5.74 Introductory Quantum Mechanics II
Spring 2009

Nonlinear Spectroscopy Problems, Part 1
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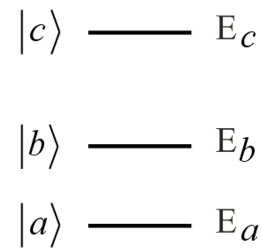
1. Nonlinear Response Function

In analogy to the derivation of the linear response function, derive the quantum form of the second-order (nonlinear) response function.

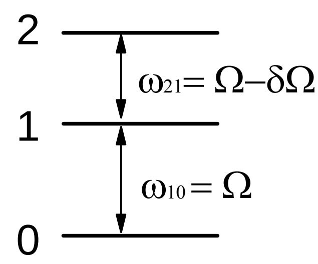
2. Second Order Response Functions

Draw the Feynman and ladder diagrams for the two correlation functions of the second order nonlinear response, Q_1 and Q_2, and write expressions for the phenomenological time-domain response functions of these systems and corresponding frequency-domain nonlinear susceptibility. Assume that you have a three level system for which the eigenstates of the system Hamiltonian are $|a\rangle$, $|b\rangle$, and $|c\rangle$, and also assume that $E_a < E_b < E_c$.

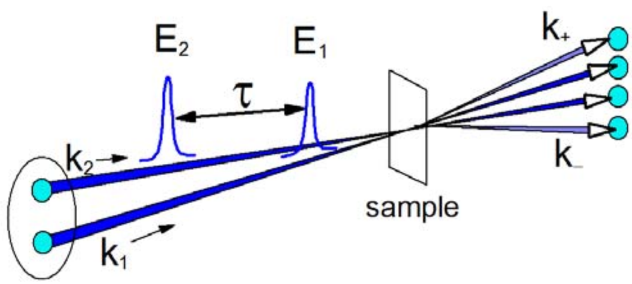


3. Nonlinear Experiments on an Anharmonic Vibration

Here we will consider two time-domain third-order nonlinear experiments on an anharmonic vibration. For high vibrational frequencies we will only occupy the ground state at equilibrium (ρ_{eq} = |0><0|), and the response can be represented by a three level system for the n=0, 1, and 2 vibrational states. For a weakly anharmonic oscillator, we will have only a very small shift between the fundamental transition frequency $\omega_{10} = \Omega$ and the n=1→2 transition, $\omega_{21}=\Omega-\delta\Omega$.



We want to describe the behavior of two experiments shown here. Two pulses, both with frequency ω resonant with the $\Delta n = \pm 1$ transitions ($\omega \approx \omega_{10} \approx \omega_{21}$) and separated by τ are crossed at a small angle, to generate two background free signals after the sample. The field E_1 incident along $\mathbf{k_1}$ preceeds the second pulse E_2 along $\mathbf{k_2}$. On a plane after the sample the two signals $\mathbf{k_+}$ and $\mathbf{k_-}$ are observed as equally spaced spots on either side of the transmitted beams. $\mathbf{k_+}$ lies next to the transmitted $\mathbf{k_1}$.



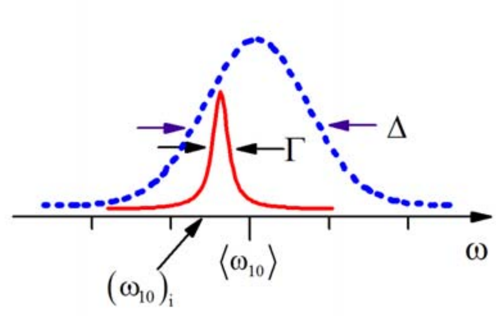
(a) Give the wavevector matching condition that leads to the signals radiated in the $\mathbf{k_+}$ and $\mathbf{k_-}$ directions. What is the frequency of each radiated signal?

(b) Draw all Feynmann and Ladder diagrams that contribute to the $\mathbf{k_+}$ and $\mathbf{k_-}$ signals, assuming that the system starts in the ground state.

(c) Write the correlation function corresponding to each diagram, assuming a phenomenological damping for propagation under H_0.

