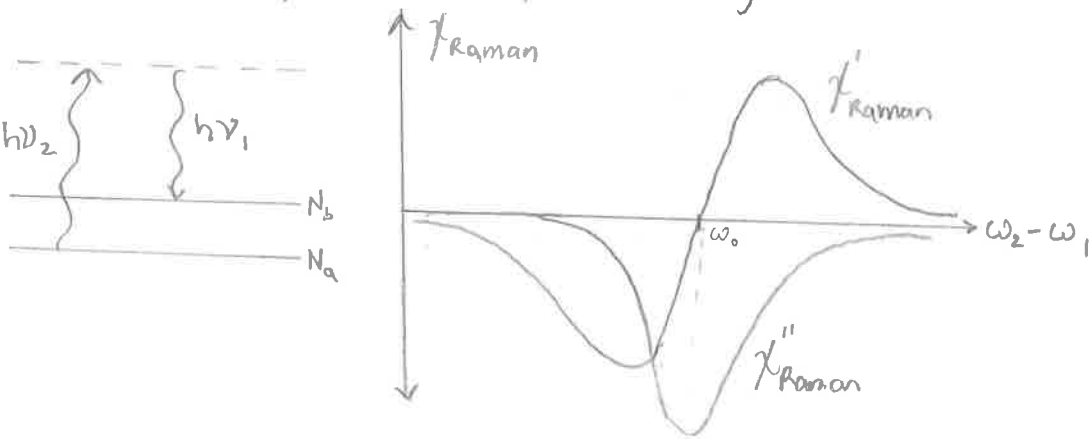
This nonlinear susceptibility corresponds to the <u>stimulated Raman effect</u>. To understand the effect, it is instructive to compute the real and imaginary parts of $\chi^{NL}_{Raman} \doteq \chi'_{Raman} + i\chi''_{Raman} = \chi^{(3)}(-\omega_1, \omega_2, -\omega_2, \omega_1)$:

⚠ It is unclear how these equations were obtained from χ^{NL} ...

$$\chi'_{Raman} = \frac{(\epsilon_0 N \gamma'^2/16m\omega_0)(\omega_0 - \omega_2 + \omega_1)}{(\omega_0 - \omega_2 + \omega_1)^2 + 1/4\Gamma^2} \qquad (6.37)$$

$$\chi''_{Raman} = \frac{-(\epsilon_0 N \gamma'^2/16m\omega_0)(1/2\Gamma)}{(\omega_0 - \omega_2 + \omega_1)^2 + 1/4\Gamma^2}$$

Notice that there is a negative sign in front of χ''_{Raman}, which resulted from the assumption that $\omega_2 > \omega_1$. Graphically, χ^{NL}_{Raman} resembles the linear harmonic oscillator χ except χ'' is negative:



Because $\chi''_{Raman} < 0$, we have <u>Raman Gain</u> at the lower frequency ω_1.

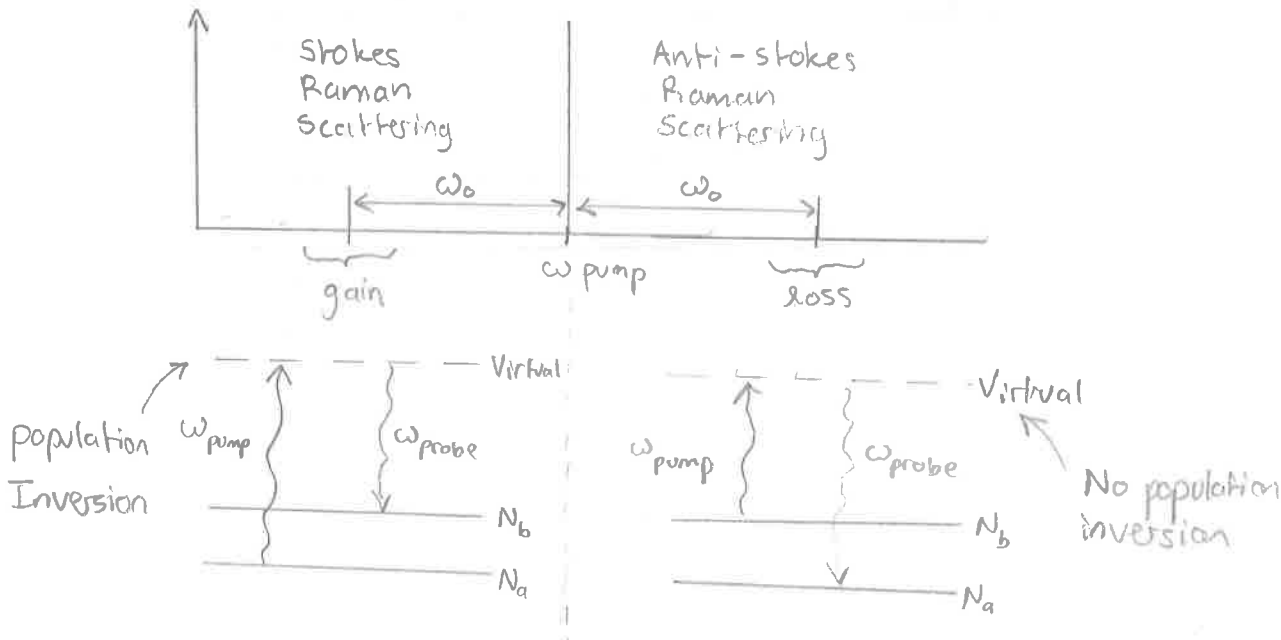
If instead we were to pump at the lower frequency ω_1 such that the polarization is

$$P(\omega_2) = \frac{(\epsilon_0 N \gamma'^2/4m)|E_1|^2}{\omega_0^2 - (\omega_2 - \omega_1)^2 - i\frac{(\omega_2 - \omega_1)}{\Gamma}} E_2 \qquad (6.38)$$

This is now changes sign

We will get a positive χ''_{Raman} and thus the probe frequency will experience loss.

The result of this is that a pump wave will generally produce gain on the lower frequency side and attenuation on the higher frequency side:



Notice that we can interpret Stokes Raman Scattering as a population inversion generated at a "virtual" level. In the case of anti-stokes Raman scattering, this population inversion is not present. In general there is no gain on the high frequency side.

In the case of Stokes Raman scattering, we can write down a gain coefficient:

$$\alpha_{Raman} = \frac{\omega_1}{n'c}\chi''_{Raman}|E_2|^2 = \text{Raman Gain} \qquad (6.39)$$

Which gives the growth of the field intensity of E_1

$$\frac{dI_1}{dz} = -\alpha_{Raman} I_1 \Rightarrow I_1 = I_{1,0}\, e^{\alpha_R z}$$

Next, given that we have a pump frequency ω_2 and a probe frequency ω_1 such that $\omega_2 - \omega_1 = \omega_0$ of the material, there are additional χ^{NL} terms corresponding to different mixtures of ω_1 and ω_2. In particular, there will be a process that generates an $\omega_3 = 2\omega_2 - \omega_1$. This process has a polarization of the form:

$$P(\omega_3 = 2\omega_2 - \omega_1) = \chi^{(3)}(-2\omega_2 + \omega_1, \omega_2, \omega_2, -\omega_1) E_2^2 E_1^* e^{i(2\omega_2 - \omega_1)t}$$

Including the spatial dependence:

$$P(\omega_3) = \chi^{(3)} E_2^2 E_1^* e^{i\omega_3} e^{i(2\bar{k}_2 - \bar{k}_1)\cdot\bar{r}}$$

As we have done previously w/ 2nd harmonic generation, we can plug this into Maxwell's Equations and apply the slowly varying amplitude approximation:

$$\frac{dE_3}{dz} = \frac{i}{\sqrt{\epsilon_3}} \frac{\omega_3}{2c} \chi^{(3)} E_2^2 E_1^* e^{i(2\bar{k}_2 - \bar{k}_1 - \bar{k}_3)\cdot\bar{r}} \qquad (6.40)$$

As with 2nd harmonic generation, we get a phase mismatch:

$$\Delta k \equiv 2k_2 - k_1 - k_3 = (2n_2 - n_1 - n_3)\frac{\omega}{c} \qquad (6.41)$$

For the process to be efficient, we want to find a way to achieve phase matching. There are two ways of doing this: (1) select the right pump frequencies for the given material or (2) inject the two pump beams such that they form a small angle w/ one another.

To figure out which frequencies to use, let's consider the taylor expansion of n_1 and n_3 about ω_2:

$$n(\omega) \simeq n(\omega_2) + \left.\frac{dn}{d\omega}\right|_{\omega_2}(\omega-\omega_2) + \frac{1}{2}\left.\frac{d^2n}{d\omega^2}\right|_{\omega_2}(\omega-\omega_2)^2 + \dots$$

$$\Rightarrow n(\omega_1) \simeq n(\omega_2) + \left.\frac{dn}{d\omega}\right|_{\omega_2}(\omega_1-\omega_2) + \frac{1}{2}\frac{d^2n}{d\omega^2}(\omega_1-\omega_2)^2 + \dots$$

$$n(\omega_3) \simeq n(\omega_2) + \left.\frac{dn}{d\omega}\right|_{\omega_2}(\omega_3-\omega_2) + \frac{1}{2}\frac{d^2n}{d\omega^2}(\omega_1-\omega_2)^2 + \dots$$

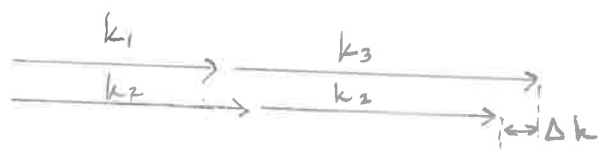
Substituting these results into (6.41)

$$2n_2 - n_1 - n_3 = -\left.\frac{dn}{d\omega}\right|_{\omega_2}\cancelto{0}{(\omega_1+\omega_3-2\omega_2)} - \frac{5}{2}\left.\frac{d^2n}{d\omega^2}\right|_{\omega_2}(\omega_1-\omega_2)^2 + \dots$$

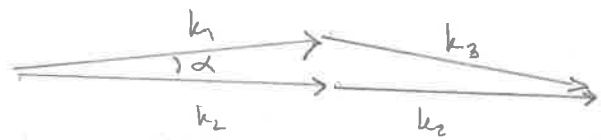
In order to get phase matching, $\Delta k = 0$. To 2nd order, this is possible given that

$$\left.\frac{d^2n}{d\omega^2}\right|_{\omega_2}(\omega_1-\omega_2)^2 = 0 \Rightarrow \left.\frac{d^2n}{d\omega^2}\right|_{\omega_2} = 0 \qquad (6.42)$$

Thus if we choose ω_2 correctly for the medium, phase matching is possible. Notice that this requirement happens to be the same requirement for dispersionless propagation As discussed in section 3 since $\frac{d^2n}{d\omega^2} = \frac{d^2(\omega n)}{d\omega^2}$.
If we operate above this inflexion point, we get a phase-mismatch:



In practice, this phase mismatch is easily accomodated by injecting the pump beams at an angle:



Here α denotes the real-space angle between the pump beams.

