4.3 Multi-photon transitions

We consider higher fields here.

4.3.1 Two-photon transitions using TDPT

If we look at E1-forbidden transitions (e.g., quadrupole) at large power enough, 2-photon higher-order term will dominate (if allowed).

We consider 2 different fields of frequency \( \omega_1 \) and \( \omega_2 \). We have the following possible diagrams:

\[ A: \]
\[ B: \]
\[ C: \]

If we make the approximation that the fields vary slowly across atoms/molecules, all exponentials of the form \( e^{\pm ik_\parallel t \Delta x} \) can be set to 1, and \( (A) \) can be ignored! (See textbook in Q. Optics for details.)
To evaluate (8) & (9), we use the following labels for the 3 levels that contribute:

\[ 15 \quad \text{final state} \]
\[ 1i \quad \text{intermediate} \]
\[ 1g \quad \text{ground state} \]

The result is thus the 2nd-order TDPT amplitude; neglecting the lifetimes \( \tau_{15}, \tau_{1i}, \tau_{1g} \), we get

\[
a_{1g}^{(2)}(t) = \frac{1}{(i\hbar)^2} \int dt_1 dt_2 \ e^{-iE_1(t-t_2)} \ V_1(t_2) e^{iE_1(t_2-t_1)} \ V_1(t_1) e^{-iE_1(t_1)}
\]

\[ t > t_2 > t_1 \]

where

\[
V_1(t_2) = eE_1 \langle i | \hat{E}_1 \cdot \hat{F} | g \rangle \left( \frac{e^{-i\omega_1 t_2} + e^{i\omega_1 t_2}}{2} \right)
\]

\[
V_2(t_2) = eE_2 \langle i | \hat{E}_2 \cdot \hat{F} | i \rangle \left( \frac{e^{-i\omega_2 t_2} + e^{i\omega_2 t_2}}{2} \right)
\]

The integral over \( t_1 \), neglecting counter-rotating terms containing \( (\omega_1 - \omega_g) + \omega_1 \) or \( (\omega_1 - \omega_g) + \omega_2 \), gives

\[
\int dt_1 = eE_1 \langle i | \hat{E}_1 \cdot \hat{F} | g \rangle \ e^{i(\omega_1 - \omega_g - \omega_1) t} \ \frac{1}{2i(\omega_1 - \omega_g - \omega_1)} - \text{term}
\]

\[ + \text{same for } E_2 \]

Integrating over \( t_2 \), again neglecting fast oscillating terms, gives \( a_{1g}^{(2)}(t) \) in terms of the matrix elements

\[
M_{1g}^{(1)} = \langle i | \hat{E}_1 \cdot \hat{F} | g \rangle \quad \text{and similarly for}
\]

\[
M_{1g}^{(2)} = \langle i | \hat{E}_2 \cdot \hat{F} | g \rangle \quad \text{for } g \rightarrow f
\]
\[ \alpha_{fg}(t) = \frac{e^2}{4\hbar^2} \left\{ \frac{E_1^2 M_{\xi f}^{(1)} M_{\xi g}^{(1)}}{(w_i - w_g - w_1)(w_i - w_g - 2w_1)} \right\} 
\]
\[ + \frac{E_2^2 M_{\xi f}^{(2)} M_{\xi g}^{(2)}}{(w_i - w_g - w_2)(w_i - w_g - 2w_2)} \]
\[ + \frac{E_2 E_1 M_{\xi f}^{(2)} M_{\xi g}^{(2)}}{(w_i - w_g - w_1)(w_i - w_g - w_1 - w_2)} \]
\[ + \frac{E_1 E_2 M_{\xi f}^{(2)} M_{\xi g}^{(2)}}{(w_i - w_g - w_2)(w_i - w_g - w_1 - w_2)} \right\} \]

Note: in principle, a sum over all \( \xi \) intermediate states is required, although only the states near resonance are really contributing.

The 1st 2 terms correspond to process (c) while terms 3 & 4 to process (b).

