MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.74 Quantum Mechanics II
Spring, 2004

Professor Robert W. Field

Problem Set #7

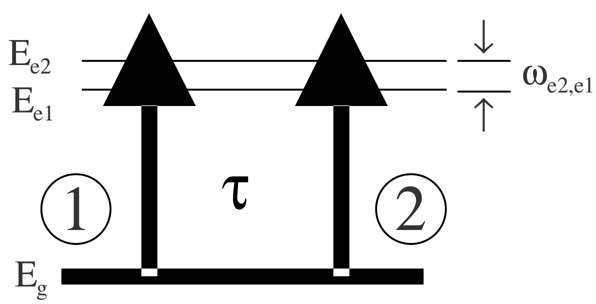
DUE: At the start of Lecture on Friday, April 23.

Reading: HLB-RWF 9.1.7, 9.1.8, 9.4.9, 9.2.1, 9.2.2, 9.2.3, 9.2.4

Problems:

I. One-Color Pump-Probe Experiment.

Consider a three-level system.



Pulses (1) and (2) are obtained by splitting a 100fs laser pulse into two identical pulses and systematically delaying pulse (2) relative to pulse (1) using a delay line.

The intensity of pulse (1) is set so that, immediately after pulse (1) has exited the sample

$$\Psi(0) = [1-0.02]^{1/2}\psi_g + 0.1\psi_{e1} + 0.1\psi_{e2}.$$

A. For excitation by pulse (1) only, what does $P(t) = |\langle\Psi(t)|\Psi(0)\rangle|^2$ look like?

B. For excitation at $t = 0$ by both pulses ① and ②, with zero delay between the two pulses, what is $\Psi(0)$? Be extremely careful to justify your value for the coefficients in front of ψ_{e1} and ψ_{e2}.

C. For excitation at $t = 0$ by pulse ① and $t = \tau$ by pulse ②, what is $\Psi(\tau)$?

D. Compute $P(t-\tau) = \left|\langle \Psi(t-\tau) | \Psi(\tau) \rangle\right|^2$ for $t = 0$, $\tau = \frac{2\pi}{\omega_{e2,e1}}(1/4)$, and $\tau = \frac{2\pi}{\omega_{e2,e1}}(1/2)$.

E. Suppose you were going to monitor P(t - τ) in a fluorescence-dip scheme. Describe this one-color pump-probe fluorescence-dip experiment in the $\boldsymbol{\rho}(0)$, **E, U, D** formulation.

F. Consider an experiment in which you have a cw laser oscillating at $\left(\frac{E_{e2} + E_{e1}}{2} - E_g\right)\Big/\hbar = \omega_{\mathrm{cw}}$. Your excitation pulse at $t = 0$ is obtained by pulse amplifying ω_{cw} from ~1mW cw to a 100fs, 1μJ pulse (peak power 10^7W). The laser beam traverses your sample and impinges on a "square law" detector. The signal is

$$I(t) \propto \left|\varepsilon_{\mathrm{laser}}(t) + \varepsilon_{\mathrm{molecule}}(t)\right|^2.$$

Use the $\boldsymbol{\rho}$, **E, U, D** formulation to describe $I(t)$ at $t > 0$ for a single amplified pulse at $t = 0$.

II. Anharmonic Coupling

$\mathbf{H} = \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_{12}$

$$\mathbf{h_1}/hc = (\omega_1/2)\left(\mathbf{a}_1^\dagger\mathbf{a}_1 + \mathbf{a}_1\mathbf{a}_1^\dagger\right) + (x_{11}/4)\left(\mathbf{a}_1^\dagger\mathbf{a}_1 + \mathbf{a}_1\mathbf{a}_1^\dagger\right)^2$$

$$\mathbf{h_2}/hc = (\omega_2/2)\left(\mathbf{a}_2^\dagger\mathbf{a}_2 + \mathbf{a}_2\mathbf{a}_2^\dagger\right) + (x_{22}/4)\left(\mathbf{a}_2^\dagger\mathbf{a}_2 + \mathbf{a}_2\mathbf{a}_2^\dagger\right)^2$$

$$\mathbf{h_{12}}/hc = k_{122}\left(\mathbf{a}_1^\dagger + \mathbf{a}_1\right)\left(\mathbf{a}_2^\dagger + \mathbf{a}_2\right)^2$$

where ω_1, x_{11}, ω_2, x_{22}, and k_{122} are in cm^{-1} units.

The goal of this problem is to discover how (or whether) it is possible to determine experimentally the sign of k_{122}. This sign is physically significant because, if $k_{122} > 0$, then when bond 1 ($\mathbf{Q}_1$) is stretched the oscillation frequency of bond 2 is *increased*, and, if $k_{122} < 0$, stretching bond 1 *decreases* the oscillation frequency of bond 2.

The energy levels of this two-mode oscillator are described by an $\mathbf{H}^{\text{eff}}$ that has diagonal elements

$$\begin{aligned} E^{(0)}(v_1,v_2)/hc = {} & \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2) + x_{11}(v_1 + 1/2)^2 \\ & + x_{22}(v_2 + 1/2)^2 + x_{12}(v_1 + 1/2)(v_2 + 1/2) \end{aligned}$$

and, because $\omega_1 \approx 2\omega_2$, is arranged in quasi-degenerate polyad blocks, each block with polyad quantum number $P = 2v_1 + v_2$. The off-diagonal matrix elements within each polyad block are

$$\mathbf{\Omega} + \mathbf{\Omega}^\dagger \equiv k_{122}\left[\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger + \mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2\right]$$

and the nonzero elements follow the selection rule $2\Delta v_1 = -\Delta v_2$.

A. Set up the $P = 10$ polyad block of $\mathbf{H}$. This is a 6×6 matrix. Let $\omega_1 = 1000\ cm^{-1}$, $\omega_2 = 500\ cm^{-1}$, $x_{11} = 10\ cm^{-1}$, $x_{22} = 5\ cm^{-1}$, $x_{12} = 0$, and $k_{122} = \pm 100\ cm^{-1}$. Solve for the energy levels for $k_{122} = 100\ cm^{-1}$ and $k_{122} = -100\ cm^{-1}$. Is the sign of k_{122} an observable quantity? If it is not, you can skip part B, unless you have a clever idea for how to sample the sign of k_{122} in the time domain.

B. Use the operator algebra from Lecture #8 (Resonance Operators: Equations of Motion) to propose a time domain observable quantity that is sensitive to the sign of k_{122}.

C. Examine the time dependence of $\left\langle \mathbf{a}_1^\dagger \mathbf{a}_1 \right\rangle_t$ for each of the six possible single basis-state plucks of the $P = 10$ polyad. Which pluck is most sensitive to the value of k_{122}?

D. Examine the time dependence of the expectation value $\langle \mathbf{\Omega} + \mathbf{\Omega}^\dagger \rangle_t$ for each of the six possible single basis-state plucks of the $P = 10$ polyad. Which pluck is most sensitive to the value of k_{122}?

E. If you conclude that the sign of k_{122} is not an observable quantity, replace $\mathbf{h}_{12}$ by

$$\mathbf{h}_{12} = k_{1122}\left(\mathbf{a}_1^\dagger + \mathbf{a}_1\right)^2\left(\mathbf{a}_2^\dagger + \mathbf{a}_2\right)^2$$

and let $\omega_1 = \omega_2 = 1000\ \mathrm{cm}^{-1}$, $x_{11} = x_{22} = 10\ \mathrm{cm}^{-1}$, and $k_{1122} = \pm\ 100\ \mathrm{cm}^{-1}$. Show that the sign of k_{1122} is an observable quantity.