7. Interaction of Radiation With A Two Level System

Here, we will consider a simple quantum system consisting of two energy levels. The most general wavefunction for this system is a linear combination of the wavefunction of each energy level:

$$\psi = c_1 \psi_1 + c_2 \psi_2 \qquad (7.1)$$

The probability of measuring the wavefunction ψ is given by:

$$\psi \psi^* = |c_1|^2 |\psi_1|^2 + |c_2|^2 |\psi_2|^2 + c_1^* c_2 \psi_1^* \psi_2 + c_1 c_2^* \psi_1 \psi_2^* \qquad (7.2)$$

In general we should expect these terms to integrate up to 1. Notice that the 1st two terms correspond to the probabilities of finding ψ is ψ_1 or ψ_2 while the second two terms correspond to wave interference. If ψ_1 & ψ_2 are orthogonal, then these two terms will be zero when integrated across all space.

An alternative way of representing the wavefunction of a two level system is the density operator:

$$\hat{\rho} = \begin{pmatrix} |c_1|^2 & c_1^* c_2 \\ c_1 c_2^* & |c_2|^2 \end{pmatrix} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \qquad (7.3)$$

If the interference terms, are orthogonal the off-diagonal terms go to zero

$$\hat{\rho} \rightarrow \begin{pmatrix} |c_1|^2 & 0 \\ 0 & |c_2|^2 \end{pmatrix}$$

Given an operator $\hat{P}$, its expectation can be found using the trace operator & density matrix:

$$\langle \hat{P} \rangle = \text{trace}\{\hat{\rho}\hat{P}\} \qquad (7.4)$$

For our two level system, the Hamiltonian will take the form:

Quadrupole

$$\hat{H} = \hat{H}_0 + \hat{p}\cdot\hat{E} + \hat{\mu}\cdot\hat{B} \; \left(+ \hat{Q}\nabla\hat{E} + \dots\right) \qquad (7.5)$$

Mutipole expansion

We seek to understand how our two level system will evolve in time. We will therefore need to compute $d\rho/dt$. This is given by the Heisenberg picture:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] \qquad (7.6)$$

Since we have chosen to work with a density matrix, it is also convenient to express the Hamiltonian as a matrix. We can accomplish this using a clever application of identity operators:

$$\hat{\mathcal{H}} = \hat{I}\hat{\mathcal{H}}\hat{I} = \sum_i \sum_j |i\rangle\langle i|\hat{\mathcal{H}}|j\rangle\langle j|$$

~~where $|i\rangle$ and $|j\rangle$ are the set of eigenvectors of $\hat{\mathcal{H}}$.~~

From this, we see that the $\mathcal{H}_{ij}$ element of the matrix representation of the Hamiltonian is given by $\langle i|\hat{\mathcal{H}}|j\rangle$.

For the two level system, we will consider a Hamiltonian which includes the electric dipole term only:

Energy of 1st level

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{p}\hat{E} \longrightarrow \begin{pmatrix} E_1 & p_{21}E \\ p_{12}E & E_2 \end{pmatrix} \qquad (7.7)$$

Energy of 2nd level

Combining (7.6) and (7.7) yields system of equations for $d\rho/dt$:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}\begin{pmatrix} \hbar\omega_1 & p_{21}E \\ p_{12}E & \hbar\omega_2 \end{pmatrix}\begin{pmatrix} \rho_{11} & \rho_{21} \\ \rho_{12} & \rho_{22} \end{pmatrix} - \text{revese order} \qquad (7.8)$$

Here we have chosen to write the energies of each level in terms of a frequency ω_i.

In the following analysis, we will consider how each element of $\hat{\rho}$ will evolve in time. First consider the ρ_{21} element:

$$\frac{d\rho_{21}}{dt} = -i\omega_0\rho_{21} + i\frac{p_{12}}{\hbar}E(t)(\rho_{11}-\rho_{22}) \qquad (7.9)$$

The remaining elements fall out in a similar way. For example, consider $\dot{\rho}_{22}$:

$$\frac{d\rho_{22}}{dt} = -\frac{i}{\hbar} P_{12} E \left(\rho_{21} - \rho_{21}^*\right) \qquad (7.10)$$

$\dot{\rho}_{11}$ takes on a similar form. It is straightforward to find the difference $\dot{\rho}_{11} - \dot{\rho}_{22}$, which we can interpret as the rate at which the difference in populations of level 1 and level 2 change:

$$\frac{d}{dt}\left(\rho_{11} - \rho_{22}\right) = 2i \frac{P_{12}}{\hbar} E(t) \left(\rho_{21} - \rho_{21}^*\right) \qquad (7.11)$$

The $\dot{\rho}_{21}$ and $\dot{\rho}_{11} - \dot{\rho}_{22}$ terms will be important for understanding the two level system. Before continuing, we need to tweak our density matrix. In reality, due to interaction with the environment, or what have you, the off diagonal terms of $\hat{\rho}$ will decay to zero. We can manually insert this behavior into $\hat{\rho}$:

$$\hat{\rho} \longrightarrow \begin{pmatrix} |c_1|^2 & c_2^* c_1 e^{-t/T_2} \\ c_1 c_2^* e^{-t/T_2} & |c_2|^2 \end{pmatrix} \qquad (7.12)$$

Here T_2 is called simply the "T_2 Time" and is the characteristic time of decay of the off-diagonal elements.

Furthermore, in reality we expect the populations ρ_{22} and ρ_{11} to move towards equilibrium. As is such, the ratio of the two should follow the Boltzmann distribution:

$$\left.\frac{\rho_{22}}{\rho_{11}}\right|_0 = e^{-\hbar\omega_0/kT} \qquad (7.13)$$

This process occurs in a characteristic time T_1. Applying these corrections manually to (7.9) and (7.11) yields two equations of interest:

$$\frac{d}{dt}(\rho_{11}-\rho_{22}) = 2\frac{i}{\hbar}P_{12}E(\rho_{21}-\rho_{21}^*) - \frac{(\rho_{11}-\rho_{22})-(\rho_{11}-\rho_{22})_0}{T_1} \leftarrow \text{energy loss}$$

$$\frac{d}{dt}\rho_{21} = -i\omega_0\rho_{21} + \frac{i}{\hbar}P_{12}E(\rho_{11}-\rho_{22}) - \frac{\rho_{21}}{T_2} \leftarrow \text{"de-phasing"} \qquad (7.14)$$

Next, we introduce a slowly varying amplitude $\sigma(t)$:

$$\rho_{21}(t) = \sigma_{21}(t)\,e^{-i\omega_0 t} \qquad (7.15)$$

The harmonic time depence helps simplify things. Substituting (7.15) into the two expressions in (7.14) and setting the time-derivatives to zero (steady state). allows us to solve for $\sigma_{21}(t)$:

$$\mathrm{Re}\{\sigma_{21}\} = \frac{\Omega_s T_2(\rho_{11}-\rho_{22})_0}{1+(\omega-\omega_0)^2T_2^2+4\Omega_s^2T_2T_1}$$

$$\mathrm{Re}\{\sigma_{21}\} = \frac{(\omega_0-\omega)T_2^2\Omega_s(\rho_{11}-\rho_{22})_0}{1+(\omega-\omega_0)^2T_2^2+4\Omega_s^2T_2T_1} \qquad (7.16)$$

similarly, we can solve for $(\rho_{11}-\rho_{22})$:

$$\rho_{11}-\rho_{22} = (\rho_{11}-\rho_{22})_0 \frac{1+(\omega-\omega_0)^2 T_2^2}{1+(\omega-\omega_0)^2 T_2 + 4\Omega_s^2 T_2 T_1} \quad (7.17)$$

In both expressions, Ω_s is the Rabi Frequency

$$\Omega_s \equiv \frac{P_{21} E_0}{2\hbar} \quad \text{where } E_0 \mid E = E_0 \cos\omega_0 t \quad (7.18)$$

Which can be interpretted as the rate of fluctuation of the occupation population between the two levels, and is a measure of the strength of the incident EM wave.

Notice that Equation (7.17) describes the relative probabilities of the two levels. Intuitively, we can multiply it by N, the number of two level systems, to get the total difference in populations of level 2 vs level 1 systems:

$$\Delta N = N(\rho_{11}-\rho_{22}) = \underbrace{N(\rho_{11}-\rho_{22})_0}_{\Delta N_0} \frac{1+(\omega-\omega_0)^2 T_2^2}{1+(\omega-\omega_0)^2 T_2 + 4\Omega_s T_2 T_1} \quad (7.19)$$

Next, although it's not necessarily obvious, the dipole moment is directly related to $\rho_{21}(t)$. In particular, the dipole moment can be written in terms of $\sigma(t)$:

$$P = P_{12}\, \sigma_{21}(t) e^{-i\omega_0 t} \quad (7.20)$$

We can thus obtain the polarization of a system of two level atoms by by multiplying the dipole moment by N.

Substituting (7.16) into (7.20) yields:

$E(t) = E_0 \cos\omega_0 t$

$$P = \frac{|P_{12}|^2 \Delta N_0 T_2}{\hbar}\left[\frac{1 + i(\omega_0 - \omega)T_2}{1 + (\omega-\omega_0)^2 T_2^2 + 4\Omega_s^2 T_2 T_1}\right] E_0 e^{-i\omega_0 t}$$

Notice that our polarization takes the form "something times Electric field". We can thus write down the complex susceptibility for our ensemble of two level systems:

$$\chi'(\omega) = \frac{|P_{12}|^2 T_2 \Delta N_0}{\epsilon_0 \hbar} \frac{(\omega_0 - \omega) T_2}{1 + (\omega-\omega_0)^2 T_2^2 + 4\Omega^2 T_2 T_1}$$

$$\chi''(\omega) = \frac{|P_{12}|^2 T_2 \Delta N_0}{\epsilon_0 \hbar} \frac{1}{1 + (\omega-\omega_0)^2 T_2^2 + 4\Omega_s^2 T_2 T_1} \qquad (7.21)$$

Recall that the Rabi frequency depends on the magnitude of the Electric field $\Omega_s \propto E_0$. Thus as the power of the incident wave increases, the susceptibility decreases. This is <u>saturation</u>.