(d) Now let's look more carefully at the signal $\mathbf{k_-}$, for an inhomogeneously broadened system. Assume that the homogeneous damping of all coherences is $\Gamma=\Gamma_{10} = \Gamma_{21}$, and there are a Gaussian distribution of resonance frequencies

$$Z(\omega_{10}) = \exp\left(-\frac{\left(\omega_{10} - \langle\omega_{10}\rangle\right)^2}{2\Delta^2}\right)$$



Also, for each member of the ensemble, $(\omega_{21})_i = (\omega_{10})_i - \delta\Omega$.

The integrated signal observed by a photodetector as a function of the pulse separation τ is

$$S(\tau) \propto \int_0^\infty d\tau_3 \left|P^{(3)}(\tau, \tau_3)\right|^2 .$$

Assuming that the experiment is performed with delta function pulses, derive an analytical expression for *S(τ)*, and explain and interpret the features of this signal for the limits Δ>>Γ and Δ<<Γ. (To understand what you see it might help to plot $P^{(3)}$ as a function of τ_1 and τ_3.) You can assume $\omega \approx \Omega >> \delta\Omega > \Gamma$. Also from harmonic oscillator selection rules, we can say $\mu_{21} = \sqrt{2}\mu_{10}$.

Nonlinear Spectroscopy Problems, Part 2

Spring 2009

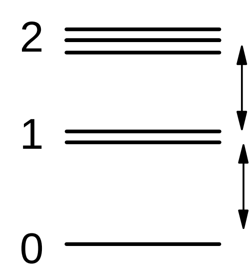
4. <u>2D Spectrum of Coupled Oscillators</u>

Calculate the 2D spectrum obtained from a third-order nonlinear experiment for a degenerate pair of coupled anharmonic vibrations. Imagine that you have two anharmonic oscillators described by the with vibrational levels in problem 3. For each oscillator, the transition energy for the v=0-1 transition is ε and the 1-2 transition is $\varepsilon - \Omega$. Then, these are coupled through a linear coupling of magnitude V: $V\left(a_1^\dagger a_2 + a_1 a_2^\dagger\right)$. Similar to before, we take $\Omega, V \ll \varepsilon$.

(a) Obtain the v=0,1,2 energy eigenvalues for the coupled oscillators. First explain why the matrix form of the Hamiltonian can be written as

$$H_0 = \begin{pmatrix} 0 & & & & & \\ & \varepsilon & V & & & \\ & V & \varepsilon & & & \\ & & & 2\varepsilon-\Omega & & \sqrt{2}V \\ & & & & 2\varepsilon-\Omega & \sqrt{2}V \\ & & & \sqrt{2}V & \sqrt{2}V & 2\varepsilon \end{pmatrix}.$$

Where the rows refer to the states $|0,0\rangle, |0,1\rangle, |1,0\rangle, |0,2\rangle, |2,0\rangle, |1,1\rangle$. The states refer to the quantum number for each oscillator, and the $|1,1\rangle$ state is the combination band in which one quantum of excitation is in each oscillator. Show how the states correspond to the bands shown to the right.



(b) Considering allowed resonances between the adjacent bands, draw the ladder diagrams that correspond to the R_2 and R_3 (rephasing) terms of the third-order nonlinear response. You can assume that only the following transitions (which change state by one quantum) are allowed: $\mu_{00,10}, \mu_{00,01}, \mu_{10,20}, \mu_{01,02}, \mu_{01,11}, \mu_{10,11}$. Also, you may assume that $\sqrt{2}\mu_{00,10} = \mu_{01,02}$, $\sqrt{2}\mu_{00,01} = \mu_{10,20}$, and $\mu_{01,11} = \mu_{10,11}$. Also write out the response obtained for each diagram setting τ_2=0.

(c) Fourier transform the responses in both the τ_1 and τ_3 variables, setting $\Gamma_{ij} \to 0$. This leads to each diagram contributing to a delta-function peak in a two dimensional spectrum plotted as a function of ω_1 and ω_3. Show where the peaks are and how their positions are dictated by the parameters ε, V and Ω.