MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
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Problem Set #7

DUE: At the start of Lecture on Friday, November 1.

Reading: CTDL, Pages 290 - 307, 643 - 662, 712 - 741

Problems:

1. Consider the two-level problem

$$H = \begin{pmatrix} E_B^{(0)} & V \\ V & E_D^{(0)} \end{pmatrix} = \overline{E}^{(0)}\mathbb{1} + \begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix}$$

$$\overline{E}^{(0)} \equiv \frac{E_B^{(0)} + E_D^{(0)}}{2}, \quad \Delta \equiv \frac{E_B^{(0)} - E_D^{(0)}}{2}$$

where $E_B^{(0)}$ and $E_D^{(0)}$ are respectively the zero-order energies of a "bright" and a "dark" state. The names bright and dark refer to the ability to absorb and emit a photon.

A. Solve for the eigenstates

E_+, ψ_+, and E_-, ψ_-

in terms of $E_B^{(0)}$, $\psi_B^{(0)}$, and $E_D^{(0)}$, $\psi_D^{(0)}$, where, by definition $E_+ > E_-$ and let V be real and $V > 0$.

Use the standard notation for the two level problem

$$|\psi_+\rangle = \cos(\theta/2)|\psi_B^{(0)}\rangle + \sin(\theta/2)|\psi_D^{(0)}\rangle$$
$$|\psi_-\rangle = -\sin(\theta/2)|\psi_B^{(0)}\rangle + \cos(\theta/2)|\psi_D^{(0)}\rangle$$

where

$$\tan\theta = V/\Delta.$$

B. By definition, at the instant of pulsed-excitation by a photon pulse,

$\Psi(x, t=0) = \psi_B^{(0)}(x)$.

Solve for $\Psi(x,t) = a_+(t)\psi_+(x) + a_-(t)\psi_-(x)$.

C. Construct the 2×2 density matrix, $\boldsymbol{\rho}(t)$, that corresponds to $\Psi(x,t)$ in the $\psi_B^{(0)}$, $\psi_D^{(0)}$ basis set.

D. The detection operator, $\hat{D} = \left|\Psi_B^{(0)}\right\rangle\left\langle\Psi_B^{(0)}\right|$, is a projection operator, which projects out the bright state character. Write the matrix representation of $\hat{D}$, $\mathbf{D}$, in the $\psi_B^{(0)}$, $\psi_D^{(0)}$ basis set.

E. Calculate the expectation value of $\mathbf{D}$ for the $\Psi(x,t)$ state represented by the $\boldsymbol{\rho}(t)$ from part C, as

$$\langle D \rangle = \mathrm{Trace}(\boldsymbol{\rho}\mathbf{D}).$$

You have just re-discovered "Quantum Beats"!

F. Plot the (time-independent) fractional modulation, $\dfrac{\langle \mathbf{D} \rangle_{MAX} - \langle \mathbf{D} \rangle_{MIN}}{\langle \mathbf{D} \rangle_{MAX}}$, vs. $\dfrac{V}{E_B^{(0)} - E_D^{(0)}}$.

It is common to talk about the time evolution as if the system is moving in *state space* (as opposed to coordinate space) back and forth between the Bright and Dark states.

G. Suppose you could make some sort of magical change in the experimental apparatus so that the original Bright state is still excited at $t = 0$ but that the detector operator now exclusively "sees" the original dark state. How does this alter the form of **D** and $\langle \mathbf{D} \rangle$ and the amplitude and phase of the quantum beats?

2. Consider a molecule with two identical anharmonic *local* R-H stretch oscillators. The two local oscillators are anharmonically coupled by the simplest possible coupling term:

$$\mathbf{H} = \mathbf{H}_L + \mathbf{H}_R + \hbar k_{LR}\mathbf{q}_L\mathbf{q}_R$$

$$\mathbf{H}_L = \frac{1}{2}\hbar\omega\left[\mathbf{a}_L\mathbf{a}_L^\dagger + \mathbf{a}_L^\dagger\mathbf{a}_L\right] + \frac{1}{4}\hbar x\left[\mathbf{a}_L\mathbf{a}_L^\dagger + \mathbf{a}_L^\dagger\mathbf{a}_L\right]^2$$

$$\mathbf{H}_R = \frac{1}{2}\hbar\omega\left[\mathbf{a}_R\mathbf{a}_R^\dagger + \mathbf{a}_R^\dagger\mathbf{a}_R\right] + \frac{1}{4}\hbar x\left[\mathbf{a}_R\mathbf{a}_R^\dagger + \mathbf{a}_R^\dagger\mathbf{a}_R\right]^2$$