On a final note, consider the real part of the susceptibility if we factor a T_2 out of the denominator:

$$\chi'(\omega) = \frac{|P_{12}|^2 T_2 \Delta N_0}{\epsilon_0 \hbar} \frac{1/T_2^2}{(\omega-\omega_0)^2 + 1/T_2^2 + 4\Omega_s T_1/T_2} \qquad (7.22)$$

This very closely resembles the harmonic oscillator model. A quantum mechanical treatement, however introduces an additional term into the denominator which accounts for the quantum mechanical oscillation between energy levels.

One final comment from the class notes which is rather confusing.

Apparently it turns out that when the condition

$$\frac{|P_{12}|^2 E_0 T_2 T_1}{\hbar^2} > 1 + (\omega - \omega_0)^2 T_2^2 \qquad (7.23)$$

is true, then absorption goes down, which is an example of absorption saturation. Absorption saturation is a $\chi^{(3)}$ process described by

$$\mathrm{Im}\{\chi^{(3)}(-\omega, \omega, -\omega, \omega)\} \qquad (7.24)$$

7.1 Magnetic Resonance

It turns out that the precession of a magnetic moment about a strong magnetic field is analogous to the two level system that we just described.

For a precessing magnetic moment, the Bloch Equations are given by (no damping included):

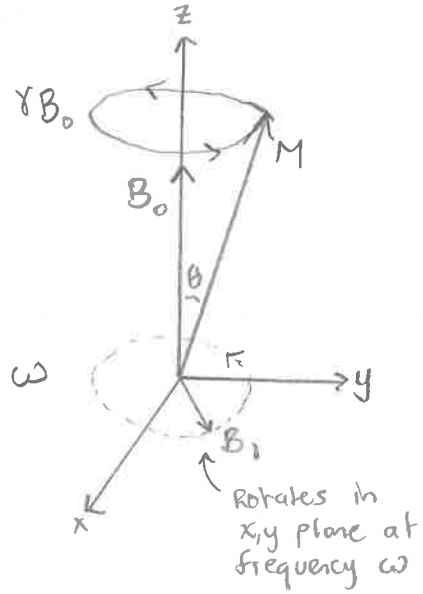
$$\frac{d\bar{M}}{dt} = \gamma \bar{M} \times \bar{B} \qquad (7.25)$$

Including damping:

$$\frac{dM_z}{dt} = \gamma(\bar{M} \times \bar{B})_z - \frac{M_z - M_0}{T_1}$$

$$\frac{dM_{x,y}}{dt} = \gamma(\bar{M} \times \bar{B})_{x,y} - \frac{M_{x,y}}{T_2} \qquad (7.26)$$

The graphical depiction of these equations as well as the equivalence between classical and quantum mechanical quantities is given below.



$$M_z \rightarrow |c_1|^2 - |c_2|^2 \qquad \gamma B_0 = \frac{E_1 - E_2}{\hbar}$$

$$M_x \rightarrow 2\,\mathrm{Re}\{c_2 c_1^*\} \qquad \gamma = |P_{12}|/\hbar$$

$$M_y \rightarrow 2\,\mathrm{Im}\{c_2 c_1^*\}$$

$$B_{1x} \rightarrow \mathrm{Re}\{E(t)\} \qquad (7.27)$$

$$B_{1y} \rightarrow \mathrm{Im}\{E(t)\}$$

If we solve the classical equations for magnetic precession and then insert the expressions in (7.27), we should end up with the solution to our two level system that we found in the previous section.

The solution to the classical problem is pretty interesting and has been very important to the field of MRI. As is such, we will consider some of the classical magnetic precession here.

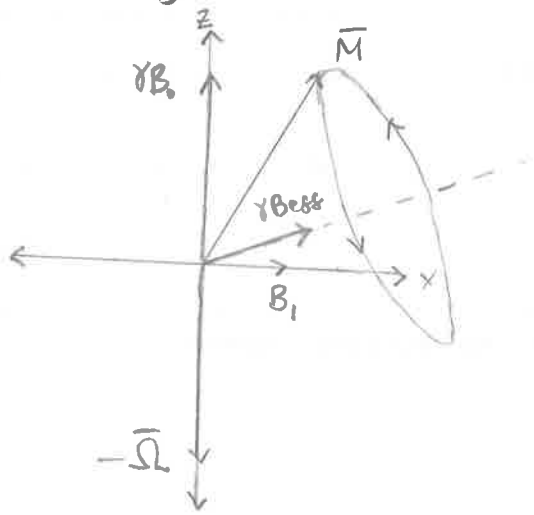
Our 1st step is to move into a rotating coordinate system which makes $\bar{B}_1$ appear stationary. dM/dt in this new frame is given by:

$$\left.\frac{d\bar{M}}{dt}\right|_{rot} = \left.\frac{d\bar{M}}{dt}\right|_{orig} + \bar{\Omega} \times \bar{M} \qquad (7.28)$$

Here, $\bar{\Omega} = \omega \hat{z}$ which describes the angular frequency of $\bar{B}_1$ as it rotates about $\hat{z}$. In the original frame, $d\bar{M}/dt$ is given by Equation (7.25), thus we can further simplify (7.28):

$$\left.\frac{d\bar{M}}{dt}\right|_{rot} = \bar{M}\times(\gamma\bar{B}-\overset{\omega\hat{z}}{\bar{\Omega}}) \qquad (7.29)$$

Graphically, the rotated coordinate system looks a bit different than the original:



(F 7.1)

At this point, we should pause and talk about why this rotating reference frame is necessary. In the case of a static applied magnetic field, a magnetic dipole will simply precess at a constant rate (excluding damping) for an indefinite period of time. However, we are interested in making an analogy to the two-level system which has time evolution between two separate states of the system. In order to achieve a similar effect w/ precessing magnetic dipoles, we must perturb the magnetic field in some predictable way. In practice, this is achieved by applying an oscillating radial magnetic field. This oscillating radial magnetic field can be expressed as two rotating magnetic fields in the xy plane (one clockwise, one counterclockwise). Thus in our problem, we technically have 2 magnetic fields: $B_0\hat{z}$ + CW field and $B_0\hat{z}$ + CCW field.

For our purposes, it turns out to be sufficient to consider only one of these rotating fields, which we choose to be the counter-clockwise rotating field which we have written as $\bar{B}_1$.

In the rotating reference frame depicted in (F7.1), the magnetic dipole precesses about an effective magnetic field (labeled as $\bar{B}_{eff}$). Looking at Equation (7.29) we see that the effective magnetic field is given by:

$$\bar{B}_{eff} = \bar{B} - \frac{\bar{\Omega}}{\gamma} \qquad (7.30)$$

Which allows us to rewrite (7.29) as

$$\left.\frac{dM}{dt}\right|_{rot} = \gamma \bar{M} \times \bar{B}_{eff} - \text{damping terms} \qquad (7.31)$$

Which places the system, once again, in a form to which we can relate our quantum mechanical 2 level system.

Recall that $\bar{\Omega} = \omega \hat{z}$ so $\bar{\Omega}/\gamma = \frac{\omega}{\gamma}\hat{z}$. If we drive the system at a frequency $\omega = \gamma B_0$, then the effective magnetic field will be equal to $\bar{B}_1$ and the magnetic dipole will precess around the x-axis at a frequency $\gamma |\bar{B}_1|$.

Recall that we made the equivalence between M_z and the difference in population of a two level system $|c_1|^2 - |c_2|^2$. If we start out with all of the

population in the 1st level, $|c_1|^2 = 1$ & $M_z = 1$, thus $\bar{M}$ points along the $\hat{z}$ direction. Then, as $\bar{M}$ precesses about $\hat{z}$, it will eventually point along the $-\hat{z}$ direction. This corresponds to a 2-level quantum system in which $|c_2|^2 = 1$ and $|c_1|^2 = 0$. All of the population is in the higher energy level implying that we have a <u>total population inversion</u>. As the magnetic dipole precesses, we oscillate between having a population inversion and not having one. This oscillation applies to any 2 level system of spin $\frac{1}{2}$ particles.

Notice that if we apply a pulsed $\bar{B}_1$ for a time equal to

$$\gamma |B_1| t_\pi = \pi \Rightarrow t_\pi = \frac{\pi}{\gamma |B_1|} \qquad (7.32)$$

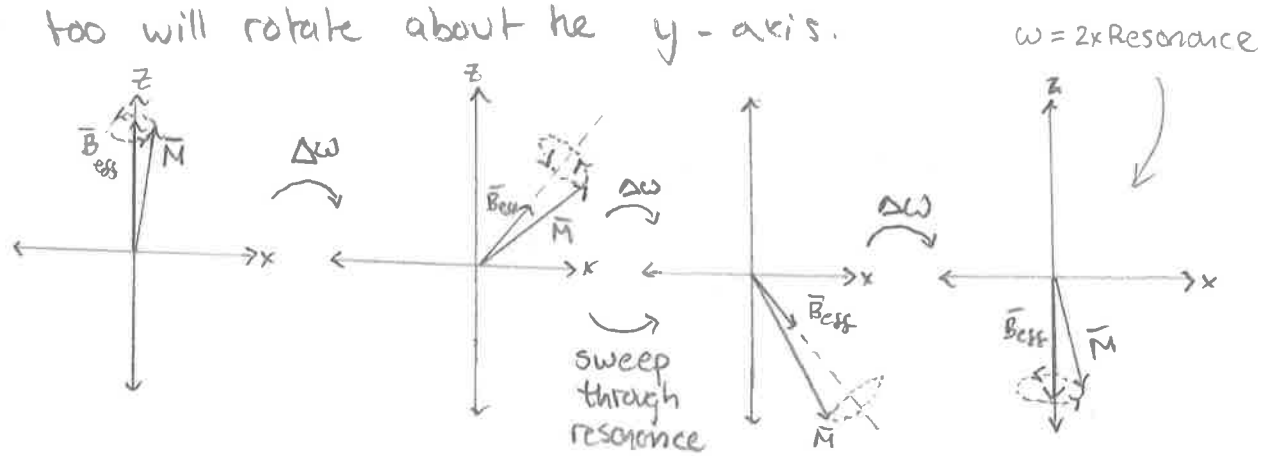
M will have precessed 180°. This is called a <u>π-pulse</u>. Similarly we can apply a pulse for a period of time $t_{\pi/2} = \frac{\pi}{2\gamma |B_1|}$ which results in rotating $\bar{M}$ by 90° and is called a <u>$\frac{\pi}{2}$ pulse</u>.