The relative importance of terms (a) ... (d) depends on the conditions such as \( w_1 \) & \( w_2 \). For example, if \( w_1 \) is chosen fairly close to \( i - g \) resonance, then the (c) terms dominate, so

\[ P_{fg}(t) = e^4 E_1^2 E_2^2 \left| \sum_i \frac{\langle \xi | \hat{E}_2 \hat{r} \hat{L}_i \rangle \langle \epsilon | \hat{E}_1 \hat{r} \hat{L}_g \rangle}{(w_i - w_g - w_1)(w_i - w_g - w_1 - w_2)} \right| \]

\[ \text{sum over all intermediate states = total } P_{fg}. \]
If we compare to the 1-photon result, we note:

1. \( P_{\text{fg} \to \text{I}_1 \text{I}_2} \propto E_1^2 E_2^2 \propto I_1 I_2 \) if \( \omega_1 = \omega_2 \) \( P_{\text{fg} \to \text{I}_1^2} \)

2. Same time dependence \( \Rightarrow \) same limits apply.

3. It suggest the excitation of a "virtual" state.
   Not to take literally though.

4. Extreme enhancement at resonance with the intermediate state \( \Rightarrow \) need to take its lifetime into account.

5. Selection rules: dictated by
   \[ \langle \text{I}_2^* | \text{I}_1 \rangle \text{ and } \langle \text{I}_1^* | \text{I}_2 \rangle \]
   \[ \Rightarrow \begin{cases} \Delta J = 0, \pm 1, \pm 2 \quad (L-S \text{ coupling}) \\ \Delta L = 0, \pm 1, \pm 2 \\ \Delta m_J = 0, \pm 1, \pm 2 \end{cases} \]
   For 1e^- atom, \( \Delta L = 0, \pm 2 \) (even parity)

6. The position of \( |\text{I}_1 \rangle \) can be anywhere (above or below \( |\text{g}\rangle \)):

\[ \begin{array}{c} |\text{I}_1 \rangle \quad \text{or} \quad |\text{g}\rangle \\
\end{array} \]
We return to

Approximate $P_{fg}$:

If large times, and assuming the example above is valid, i.e.

$$P_{fg}(t) = \frac{e^{4E_{1}E_{2}^{2}}}{4\pi^{4}} \left| \sum_{c} \frac{\langle \delta E_{2} \cdot F \rangle \langle c | E_{1} \cdot F | g \rangle \sin[(\omega_{c} - \omega_{g} - \omega_{1})/2]}{[\omega_{c} - \omega_{g}] - \omega_{1}]^{2}} \right|^{2}$$

$$\Rightarrow t \gg \frac{1}{\omega_{s} - \omega_{g} - (\omega_{1} + \omega_{2})}$$

Using $\lim_{t \to 0} \frac{1}{\pi t} \sin\left(\frac{t}{\pi}ight) = \delta(t)$, with $E = \frac{1}{2\omega_{s} - \omega_{g} - \omega_{1}}$ and $t = \frac{E}{2}$

$$P_{fg}(t) = \frac{e^{4E_{1}E_{2}^{2}}}{4\pi^{4}} \left| \sum_{c} \frac{\langle \delta E_{2} \cdot F \rangle \langle c | E_{1} \cdot F | g \rangle}{[\omega_{c} - \omega_{g}] - \omega_{1}]^{2}} \right|^{2} \frac{\pi}{2} \delta(\omega_{s} - \omega_{g} - \omega_{1})$$

This is an infinitely sharp resonance!

Note: we can now integrate easily now over $\omega$'s to get a rate.

Note: White light would require very large intensities to observe $2-\nu$ processes, and thus we are focusing on narrow-band sources instead.
Two-photon rate: (monochromatic light)

To determine the transition rate for realistic systems, we must include the lifetime of the upper state.

