Exercise 8: Third-Order Vibrational Spectroscopy

1 Homework

1.1 Third-Harmonic Generation

Consider a three-level system with the energy level structure pictured in Figure 1 and in which transitions are allowed only between consecutive eigenstates, i.e. dipole moment matrix elements μ_{mn} are identically zero unless $m = n \pm 1$. This forms a simple model for vibrational spectroscopy. Draw the third-harmonic ($\boldsymbol{k}_{\text{sig}} = \boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$) arrow-ladder diagram for this system. Can this system produce a third-harmonic signal? Why or why not? Assume that the appropriate phase-matching requirements *are* satisfied, and explain your answer by explicitly writing down the response-function term corresponding to this diagram.

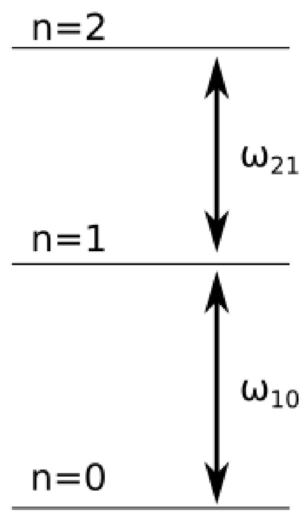

Figure 1: Energy level diagram for a vibrational three-level system.

1.2 Double-Quantum Coherence

Suppose that

$$\|\mu_{21}\|^2 = 2\|\mu_{10}\|^2. \tag{1}$$

This is a harmonic-scaling assumption for the transition dipole moments, which is satisfied exactly for the harmonic oscillator. Draw the two diagrams corresponding to the double-quantum coherence pathway ($\boldsymbol{k}_{\text{sig}} = \boldsymbol{k}_1 + \boldsymbol{k}_2 - \boldsymbol{k}_3$) and write down the corresponding response-function terms. Under what conditions on ω_{21} and ω_{10} will the double-quantum coherence signal vanish? What does this tell you about the nonlinear response properties of the harmonic oscillator?

1.3 Two-Dimensional Spectroscopy

Draw all six arrow-ladder diagrams that contribute to the 2D IR spectrum for the vibrational three-level system of Figure 1 and classify them as corresponding to the rephasing ($\boldsymbol{k}_{\text{sig}} = -\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$) or nonrephasing ($\boldsymbol{k}_{\text{sig}} = \boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$) pathways. Finally, classify each diagram as contributing to either the positive (blue) or red (negative) peak in the 2D IR spectrum shown in Figure 2 and label the frequencies of each peak in Figure 2 as ω_{21} or ω_{10}.

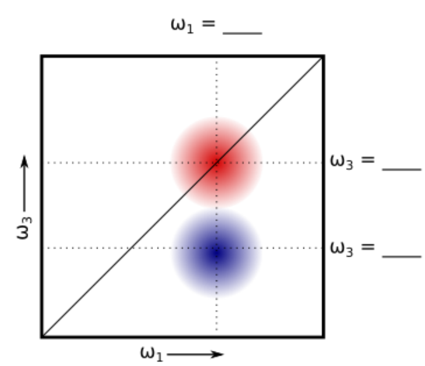

Figure 2: 2D IR spectrum for a vibrational three-level system.

2 Extra Credit

The six-level system whose energy diagram is depicted in Figure 3 is a common model for the vibrational dimer, i.e., a pair of coupled vibrational modes denoted a and b in the diagram. The states a and $2a$ consist primarily of vibrational motion on oscillator a, while the states b and $2b$ consist primarily of vibrational motion on oscillator b. State ab is the jointly-excited state featuring vibrational motion of both oscillators. The arrows in the diagram indicate selection rules, i.e., transitions are allowed *only* between the states connected by arrows. There are 28 arrow-ladder diagrams that contribute to the 2D IR spectrum of this system. Draw them.

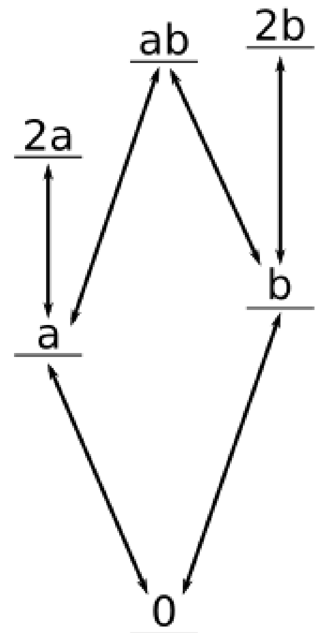

Figure 3: Energy level diagram for a vibrational six-level system.