Adiabatic Fast Passage

The $\frac{\pi}{2}$-pulse is particularly useful for MRI – if we can make the magnetic precess perpendicular to the applied magnetic field, it will radiate RF waves.

The π pulse is not the only way to achieve a population inversion. Alternatively, we can slowly sweep the

Frequency of $\bar{B}_1$ as depicted below. As we do so, the $\bar{B}_{eff}$ will essentially rotate about the y axis. Because $\bar{M}$ always precesses about the $\bar{B}_{eff}$, it will follow it too will rotate about the y-axis.



If we sweep the frequency far enough, we can point $\bar{M}$ along the $-\hat{z}$ direction, thus preparing a population inversion.

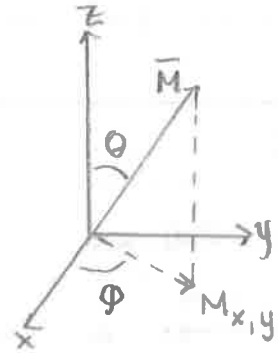
Completing the 2-Level Analogy

We have discussed how $\bar{M}$ pointing along the $+\hat{z}$ & $-\hat{z}$ directions is similar to a two level system. We can further clarify this relationship by writing a wavefunction which directly relates to the magnetic dipole system:

$$|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle = e^{i\Phi/2}\cos\frac{\theta}{2}|\psi_1\rangle + e^{-i\Phi/2}\sin\frac{\theta}{2}|\psi_2\rangle \quad (7.33)$$

Here, $|\psi_1\rangle$ and $|\psi_2\rangle$ correspond to the wave functions of energy level 1 and 2, respectively. Notice that as long as $|\psi\rangle$ is normalized and we have two degrees of freedom present when defining c_1 & c_2, we can choose them as we please without sacrificing generality.

Notice that if we define two angles θ & φ in the magnetic system such that



then we have formed a direct correspondence between the quantum and classical picture. We can see this because

$$|c_1|^2 - |c_2|^2 = \cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2} = \cos\theta = M_z$$

$$2c_2c_1^* = 2\cos\frac{\theta}{2}\sin\frac{\theta}{2}e^{-i\varphi} = \sin\theta e^{-i\varphi} = M_x - iM_y \qquad (7.34)$$

(where we assume $|\bar{M}| = 1$). Note that this implies that any 2d Hilbert space can be cast as a 3D vector and vice versa. Furthermore notice that θ and/or φ must make two full rotations in 3D space to return the 2d Hilbert space to its original value.

To take the correspondence further, we can rewrite the density matrix in terms of M_x, M_y, and M_z:

$$\rho = \frac{1}{2}\begin{pmatrix} 1 + M_z & M_x - iM_y \\ M_x + iM_y & 1 - M_z \end{pmatrix} \qquad (7.35)$$

Recall that in both systems, we are concerned w/ finding $d\rho/dt$ and $\frac{dM}{dt}$. Thus to complete the correspondence, we must define the Hamiltonian in terms of the classical magnetic system quantities. This turns out to be

$$\hat{H} \rightarrow \frac{\gamma}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \qquad (7.36)$$

Ideally, we want the hamiltonian to be written in terms of a magnetic moment $\hat{H} \sim -\bar{\mu}\cdot\bar{B}$. This is accomplished using pauli spin matrices:

$$\hat{H} = -\frac{\gamma}{2}\underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\mu_z} B_z - \frac{\gamma}{2}\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\mu_x} B_x - \frac{\gamma}{2}\underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\mu_y} B_y$$

7.2 Merging the 2-level System and the Multi-Oscillator Model

Our analysis of the two level system yielded a result that was similar to the harmonic-oscillator model but included additional phenomena such as saturation. Now we would like to explicitly draw a connection between the multi-oscillator model discussed in section 4 and the two level system.

Our starting point is Equation (4.12) which we recall here in a slightly different form for reasons that will soon become apparant:

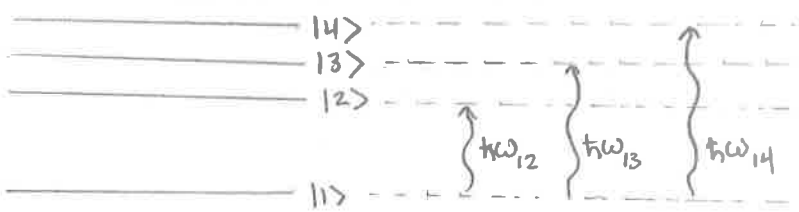
$$\chi(\omega) = \sum_i \chi_i(\omega) = \sum_i \frac{Nq^2/m\epsilon_0 \times S_i}{(\omega_i - \omega)^2 - i\frac{\omega}{\tau}}$$

Taking the imaginary part and assuming $\omega \simeq \omega_i$ (Note: it seems *very* incorrect to do this for all terms in the sum) yields

$$\chi''_{cl}(\omega) = \sum_i \chi''_i \simeq \sum_i \frac{(Nq^2/m\epsilon_0)(1/4\omega_i\tau)}{(\omega_i - \omega)^2 + \left(\frac{1}{2\tau}\right)^2} S_i \qquad (7.37)$$

Where the subscript cl stands for "Classical".

Recall that in our two level system, we considered only a single set of levels and hence a single resonce. We are not, however limited to a single set of levels – We can easily extend our model to include transitions between multiple sets of levels (this is actually kind of questionable). For example we might have



So long as each pair of levels (|1> + |2>), (|1> + |3>), (|1> + |4>), etc does not interact with the other pairs of levels, we may freely extend our model to accomodate these new resonances.

Modifying Equation (7.21) to include the multiple resonances gives

$$\underset{\text{"Quantum mechanical"}}{\chi''_{QM}(\omega)} = \sum_i \chi_i^{QM}(\omega) = \sum_i \frac{|P_{12}|^2 \Delta N}{\epsilon_0 \hbar} \frac{1/T_2}{(\omega_i - \omega)^2 + \frac{1}{T_2}}$$

Notice that we have neglected the saturation term in the denominator. This because saturation is a non linear effect not included in the multi-oscillator model. If we assume a weak incident field, this term can be neglected and the two can be compared.

As will become evident soon, it is convenient to integrate out the frequency dependence before directly comparing them. We thus seek to evaluate

$$\int_{-\infty}^{\infty} \sum_i \omega_i \chi_i'' \, d\omega = \sum_i \int_{-\infty}^{\infty} \omega_i \chi_i''(\omega) d\omega \qquad (7.38)$$

Consider first (7.38) using our classical expression

$$\sum_i \int_{-\infty}^{\infty} \omega_i \chi_i^{''cl} d\omega = \frac{Nq^2}{m\epsilon_0} \sum_i \int_{-\infty}^{\infty} d\omega \frac{1/4\tau}{(\omega_i - \omega)^2 + 1/4\tau^2} S_i$$

$$= \frac{Nq^2}{m\epsilon_0} \sum_i \pi S_i = \frac{\pi N q^2}{2 m \epsilon_0} \qquad (7.39)$$

Here we use the face that $\sum S_i = 1$ as discussed in Section 4. Next consider the Quantum mechanical χ'' in (7.38):

$$\sum_i \int_{-\infty}^{\infty} \omega_i \chi_i^{''QM} d\omega = \sum_i \frac{\Delta N q^2 |\langle 1 | x | i \rangle|^2 \omega_i}{\epsilon_0 \hbar} \pi \qquad (7.40)$$

Here we have replaced $|p_{12}|^2$ w/ the explicit matrix element. In order to link the classical and Quantum pictures, we need to evaluate this matrix element.

(Note: At this point in the notes we introduce the canonical potential and assert the dipole approximation ie $\langle 1|qx\cdot E|2\rangle \approx \langle 1|\frac{q}{m}p\cdot A|2\rangle$. This however does not seem super important for the task at hand so we exclude it here).

To better understand the matrix element, we make use of the commutator identity

$$\left[[\hat{x},\hat{H}],\hat{x}\right] = \frac{\hbar^2}{m}\hat{I} \qquad (7.41)$$

It follows that the expectation is

$$\langle 1|[[\hat{x},\hat{H}],\hat{x}]|1\rangle = \frac{\hbar^2}{m} \qquad (7.42)$$

Next, recall that any any wavefunction can be expanded in terms of a complete basis $|i\rangle$. For example, $|1\rangle$ can be expanded such that:

$$|1\rangle = \hat{I}|1\rangle = \sum_i |i\rangle\langle i|1\rangle$$

Similarly, we can multiply any operator by $\hat{I} = \sum_i |i\rangle\langle i|$ without changing it.

Remember that we are trying to find some sort of expression for the matrix element $|\langle 1|x|i\rangle|^2$.

It is a straight forward process of expanding the commutator in (7.42) and inserting identity into each of the terms to show that (7.42) reduces to:

$$\langle 1|[[\hat{x},\hat{H}],\hat{x}|1\rangle = 2\sum_i (E_i - E_1)|\langle 1|\hat{x}|i\rangle|^2 \qquad (7.43)$$

Writing the energy difference $E_i - E_1$ as a frequency ω_i, ie $E_i - E_1 = \hbar\omega_i$, it follows that:

$$\sum_i \omega_i |\langle 1|\hat{x}|i\rangle|^2 = \frac{\hbar}{2m} \qquad (7.44)$$

Notice that this expression appears in (7.40). Substituting in $\hbar/2m$ to (7.40) yields:

$$\sum_i \int_{-\infty}^{\infty} \omega_i \chi_i^{QM} d\omega = \frac{\Delta N q^2}{2m\epsilon_0}\pi \qquad (7.45)$$

This is the exact same result as the classical case! knowing that the two expressions are true lets us relate the classical weights S_i to the Quantum mechanical matrix elements $|\langle 1|\hat{x}|i\rangle|^2$. Rewriting Equation (7.40) to match (7.39) gives

$$\frac{\pi\Delta N q^2}{2m\epsilon_0}\sum_i S_i = \frac{\pi\Delta N q^2}{2m\epsilon_0}\sum_i \frac{2m|\langle 1|\hat{x}|i\rangle|^2}{\hbar}\omega_i \qquad (7.46)$$

Thus we conclude that

$$S_i = \frac{2m|\langle 1|\hat{x}|i\rangle|^2}{\hbar}\omega_i \qquad (7.47)$$

8. Polaritons: The Coupled Mode Picture

As EM waves propogate through matter, they may interact to form a so called "Polariton." In this section, we will derive the characteristics of polaritons and the conditions which must be satisfied for a polariton to form.