As before, we simply substitute:

\[
\frac{\sin[(\omega_g - \omega_1 - \omega_2)t/\hbar]}{(\omega_f - \omega_g - \omega_1 - \omega_2)} \rightarrow e^{-\gamma_f t/2} \left| \frac{\sin[(\omega_f - \omega_1 - \omega_2)t/\hbar]}{(\omega_f - \omega_g - \omega_1 - \omega_2)^2 + (\gamma_f/2)^2} \right|^2
\]

\[\Rightarrow \text{ in TDPST, the lineshape for monochromatic light is a lorentzian}\]

The rate is found by integrating over \( \omega_1 + \omega_2 = \omega_f \)

\[
R_{fg} \approx \left( \frac{\Omega_R^2}{\gamma_0} \right)^2 \gamma_f \frac{\hbar^4}{\hbar^4 + (\gamma_f/2)^2} \times \sum_i \frac{\langle 
abla (E_i - v_i) | i \rangle^2 \langle i | \nabla (E_i - v_i) | f \rangle^2}{(w_f - \omega_g - \omega_i)^2}
\]

\( \Omega_R \): effective two-photon Rabi frequency

\( S = \omega_1 + \omega_2 - (\omega_f - \omega_g) \): detuning

This result is valid for \( t >> \gamma_f \) and ignores counter-rotating terms and contributions to \( |i\rangle + |f\rangle \) from \( \omega_2 \).
Identifying
\[ \Omega_R(g \rightarrow i) = \frac{eE_1}{\hbar} \langle g | \mathbf{E}_1 \cdot \mathbf{n} | i \rangle \]
\[ \Omega_R(c \rightarrow s) = \frac{eE_2}{\hbar} \langle s | \mathbf{E}_2 \cdot \mathbf{n} | c \rangle \]
we can rewrite \( \Omega_R^{2 \nu} \) as

\[ \Omega_R^{2 \nu} = \sum_i \frac{\Omega_R(c \rightarrow s) \Omega_R(g \rightarrow i)}{2 \Delta_i} \]

\( \Delta_i = \omega_c - \omega_g - \omega_i \)

: intermediate-state detuning

So, the result for the rate looks like the 1-\( \nu \) case: apart from the resonant denominator, the extra factor of \( E^2 \), and the sum over states, all now included in \( \Omega_R^{2 \nu} \).

**Note:** Stimulated 2-\( \nu \) decay can take place, if one of the photons is emitted at frequency \( \omega_i \), the 2-\( \nu \) decay rate is

\[ \delta \omega_i = \frac{4e^4}{\hbar^2 c^6 \varepsilon_0^2} \omega_1^3 \omega_2^3 d\omega_1 \times \left| \sum_i M_{ci} M_{ig}^{(1)} + \sum_i M_{ci} M_{ig}^{(2)} \right|^2 \]

\[ \omega_s - \omega_i + \omega_2 \]

This must be integrated over \( \omega_i \), with \( \omega_1 \omega_2 = \omega_s - \omega_g \)

and averaged over the direction of propagation & polarization \( \hat{e}_1 \) and \( \hat{e}_2 \).

**Very slow:** \( T_{1/2} (2^3 S) = 2.4 \times 10^8 \) s

\( \approx 10 \) years.
4.3.2 Multiphoton Transitions using TDPT

We can generalize the previous treatment to N-photon

\[ |g\rangle \rightarrow |c\rangle \rightarrow |d\rangle \rightarrow |f\rangle \]

3-photon

e... For this example, the 3rd-order TDPT amplitude has several terms: the one near resonance (as illustrated left) has the form

\[ a^{(3)}_{fg} = \frac{\omega^3}{8\hbar^3} E_1^3 M_{cj}^{(1)} M_{dj}^{(1)} M_{fg}^{(1)} \left[ e^{i(\omega_f - \omega_g - 3\omega)t} - 4 \right] \]

\[ \frac{1}{(\omega_f - \omega_j - \omega)(\omega_j - \omega_g - 2\omega)(\omega_f - \omega_g - 3\omega)} \]

The square modulus, \( |a^{(3)}_{fg}|^2 \), gives a transition probability with the familiar \( 1\sin^2() \), but proportional to \( E^6 \Rightarrow I^{3/2} \).

