1. $\chi^{(3)}(\omega; \omega, \omega, -\omega)$ in Na vapor
With reference to the spectrum of $|\chi^{(3)}(3\omega; \omega, \omega, \omega)|$ in atomic sodium given in Boyd, page 150 (3rd ed.), sketch (neatly and clearly) what would you think might be the spectrum of $|n_2| \propto |\chi^{(3)}(\omega; \omega, \omega, -\omega)|$. Explain the primary differences between the two. (You may be only qualitative regarding the magnitude of the nonlinearity) (10 points)

2. Two-Photon Spectroscopy

In this problem we consider the nonlinear absorption spectroscopy of the fictional element $\text{Trilevelium}$ whose energy levels are shown below. In such an experiment, the transmission of a tunable high power laser is recorded as a function of the wavelength $\lambda$. As we all know, ignoring the linear absorption, the governing equation assuming two-photon absorption (TPA) is:

$$\frac{dI}{dz} = -\beta(\lambda) I^2$$

where $I$ is the irradiance, $\beta$ is the TPA coefficient, and $z$ denotes the depth along the sample.

(a) Write down the quantum mechanical expression for $\beta$ for this particular element. (5 points)

(b) Qualitatively, plot the transmission vs $\lambda$ and explain the mechanism and the resonance(s). (5 points)

Briefly compare your TPA spectrum with that of the linear absorption spectrum on the same sample and identify the differences and advantage(s). (5 points)

Note (as we derived in the class):

$\beta \propto \text{Im} \left\{ \chi^{(3)}(\omega; \omega, \omega, -\omega) \right\}$

Also use the identity:

$$\frac{1}{\Delta \omega} \to \Phi \left( \frac{1}{\Delta \omega} \right) + i\pi \delta(\Delta \omega)$$

Trilevelium with 1s ground state and 2s and 2p excited states.
3. **NLO susceptibilities: resonances and selection rules**

A fictional molecule has the following energy levels. Draw the spectrum (for $0 < \hbar \omega < 8 \text{ eV}$) for the (a) linear absorption coefficient $\alpha$, (b) two-photon absorption (TPA) coefficient $\beta$, (c) SHG: $|\chi^{(2)}(2\omega; \omega, \omega)|$ and (d) THG: $|\chi^{(3)}(3\omega; \omega, \omega, \omega)|$.

*Be quantitative in your x-axis. Assume a finite broadening in your drawings. Point out the resonances (diagrammatically) on your graph for each case and show the relative strengths if obvious. Note: no calculations needed for this problem either.*

![Energy level diagram](image)

- **E (eV)**
  - 7: $|4\rangle$, S-type
  - 3.4: $|3\rangle$, P-type
  - 2: $|2\rangle$, S-type
  - 0.0: $|1\rangle$, S-type (ground state)
Problem 4: $X^{(3)}$ in Na Vapors.

The transitions involved in $X^{(3)}(\omega, \omega, \omega, -\omega) \propto n_2$ are:

- Therefore, there are only one-photon and two-photon resonances.
- There is no three-photon ($3\omega$) resonance.
- The spectrum of $\text{[Na]}$ must therefore look like Fig. in Boyd (p. 143) without the $3\omega$ resonances!
Two-photon spectroscopy:

\[ |i\rangle \rightarrow |i\rangle \rightarrow |f\rangle \rightarrow |f\rangle \]

\[ 0.5 \text{ ev} \]

\[ 1.24 \text{ ev} \]

- TPA corresponds to the \( \text{Im} \{ X^{(3)} (\omega; \omega, \omega, -\omega) \} \) that involves the transition:

\[ i \rightarrow k \]

(only)

\[ |i\rangle = g \]

- Because of parity consideration (\( M_{ss} = 0 \) & \( M_{sp} \neq 0 \)),

\[ i = |p\rangle \]

\[ k = |p\rangle \]

\[ j = |2s\rangle \] (there is no other route permissible)

- Thus, two photon resonance corresponds to:

\[ |i\rangle \rightarrow |2s\rangle \] transitions \( \rightarrow \) where \( 2\omega = \frac{1.24}{\hbar} \)

\[ \Rightarrow \lambda^{(\text{Im})} = \frac{1.24}{2 \times \omega(\text{ev})} = 2 \text{ \mu m} \]

Part (b) T

\[ \lambda [\text{\mu m}] \]

\[ 2 \text{ \mu m} \]
Problem 2-(a)

As derived in the class,

\[ \beta = \frac{\omega}{\eta_0 c e_0} \text{Im} \left\{ \chi^{(3)}(\omega; \omega, \omega, -\omega) \right\} \]

where, \( \chi^{(3)} \) for TPA is (As discussed in previous page):

\[ \chi^{(3)} = \frac{N}{\hbar^3} \frac{M_{13} M_{32} M_{23} M_{33}}{(\omega_1 - \omega)(\omega_1 - \omega - \omega)(\omega_2 - \omega - \omega + \omega)} \quad ; \quad \omega_{ij} = \omega_{ij} + i\Gamma \]

Part (c)

For one-phonon (linear) absorption, IS \rightarrow P transition is allowed. (No population is in 2s at room temperature)

\[ \lambda = \frac{1.24}{E_{31}} = \frac{1.24}{1.74} \approx 0.71 \ \mu m \]

- Thus, two-photon spectroscopy allows us to probe IS \rightarrow 2s transition, while it's not allowed in the linear case!
Problem 3

\[ \alpha \]

\[ 1s \rightarrow 3p \]

\[ 1s \rightarrow 4s \]

\[ \beta \]

\[ \chi^{(3)} \]

\[ \chi^{(2)} = 0 \]

\[ |\chi^{(3)}| \]

\[ 2\omega \quad 3\omega \quad 4\omega \quad \omega \]

1s \rightarrow 4s \text{ larger, since it has a one-photon resonance enhancement.}