We begin with the harmonic oscillator that we analyzed in detail in section 4. Recall

$$m\ddot{x} - \frac{m}{\tau}\dot{x} + m\omega_0^2 x = qE_0 e^{-i\omega t}$$

$$\Rightarrow \left[m(\omega_0^2 - \omega^2) - \frac{i\omega m}{\tau}\right] x_0 = qE_0$$

where we have noticed that x must have the form $x = x_0 e^{-i\omega t}$. Since the polarization is given by $P = qNx$ which we can use to write down the "Matter Equation":

$$\left[(\omega_0^2 - \omega^2) - \frac{i\omega}{\tau}\right] P = N\frac{q^2}{m} E_0 \qquad (8.1)$$

Notice that the harmonic oscillator responds at frequency ω_0 and no wavevector is present.

We can derive a similar Electro-magnetic equation. In fact, we already know it well - it's just the wave equation:

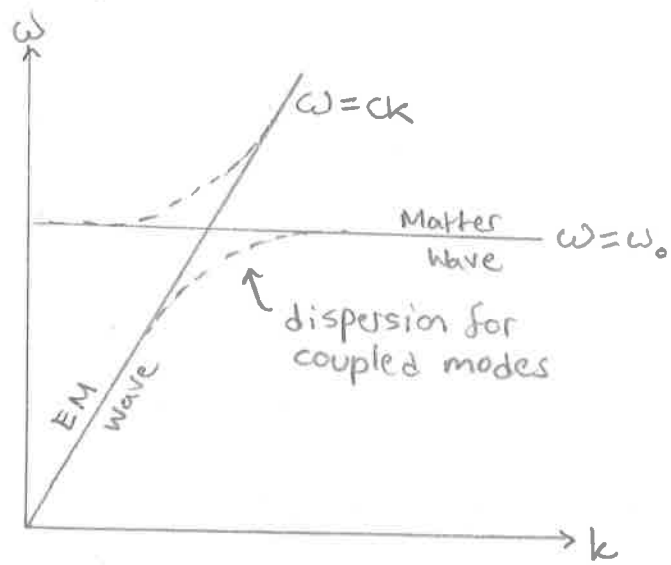
$$\left[-k^2 + \mu_0\epsilon_0\omega^2\right] E = -\mu_0\omega^2 P \qquad (8.2)$$

Putting (8.1) and (8.2) side by side demonstrates an obvious coupling between electromagnetic and matter waves:

$$\left[-k^2 + \mu_0 \epsilon_0 \omega^2\right] E = -\mu_0 \omega^2 P$$

$$\left[(\omega_0^2 - \omega^2) - \frac{i\omega}{\tau}\right] P = N \frac{q^2}{m} E \qquad (8.3)$$

Graphically, the dispersion relations corresponding to these two equations look like



(F8.1)

If we are successful in solving the coupled equations given in (8.3), we expect the dispersion relation to follow the dotted lines in (F8.1). Let's see how this pans out.

First rewrite the matter equation as the harmonic oscillator model that we explored in Section 4:

$$P = \frac{N \frac{q^2}{m} E}{(\omega_0^2 - \omega^2) - i\omega/\tau} = \epsilon_0 \chi E$$

Substituting the harmonic oscillator model into the wave equation yields

$$\left[-k^2 + \mu_0 \epsilon_0 \omega^2 \epsilon_r\right] E = 0 \qquad (8.4)$$

Where we ϵ_r is the relative permitivitty of the harmonic oscillator model:

$$\epsilon_r = 1 + \frac{N q^2 / m\epsilon_0}{(\omega_0^2 - \omega^2) - i\omega/\tau}$$

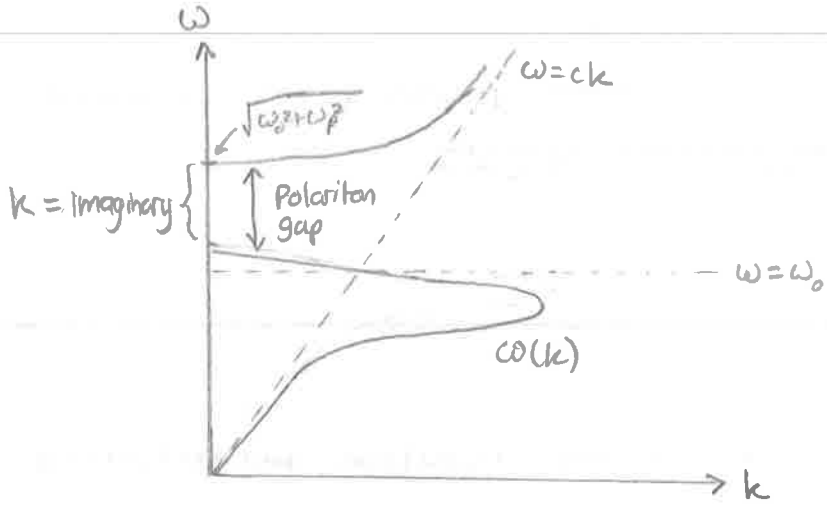
From Equation (8.4) we can find the new dispersion relation:

$$k = \frac{\omega}{c}\sqrt{\epsilon_r} = \frac{\omega}{c}\sqrt{1 + \frac{N q^2/m\epsilon_0}{(\omega_0^2 - \omega^2) - i\omega/\tau}} \qquad (8.5)$$

In the limit that the loss is small ($\omega/\tau \ll 1$) this simplifies to

$$k \simeq \frac{\omega}{c}\sqrt{\epsilon_r'} = \frac{\omega}{c}\sqrt{1 + \frac{N q^2/m\epsilon_0 \, (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2/\tau^2}} \qquad (8.6)$$

Graphically, this new dispersion relation looks very similar to what we expected:



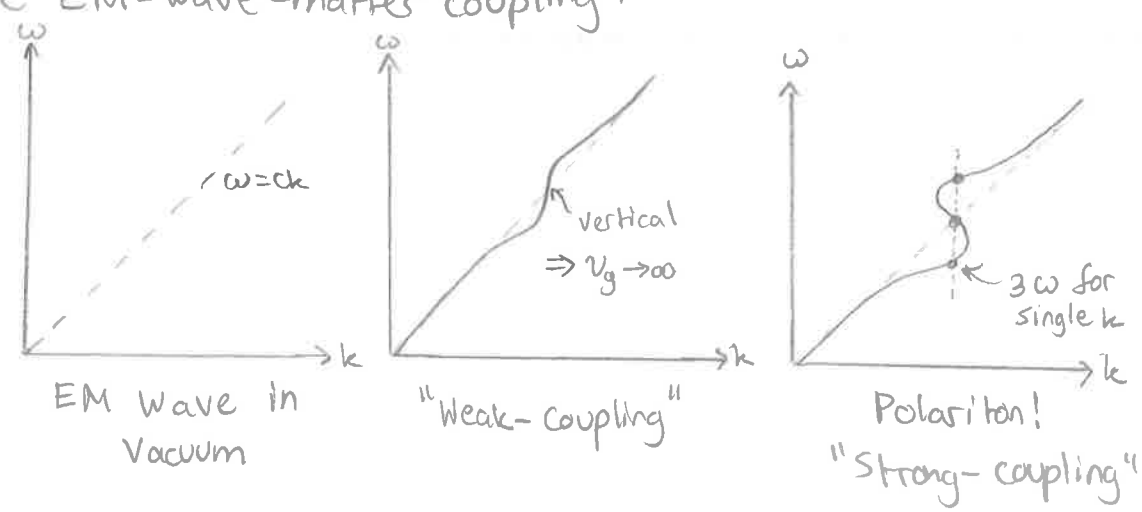
(F8.2)

Notice that if ϵ_r' goes negative (as it might near resonance in a metal) ϵ_r' becomes negative and k becomes imaginary. This results in the formation of a gap in the dispersion relation which we call the <u>polariton gap.</u> As a result, $\epsilon_r' < 0$ is sometimes used as a condition for the existence of polaritons.

A second condition for polaritons which is perhaps more commonly used is that inorder for a polariton to exist, a coupled mode must exist, that is 2 or more mode frequencies exist for a given wave vector k.

This second condition is easily demonstrated graphically by looking at the dispersion relation as we slowly turn on the EM-wave-matter coupling:

(F8.3)



Notice that just before multiple mode frequencies form for a single k, the slope of $\omega(k)$ goes to infinity. This provides us w/ a way to express the polariton condition mathematically:

$$\text{Polaritons occur when } \frac{1}{v_g} = \frac{dk}{d\omega} = 0 \qquad (8.7)$$

We can can write this condition in terms of known quantities. First, we differentiate (8.6):

$$\frac{dk}{d\omega} = \frac{\sqrt{\epsilon_r'}}{c} + \frac{1}{c\sqrt{\epsilon_r'}} \frac{\omega}{2} \frac{\partial \epsilon_r'}{\partial \omega} = 0$$

$$\Rightarrow \qquad \omega \frac{\partial}{\partial \omega} \epsilon_r'(\omega) = -2\epsilon_r' \qquad (8.8)$$

We have an expression for $\epsilon_r'(\omega)$ so we should be able to find a condition on ω for the existence of polaritons. Before continuing, however, notice that in figure 8.2, $\frac{dk}{d\omega}$ drops negative for strong coupling at resonance. A more complete condition for polariton existence would mus be:

$$\frac{dk}{d\omega} < 0 \Rightarrow \omega \frac{\partial}{\partial \omega} \epsilon_r'(\omega)\Big|_{\omega_0} < -2\epsilon_r'(\omega_0) \qquad (8.9)$$

If we now substitute ϵ_r' for equation (4.6), we find that the condition for polaritons is

$$\frac{Nq^2}{m\epsilon_0} > \frac{1}{\tau^2} \qquad \Rightarrow \qquad \omega_p^2 > \frac{1}{\tau^2} \qquad (8.10)$$

This means that in order to get polaritons, the density of oscillators N must be high and the line broadening mechanism $1/\tau$ must be weak. This usually requires a sharp single spectral line containing all the oscillator strength at the full molecular density.