In general, for N-photon processes, each new order comes in with an additional multiplicative factor of the form

\[ a^{(n)}_{fg} \sim Q^{(n)}_{fg} \left( \frac{E_1}{2\hbar} \right)^n M^{(n)} \rightarrow \text{dipole matrix element} \]

\[ \Delta \text{ intermediate state detuning} \]

The total amplitude involves a sum over \( (n-1) \) series of intermediate states (each infinite in number)

\[ \Rightarrow \text{an accurate calculation is formidable!} \]
Notes:

a) TDPT breakdown if saturation sets in.
   For example, \( I^n \) will change
   if near a resonance
   \[
   \frac{eE_1M}{2\hbar\Delta\omega} \sim 1 \quad \text{or, in a.u. with} \quad M \sim 1
   \]
   \[
   \Delta\omega \sim \frac{1}{4}
   \]
   \[
   \Rightarrow E_1 \sim \frac{1}{2} \approx 2 \times 10^9 \text{V}
   \]
   or \( I \approx \frac{1}{2} \) if \( E_1 = 5 \times 10^5 \text{V} \), fairly large!

b) Multiphoton Path frequency can be written as
   \[
   \frac{1}{2} |\omega_R^{(m)}| = \left( \frac{1}{2^m} \right) \frac{|\omega_{R1} - \omega_{R2} - \omega_{R3} - \ldots - \omega_{Rm}|}{\Delta_2 \Delta_3 \ldots \Delta_m}
   \]
   This must be summed over intermediate states as needed.
4.3.3 Other multiphoton processes

A - Raman scattering:

The levels are for a Raman process,
with
\[ \omega_1 - \omega_2 = \omega_3 - \omega_4 \]
Note: m-p possible as well.

This can be a stimulated or spontaneous process.

B - Stimulated Raman scattering (3-level)

Assume both \( \omega_1 \) & \( \omega_2 \) as monochromatic light. As before,

\[
a_{eg}(t) = \frac{e^2}{4\pi^2} \sum \left[ \frac{E_1 E_2 M_{ei} M_{eg}^{(1)}}{(\omega_1 - \omega_3 - \omega_4)} \left[ \frac{e^{i(\omega_1 + \omega_2 + \omega_3 - \omega_4) t}}{(\omega_1 - \omega_3 - \omega_4)} - 1 \right] \right] + \frac{E_1 E_2 M_{ei} M_{eg}^{(2)}}{(\omega_1 - \omega_3 + \omega_4)} \left[ \frac{e^{i(\omega_1 + \omega_2 + \omega_3 - \omega_4) t}}{(\omega_1 - \omega_3 + \omega_4)} - 1 \right] + \text{terms with } \omega_1 - \omega_4 \text{ or } \omega_2 - \omega_4 \text{ (c)+(d)}
\]

(b) can be important if \( 1c \) lies below \( 1g \), or if all states are very far from resonance

(c) \( (a) \) do not contribute in Raman scattering, although relevant to spontaneous emission, Rayleigh scattering, etc.
Note: near resonance, we can introduce lifetimes as usual with \( \omega - \omega \approx \delta / 2 \).

As before, the rate is found to be:

\[
R \text{ (sti. Raman)} = \left( \frac{\mathcal{J}_{\text{Raman}}}{2} \right)^2 \delta^2_f
\]

\[
\frac{(\omega_f - \omega_g - \omega_1 + \omega_2)^2 + (\delta_f / 2)^2}
\]

where \( \mathcal{J}_{\text{Raman}} = e^2 F_1^2 F_2^2 \left| \sum_{\ell} \frac{M_{\ell c} (\ell) M_{\ell g} (\ell)}{\omega_{\ell} - \omega_g} + \frac{M_{\ell c} (\ell) M_{\ell g} (\ell)}{\omega_{\ell} - \omega_g + \omega_2} \right|^2
\]

C - Spontaneous Raman scattering

Not here; covered in JJ class.

D - Other coherent processes

- STIRAP
- EIT
- ETC...

again in JJ class in Q. Optics