Jyvaskyla Summer School 2013
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Homework

1. Double Quantum Coherence: Let A and B denote two coupled two-level systems, described by the Hamiltonian

$$H = H_A + H_B + V \; . \qquad (1)$$

Here, H_A *(*H_B*) is the Hamiltonian of the system A (B) and* V *represents their mutual coupling.* $\{|a\rangle, |b\rangle\}$ *are the eigenstates of* H_A *with corresponding eigenvalues* $\{E_a, E_b\}$ *and* $\{|\alpha\rangle, |\beta\rangle\}$ *the eigenstates of* H_B *with eigenvalues* $\{E_\alpha, E_\beta\}$*. Consider the coupling*

$$V = \gamma \left\{ |a\beta\rangle\langle b\alpha| + |b\alpha\rangle\langle a\beta| \right\} . \qquad (2)$$

This is a model Hamlitonian that e.g. describes two weakly interacting chromophores, each approximated by a two-level system. In this case the coupling originates from dipole-dipole interaction between the charge distributions representing the two chromophores. For system A (B), state $a(\alpha)$ *is the ground state and state* $b(\beta)$ *is the excited state.*

i. Write down the matrix representation of H with respect to the basis $\{|a\alpha\rangle, |b\beta\rangle, |b\alpha\rangle, |a\beta\rangle\}$. The order of basis elements specified above guarantees a particularly simple (block diagonal) form of the Hamiltonian matrix.

ii. Calculate the first non-vanishing correction in the coupling strength, γ, to the eigenenergies of the system. (*Hint:* Use perturbation theory) Explore how your result changes for an arbitrary off-diagonal coupling by analyzing the small and large γ limits.

iii. Solve the 4×4 eigenvalue problem for the Hamiltonian of the coupled system directly. Here, it proves advantageous to redefine the energy scale such that $E_\alpha = E_a = 0$. Further assume that $E_\beta = E_b$ (e.g. identical chromophores). Show that the joint system corresponds to an effective three level system of the type shown in Fig. 1. Consider also the limiting case $\gamma \to 0$.

iv. We now expose an assembly of such coupled two level system to 3 laser pulses, $E_j(\tau) = E_{j0}(\tau - \tau_{j0})e^{i(k_j \cdot r - \omega_{j0}\tau)}$ with $j = 1,2,3$. Here, ω_{j0} denotes the carrier frequency, k_j the wavevector, and τ_{j0} the center time of the envelope $E_{j0}(\tau - \tau_{j0})$ of the j th pulse. Select the phase-matching direction $k_{III} = k_1 + k_2 - k_3$ and assume the pulses to be well separated in time where $\tau_{10} < \tau_{20} < \tau_{30}$. Within the Rotating Wave Approximation using the dipole selection rules shown in Fig., derive a formula for the third order polarization for the k_{III} -signal.

v. Show that the signal derived in (iv) vanishes for the case of zero coupling. This illustrates that the k_{III} signal is a technique that is able to probe the coupling between e.g. chromophores.

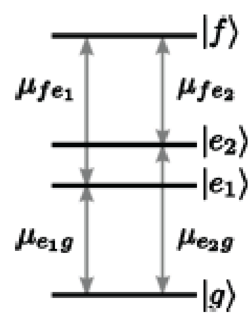
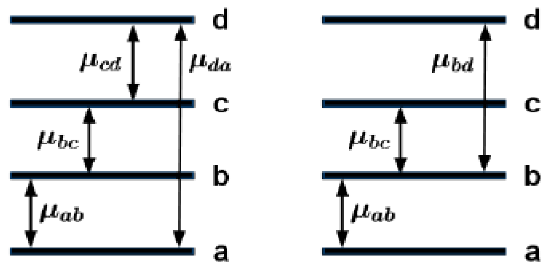


Figure 1: Level scheme

Since the coupling between the choromophores will depend on their relative distance and orientation, the k_{III} technique can provide information about the structure of e.g. the chromophores in large biomolecules. (*Hint:* In the limit $\gamma \to 0$, the following hold for the transition moments of the joint system: $\mu_{e_1 f} = \mu_{ge_2}$; $\mu_{e_2 f} = \mu_{ge_1}$)

2 *For each of the level schemes below, determine the density matrix pathways (within the RWA) for the signals,* $\mathbf{k}_{IV} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ *and* $\mathbf{k}_{III} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ *for an experiment*

which utilizes three time-ordered fields with propagation directions and frequencies $\{\mathbf{k}_j, \omega_j\}$ $j \in \{1,2,3\}$. *(Hint: Use Fig. 6.3 on page 152 in Nonlinear Spectroscopy)*



3 Define and explain

a) The rotating wave approximation

b) Pure dephasing

c) Photon echo

d) CARS

4 What is the minimum linewidth of a spectral transition between two states whose lifetime is 10 ps and 25 ps? Express the linewidth in cm-1

5 The perturbative approach to nonlinear spectroscopy applies when the optical field is weak compared to the electrostatic field in the molecule. What is the electric field acting on the electron in a hydrogen atom?

Optional: *What laser intensity* $(watt/cm^2)$ *produces such a field?*