Some examples of materials with and without polaritons are:

has Polaritons	No Polaritons
glass	GaAs (at low Temp)
silicon	CuCl
	die Molecules

9. Parametric Amplification

Parametric amplification results from a $\chi^{(2)}$ process. A pump beam at ω_3 enables the growth of a beam at ω_1 such that $\omega_3 = \omega_1 + \omega_2$. The name "parametric" arises from the fact that the pump beam is so strong that we treat it is a constant "parameter" of the system.

Since this is a $\chi^{(2)}$ process, our starting point will be the sum frequency generation equations derived in section 6. Assuming phase matching, we recall:

$$\frac{dE_1}{dz} = \frac{i}{\sqrt{\epsilon_1}} \frac{\omega_1}{2c} \chi^{(2)} E_3 E_1^*$$

$$\frac{dE_2^*}{dz} = -\frac{i}{\sqrt{\epsilon_2}} \frac{\omega_2}{2c} \chi^{(2)*} E_3^* E_2 \qquad (9.1)$$

$$\frac{dE_3}{dz} = \frac{i}{\sqrt{\epsilon_3}} \frac{\omega_3}{2c} \chi^{(2)} E_1 E_2$$

We regard E_3 as a constant parameter, thus the 1st two equations are coupled. Their are two equations & two unknowns, so we could in priciple solve for E_1 & E_2:

$$\begin{pmatrix} 0 & \frac{i}{\sqrt{\epsilon_1}} \frac{\omega_1}{2c} \chi^{(2)} E_3 \\ \frac{-i}{\sqrt{\epsilon_2}} \frac{\omega_2}{2c} \chi^{(2)*} E_3^* & 0 \end{pmatrix} \begin{pmatrix} E_1 \\ E_2^* \end{pmatrix} = \frac{d}{dz} \begin{pmatrix} E_1 \\ E_2^* \end{pmatrix} \qquad (9.2)$$

Let us assume for a moment that the spatial dependence of E_1 & E_2 is exponential growth or decay, ie $E_1 \to E_1 e^{gz}$. Substituting this in for E_1 & E_2^* yields an eigenvalue

problem of the form

$$\begin{pmatrix} 0 & \frac{i}{\sqrt{\epsilon_1}}\frac{\omega_1}{2c}\chi^{(2)}E_3 \\ \frac{-i}{\sqrt{\epsilon_2}}\frac{\omega_2}{2c}\chi^{(2)*}E_3^* & 0 \end{pmatrix}\begin{pmatrix} E_1 \\ E_2^* \end{pmatrix} = g\begin{pmatrix} E_1 \\ E_2^* \end{pmatrix} \qquad (9.3)$$

The eigenvalue g is easily determined by evaluating

$$\det\begin{pmatrix} -g & \frac{i}{\sqrt{\epsilon_2}}\frac{\omega_2}{2c}\chi^{(2)}E_3 \\ \frac{-i}{\sqrt{\epsilon_2}}\frac{\omega_2}{2c}\chi^{(2)*}E_3^* & g \end{pmatrix} = 0$$

which has the result

$$g = \pm\sqrt{\frac{\omega_1\omega_2}{4\sqrt{\epsilon_1\epsilon_2}}}\,\frac{|\chi^{(2)}E_3|}{c} \qquad (9.4)$$

If we choose the positive solution, g is a gain which depends on the incident field amplitude. This is very unusual. Choosing the negative sign results in loss. In fact both gain and loss are present. To see how this is possible, let us consider the case where $\omega_1 = \omega_2 = \omega$ and $\omega_3 = 2\omega$. Since the only pump is assumed to be at ω_3, then the 1st two Equations in (9.1) must be equivalent. This means that $E_1 = E_2$. The 1st equation in (9.1) can thus be rewritten more simply as:

$$\frac{dE_1}{dz} = \frac{\omega_1}{2\sqrt{\epsilon_1}c}\chi^{(2)}(iE_3)E_1^* \qquad (9.5)$$

Recall that the fields we actually deal with are real. Let us assume that our input beam is given by

$$\mathrm{Re}\{E_3 e^{i\omega_3 t}\} = E_3 \sin(\omega_3 t)$$

This is true if E_3 in equation is pure imaginary, ie $E_3 \to -iE_3$. Note that we are free to make this choice since we are putting ω_3 into the system, so we can choose its phase (ie whether it is a sin or cos). Making this modification to equation (9.5) produces

$$\frac{dE_1}{dz} = \frac{\omega_1}{2\sqrt{\epsilon_r}c}\chi^{(2)}|E_3|E_1^* . \qquad (9.6)$$

If we assume that $\chi^{(2)}$ is pure real (ie minimal loss), then we see that $dE_1/dz \propto E_1^*$. This implies that the real and imaginary parts of E_1 will Evolve differently.

We can quantify this difference by writing (9.6) as two equations: One for the real part of E_1 and one for the imaginary part of E_1. Substituting $E_1 = E_1' + iE_1''$ into (9.6) gives us these two equations (since the real & imaginary parts must be independently equal):

$$\frac{dE_1'}{dz} = \frac{\omega_1}{2\sqrt{\epsilon_r}c}\chi^{(2)}|E_3|E_1'$$

$$\frac{dE_2'}{dz} = -\frac{\omega_1}{2\sqrt{\epsilon_1}c}\chi^{(2)}|E_3|E_1'' \qquad (9.7)$$

From these equations, it is evident that the real part of E_1 will grow exponentially while the imaginary part will decay exponentially. Since $E_1(z,t)$ is a real quantity given by

$$E_1(z,t) = \mathrm{Re}\{E_1 e^{i\omega t}\} = E_1' \cos\omega t - E_1'' \sin\omega t$$

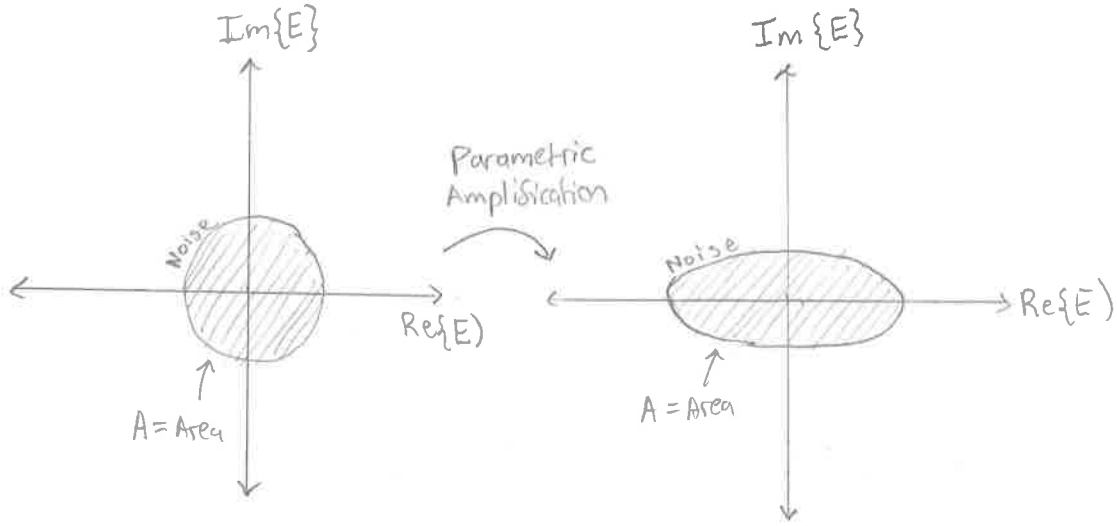
this means that the cosine component of $E_1(z,t)$ is amplified while the sine component is attenuated. Thus the phase of the generated wave is very important

From equations (9.7), it is also easy to see that the absorption/gain coefficient for the ω waves is

$$\alpha = \pm \frac{\omega}{\sqrt{\epsilon}\, c} \chi^{(2)} |E_3| \qquad (9.8)$$

It is interesting to note that parametric amplification did not require anything too fancy — just the right piece of $\chi^{(2)}$ material. If, however, we take that same $\chi^{(2)}$ material and put it in a cavity, we will get a <u>parametric oscillator</u>.

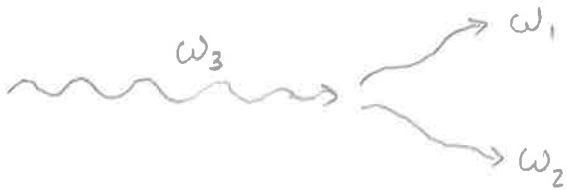
An important effect arises from parametric amplification. As w/ any system, noise is present during parametric amplification. However, as we have already seen, only the real part of the electric field is amplified, which applies to noise as well!



Under parametric amplification, Energy is transfered from the imaginary part to real part of E. This is called <u>quadrature "squeezing"</u>.

9.2 Parametric Down Conversion

In parametric amplification, we had a pump beam at ω_3 and a probe beam at ω_1 which was amplified. One might ask, however, what would happen if we only had the pump beam at ω_3 but no probe beam? The answer is that we could still get two lower energy photons due to <u>parametric down conversion</u> or <u>"spontaneous parametric decay"</u>.



This happens because vacuum fluctuations ω_1 are always present. The process is analogous to spontaneous

emission in matter.

Notice that energy and momentum of the photon at ω_3 must be conserved, thus the wave vectors of the outgoing photons must add to the $\bar{k}$ vector of the incoming photon (this would imply that the dispersive properties of the medium will select the exact values of ω_1 & ω_2).
Furthermore, angular momentum must be conserved. This necessitates that the outgoing photons be correlated, or in quantum mechanical terms, they must be entangled.

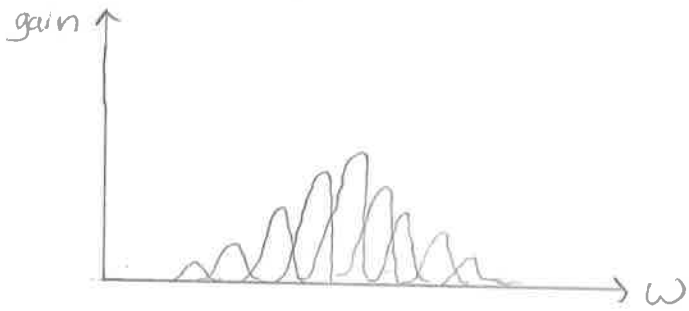
Furthermore, the net polarization of the system must remain constant. This means that if the photon at ω_3 is linearly polarized, then ω_1 and ω_2 must have left and right polarization.

Based on this, if $\omega_1 = \omega_2 = \omega$, then the two photons are effectively indistinguishable and resemble a singlet state of spin polarization.

10. Motional Narrowing

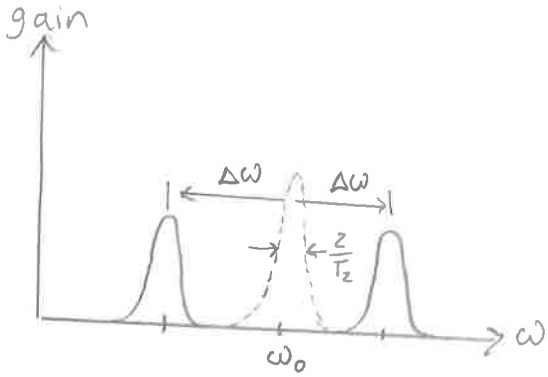
In this section, we very briefly discuss the process called motional narrowing which is very important in spectroscopy.

If we were to measure a gain spectrum, we might get something that looks like a collection of broadened spectral lines. For example.



(F10.1)

Naively, we might interpret this as each bump being a single line and calling this the Fourier transform of our signal. In reality, however, a single line can result from two separate lines which oscillate back and forth very rapidly: Consider



(F10.2)

As the spectrum jumps between $\omega_0 \pm \Delta\omega$ faster and faster, the resulting spectrum looks like the dotted line above which becomes sharper and sharper. w/ the rate of oscillation

This process of line narrowing is motional narrowing, and can occur as a result of multiple molecules inhomogenously situated or a single molecule jumping between inhomogenous situations.

When interpreting a sample spectrum, motional narrowing can be accounted for by modifying our definition of the Fourier transform:

$$\text{Time Evolution} \rightarrow \int f(\omega) e^{i\omega_0 t \pm i\Delta\omega t} e^{i\omega t} dt \qquad (10.1)$$

When measuring a spectrum, we would really like to figure out how long it takes for two oscillating lines to motionally narrow into a single line. Let us define τ to be the average time between jumps between $\omega_0 \pm \Delta\omega$ and assume that the actual time is random. In this case the average phase picked up is

$$\delta\varphi = \Delta\omega\tau \qquad (10.2)$$

Notice that the way the phase jumps around is identical to a random walk. If the frequency jumps N times, then the RMS phase that we pick up is:

$$\sqrt{\langle\varphi^2\rangle} = \sqrt{N(\delta\varphi)^2} = \sqrt{N}\,\delta\varphi \qquad (10.3)$$

After about 1 radian, we will largely have lost track of the phase and we will have a single spectral line. Thus

$$\sqrt{\langle\varphi^2\rangle} = 1 \Rightarrow \sqrt{N}\,\delta\varphi = 1 \Rightarrow N = \frac{1}{(\Delta\omega\tau)^2} \qquad (10.4)$$

The time T_2 to lose "phase memory" is $N\tau$ which

is simply given by

$$T_2 = \frac{1}{\Delta\omega^2 \tau} \qquad (10.5)$$

This T_2 time also gives the width of the single narrowed line, which is $2/T_2$. Note that this only applies to very short correlation times, i.e

$$\Delta\omega\tau \ll 1$$

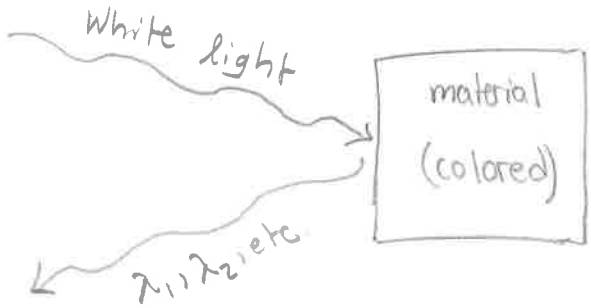
If, however $\Delta\omega\tau \gg 1$, then the two original inhomogenous broadened lines will be visible.

Finally, the most general case of Motional narrowing can be summed up by a heavily modified Fourier transform:

$$\mathcal{F}\{f(t)\} = \int_{-\infty}^{\infty} f(t)\, e^{-i\omega t}\, e^{i\int_{-\infty}^{t}\omega(t')dt'}\, dt$$

11. Opto-electronically Active Materials

A large number of materials are electronically active and have many interesting properties. To distinguish between opto-electronically "active" and "dead" materials, we say that "dead" materials are those where electronic excitations last for only a picosecond or less. For example most simple colored materials are opto-electronically "dead."



An opto-electronically active material, on the other hand, is one in which electronic excitations in a material last for a long time, i.e 1 nanosecond or longer. For example Na or Hg atoms in a gas have long lifetimes and produce yellow and UV glows, respectively.

Putting transition metals in rigid crystals such as Cr^{3+} in Al_2O_3 (ie Ruby) produces electronically active materials in which population inversions are possible, thanks to the d-electrons. Similarly, rare-earth metals in glass such as Nd^{3+} in glass can also be made to lase.

Of particular interest are materials which contain 3 and 4 level systems, as they are prime candidates for forming population inversions and hence are used in lasers. In the next few pages the many ways of forming population inversions are discussed.

Summary:

(1) 3-level Scheme (e.g. Ruby laser): Pump electrons up to energy levels which are sufficiently far from lower energy level such that they must relax radiatively $\Rightarrow$ long lifetime; Er^{3+} doped fiber

(2) 4-level scheme (e.g. N_d^{3+}:YAG lases) $\rightarrow$ similar to 3 level.

(3) CO_2 laser: Many

(4) Frank - Condon Effect: Die Molecules

(5) Excimer Laser

12. Population Inversions

Having seen some examples of sources of population inversions, it would be constructive to now provide some mathematical foundation.

To do so, we begin with the black body spectrum, which we call the "Brightness" B:

$$B = \frac{8\pi n^2 \nu^2}{c^2} d\nu \frac{1}{e^{h\nu/kT} - 1} \qquad (12.1)$$

We can solve this expression for $\frac{h\nu}{T}$ which we will soon relate to the entropy of the system:

$$\frac{h\nu}{T} = k \ln\left(1 + \frac{8\pi n^2 \nu^2}{c^2 B}\right) \qquad (12.2)$$

Next, from the second law of thermodynamics, we know $dU = TdS$. At least approximately, we can rewrite this as $\Delta U = T\Delta S$. For a single photon, $\Delta U = h\nu$, thus we can solve for the change in entropy due to the arrival of a single photon

$$\Delta S = \frac{h\nu}{T} \qquad (12.3)$$

Thus it follows from (12.2) that:

$$\Delta S = k \ln\left(1 + \frac{8\pi n^2 \nu^2}{c^2 B}\right) \qquad (12.4)$$

Next, the Free energy or chemical potential is given by $\mu = U - TS$ and represents the total amount of useful energy available. Rearranging terms we find

$$\mu = U - TS \Rightarrow S = \frac{U-\mu}{T} \Rightarrow \Delta S = \frac{h\nu - \mu}{T} \qquad (12.5)$$

where in the last step we wrote s for the case of a single photon. Equating this result to (12.4) and solving for B gives

$$B(\nu, \mu, T) = \frac{8\pi h^2 \nu^2}{c^2} \frac{1}{e^{\frac{h\nu - \mu}{kT}} - 1} \qquad (12.6)$$

Which is the blackbody spectrum in equilibrium including a correction for the non-zero chemical potential μ, which could arise from an applied voltage, an external light source, etc.

Next, we can define the Luminescence spectrum, which gives the actual spectrum of emitted light from an object. The Luminescent spectrum is given by:

$$L(\nu, \mu, T) = \alpha(\nu, \mu, T) B(\nu, \mu, T) \qquad (12.7)$$

Conceptually, the Luminescence spectrum should always be positive. Let us assume for a moment that the luminescence is known. We can then solve (12.7) for $\alpha(\nu, \mu, T)$:

$$\alpha(\nu, \mu, T) = \frac{L}{B} = \frac{c^2}{8\pi h^2 \nu^2} L \left\{ e^{\frac{h\nu - \mu}{kT}} - 1 \right\} \qquad (12.8)$$

We at last can express a condition for gain. Notice that if $h\nu < \mu$, $\alpha < 0$. A negative absorption is gain. Succinctly:

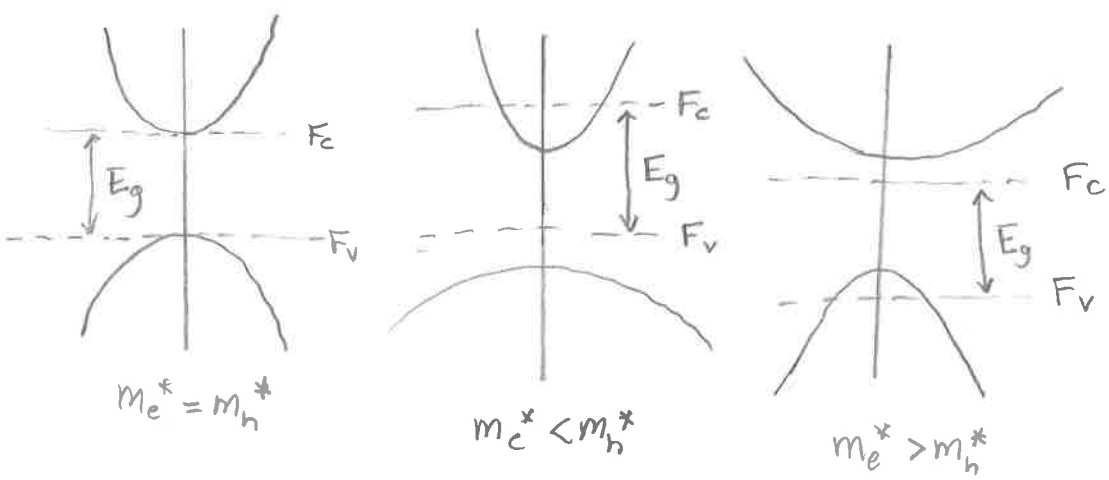
$$\text{For Gain: } h\nu < \mu \qquad (12.9)$$

This condition is known as the Bernard-Duraffourg condition. For semiconductors which have bandgaps, the condition may take an alternate form:

$$\text{For gain: } \quad E_g < \mu \qquad (12.10)$$

It is important to note that these gain conditions are equivalent to saying that we need low entropy in order to achieve gain (or a population inversion).

Notice that right at $E_g = \mu$, there is neither gain nor absorption. This is the so-called "Transparency condition." Depending on the hole and electron effective masses, the quasi fermi levels will position themselves differently:



The situation depicted in the center is the most common while the situation depicted on the left is ideal. Strain can be used to make the situation in the center more like the situation on the left.

13. Quantizing The Electromagnetic Field

As we already know well, the energy in the electromagnetic field is quantized in amounts $\hbar\omega$. This quantization can be derived mathematically, which is the goal of this section.

As is often the case, we begin our derivation w/ the harmonic oscillator. The Hamiltonian for a harmonic oscillator potential is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega_0^2}{2}\hat{x}^2 \qquad (13.1)$$

Our goal is to determine the eigenstates of this hamiltonian. To do so, we may cleverly define two new operators:

$$\hat{a}^+ = \sqrt{\frac{m\omega_0}{2\hbar}}\,\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p}$$

$$\hat{a} = \sqrt{\frac{m\omega_0}{2\hbar}}\,\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega_0}}\,\hat{p} \qquad (13.2)$$

We can choose to rewrite $\hat{x}$ & $\hat{p}$ in terms of these new operators:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega_0}}\,(\hat{a}^+ + \hat{a})$$

$$\hat{p} = i\sqrt{\frac{m\hbar\omega_0}{2}}\,(\hat{a}^+ - \hat{a}) \qquad (13.3)$$

Next substituting these expressions into Equation (13.1) yield the Hamiltonian in terms

$\hat{a}$ and $\hat{a}^+$:

$$\hat{H} = \frac{\hbar\omega_0}{2}\left(aa^+ + a^+a\right) \qquad (13.4)$$

We are not done yet. $\hat{H}$ can be further simplified by noticing that

$$[\hat{a}, \hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = \frac{i}{2\hbar}\left(-\hat{x}\hat{p} + \hat{p}\hat{x} - \hat{x}\hat{p} + \hat{p}\hat{x}\right)$$
$$= \frac{i}{\hbar}\left(\hat{p}\hat{x} - \hat{x}\hat{p}\right) = \frac{-i}{\hbar}[\hat{x}, \hat{p}]$$
$$= \frac{-i}{\hbar}(i\hbar) = 1$$

$$\Rightarrow \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1 \Rightarrow \hat{a}\hat{a}^+ = 1 + \hat{a}^+\hat{a} \qquad (13.5)$$

Here we have used the important relation that $[\hat{x}, \hat{p}] = i\hbar$. Substituting this result into (13.4) yields our final expression for the Harmonic oscillator Hamiltonian:

$$\hat{H} = \hbar\omega_0\left(\hat{N} + \frac{1}{2}\right) \qquad (13.6)$$

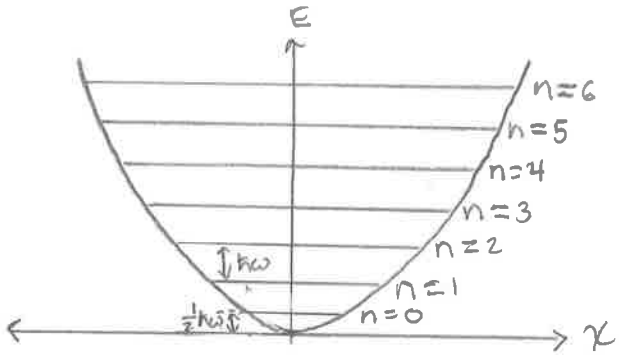
where $\hat{N} = \hat{a}^+\hat{a}$. We call $\hat{N}$ the "number operator" and define its eigenstates such that

$$\hat{N}|n\rangle = n|n\rangle \qquad (13.7)$$

These eigenstates are also eigenstates of the amiltonian:

$$\hat{H}|n\rangle = \hbar\omega_0\left(n + \frac{1}{2}\right)|n\rangle \qquad (13.8)$$

There are two important observations to make about the eigenvalues of the hamiltonian. First, the eigenenergies are evenly spaced by an amount $\hbar\omega_0$. Second, *there is no zero energy*. The minimum energy level is $\frac{1}{2}\hbar\omega_0$ corresponding to the state $|0\rangle$. This energy is known as the <u>zero point energy</u> and the state $|0\rangle$ is referred to as vacuum fluctuations.



It is worth pausing for a moment to talk a bit more about the meaning of the $\hat{a}^+$ and $\hat{a}$ operators. Their meaning is clarified using a little bit of simple math. Consider first the expression:

$$\begin{aligned}\hat{N}\hat{a}^+|n\rangle &= \hat{a}^+\hat{a}\hat{a}^+|n\rangle \\ &= \hat{a}^+(\hat{a}^+\hat{a}+1)|n\rangle \\ &= (n+1)\hat{a}^+|n\rangle \qquad (13.9)\end{aligned}$$

$\hat{a}^+|n\rangle$ is thus an eigenstate of $\hat{N}$ w/ eigenvalue $n+1$. This implies that

$$\hat{a}^+|n\rangle = |n+1\rangle \qquad (13.10)$$

The $\hat{a}^+$ thus raises $|n\rangle$ to $|n+1\rangle$. As is such, we call it the "<u>raising operator</u>".

In a similar fashion, we can show that

$$\hat{a}\,|n\rangle = |n-1\rangle \qquad (13.11)$$

We call $\hat{a}$ the "<u>Lowering Operator</u>". Next, consider the seamingly arbitrary expression $\langle n-1|\,\hat{N}\,|n-1\rangle$:

$$\langle n-1|\,\hat{a}^{+}\hat{a}\,|n-1\rangle = (n-1) \qquad (13.12)$$

Notice that if we were to plug in a value for $n \leq 0$, we would get a negative expectation value! But we know this to be impossible. This is resolved by requiring that $\hat{a}\,|0\rangle = 0$.

Second Quantization

While the harmonic oscillator appears rather simple, it nonetheless sets the foundation for some rather important results. In particular, we can draw an analogy between the harmonic oscillator and Maxwell's equations which will allow us to quantize the electromagnetic field.

We begin by considering an electric & magnetic field which are plane waves, e.g.

$$\bar{E} = E_0\, e^{ikx - i\omega t}$$

With this choice, Ampere's law & Faraday's Law can be rewritten as

$$-\bar{k}c \times \bar{E} = \frac{\partial \bar{B}}{\partial t} \qquad \text{(Faraday)}$$
$$\bar{k}c \times \bar{B} = \frac{\partial \bar{E}}{\partial t} \qquad \text{(Ampere)} \qquad (13.14)$$

Notice that these equations strongly resemble the mechanical equations of the harmonic oscillator:

$$\frac{p}{m} = \frac{dx}{dt} \qquad \text{(momentum)}$$
$$-kx = \frac{dp}{dt} \qquad \text{(Force)} \qquad (13.15)$$

Similarly, the Energy of an EM wave,

$$\frac{1}{2}\varepsilon_0 E^2 + \frac{1}{2\mu}B^2 = H \qquad (13.16)$$

is very similar to the energy of a harmonic oscillator;

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad (13.17)$$

Thus just as we quantized the harmonic oscillator, we can quantize the Electric & magnetic fields. We call this process Second Quantization.

As with x and p in the harmonic oscillator problem, $\bar{E}$ & B become operators which can be written in terms of raising & lowering operators:

$$\hat{\bar{E}} = -i\sqrt{\frac{\hbar\omega}{2V\varepsilon}}\left(\hat{a}^{+}e^{-ikr} - \hat{a}_k e^{ikr}\right)\hat{x}$$
$$\hat{\bar{B}} = \sqrt{\frac{\mu\hbar\omega}{2V}}\left(\hat{a}_k e^{-ikr} + \hat{a}_k e^{ikr}\right)\hat{y} \qquad (13.18)$$

As with $\hat{x}$ & $\hat{p}$, $\hat{E}$ & $\hat{B}$ don't commute, ie $[\hat{E}, \hat{B}] \neq 0$.

In the context of electromagnetic waves, $\hat{a}$ & $\hat{a}^+$ are annihilation and creation operators for photons. In the case of photons, the ground state has a finite energy equal to $\frac{1}{2}\hbar\omega$. The eigenfunctions corresponding to this eigen value are known as vacuum fluctuations. The 1st excited state has a single photon and thus an energy of $\frac{3}{2}\hbar\omega$. The 2nd state has energy $\frac{5}{2}\hbar\omega$, and each subsequent state has $\hbar\omega$ more energy.

Having an operator form for $\hat{E}$ & $\hat{B}$ and an eigenbasis to work with is theoretically very useful. For example, we can use this framework to calculate the spontaneous emission rate of a multi level system. Fermi's golden rule tells us:

$$R_{nk} = \frac{2\pi}{\hbar}\left|\langle 1,k|q\hat{x}\hat{E}|0,n\rangle\right|^2 \frac{dN}{dE}$$

where dN/dE is the density of states. Making the necessary substitutions, we can express R_{nk} in terms of the quantum mechanical raising and lowering operators

$$R_{nk} = \frac{2\pi}{\hbar}\left|\langle 1,k|\, q x(\hat{a}^+ - \hat{a})|0,n\rangle\right|^2 \frac{\hbar\omega}{2V\varepsilon} \times \frac{\omega^2 V}{c^3\pi^2}$$

which we could in priciple solve. In the next chapter, we will explore a variety of ways to express the spontaneous emission rate using both classical & quantum approaches.

14. Calculating Spontaneous Emission Rate

There are at least 4 different ways to calculate the spontaneous emission rate. Most of these methods are fairly tedious and require numerous assumptions that are not always easily motivated. As is such, we will present the result and then work through the derivation using one of the more insightful methods.

The spontaneous emission rate is given by:

$$R_{nk} = \frac{4}{3} \frac{|q x_{nk}|^2 n \omega^3}{4\pi \varepsilon_0 \hbar c^3} \qquad (14.1)$$

To derive this result, we will consider dipole fluctuations in a material. To begin, recall that the electric potential is given by:

$$\Phi(x) = \int \frac{\rho(x')\, d^3x'}{|x-x'|\, 4\pi\varepsilon_0} \qquad (14.2)$$

The vector potential, meanwhile, is given by

$$\bar{A}(x) = \int \frac{\mu_0 \bar{J}(x')\, d^3x'}{4\pi |x-x'|}\Bigg|_{\text{retarded}} \qquad (14.3)$$

Given the scalar and vector potentials, the electric field can be defined:

$$\bar{E} = -\bar{\nabla}\Phi - \frac{\partial \bar{A}}{\partial t} \qquad (14.4)$$

In the absence of charge, $\Phi = 0$ and we have:

$$\bar{E} = -\frac{\partial \bar{A}}{\partial t} \qquad (14.5)$$