(L = Left, R = Right)

$$\mathbf{H}^{(0)} = \mathbf{H}_L + \mathbf{H}_R$$

$$\mathbf{H}^{(1)} = \frac{1}{2}\hbar k_{LR}\left(\mathbf{a}_L + \mathbf{a}_L^\dagger\right)\left(\mathbf{a}_R + \mathbf{a}_R^\dagger\right)$$

Note that $\left[\mathbf{a}_L, \mathbf{a}_L^\dagger\right] = \left[\mathbf{a}_R, \mathbf{a}_R^\dagger\right] = 1$

$$0 = \left[\mathbf{a}_L, \mathbf{a}_R\right] = \left[\mathbf{a}_L, \mathbf{a}_R^\dagger\right] = \text{etc.}$$

All basis states may be derived from

$$\left|n_L n_R\right\rangle = \left(a_L^\dagger\right)^{n_L}\left(a_R^\dagger\right)^{n_R}|00\rangle\left[n_L!n_R!\right]^{-1/2}.$$

Since $\omega_L = \omega_R = \omega$ and $x_{LL} = x_{RR} = x$ and $x_{LR} = 0$, the two local oscillators are identical. Thus the energy levels (and basis sets) are arranged in polyads where the polyad quantum number, **P**, is

$$\mathbf{P} = \mathbf{a}_L^{\dagger}\mathbf{a}_L + \mathbf{a}_R^{\dagger}\mathbf{a}_R.$$

The selection rule for $\mathbf{H}^{(1)}$ is $\Delta n_L = \pm 1$, $\Delta n_R = \pm 1$, and the intrapolyad selection rule is $\Delta n_L = -\Delta n_R = \pm 1$.

If we treat $\mathbf{q}_L$ and $\mathbf{q}_R$ as dimensionless, then ω, x, and k_{LR} all have the same units. All parts of the following problem are to be based on [$\omega = 1000$, $m = 1$, $x = 10$, and $k_{LR} = 1$] or [$\omega = 1000$, $m = 1$, $x = 1$, $k_{LR} = 10$]. The first set of parameters is close to the normal mode limit and the second set of parameters is close to the local mode limit.

A. Set up the 11×11 $P = 10$ polyad. Solve for the energy eigenvalues and eigenvectors. Do this twice, once for each of the two parameter sets, above. Give an energy level diagram where all 11 energy states are shown on the same diagram. Specify the basis state (and its fractional character) that has the largest fractional character in each eigenstate. Are there any surprising features?

B. The *normal* mode creation and annihilation operators are

$$\mathbf{a}_s = 2^{-1/2}(\mathbf{a}_L + \mathbf{a}_R), \qquad \mathbf{a}_s^{\dagger} = 2^{-1/2}(\mathbf{a}_L^{\dagger} + \mathbf{a}_R^{\dagger})$$
$$\mathbf{a}_a = 2^{-1/2}(\mathbf{a}_L - \mathbf{a}_R), \qquad \mathbf{a}_a^{\dagger} = 2^{-1/2}(\mathbf{a}_L^{\dagger} + \mathbf{a}_R^{\dagger})$$

and the normal mode basis states are

$$|n_s n_a\rangle = (\mathbf{a}_s^{\dagger})^{n_s}(a_a^{\dagger})^{n_a}|00\rangle[n_s!n_a!]^{-1/2}.$$

The subscripts $_s$ and $_a$ stand for symmetric and antisymmetric. Calculate the expectation values of $\mathbf{a}_s^{\dagger}\mathbf{a}_s$ and $\mathbf{a}_L^{\dagger}\mathbf{a}_L$ for the highest and lowest energy eigenstates in the $P = 10$ polyad for both sets of parameters.

What does this tell you about the transition from the local mode limiting case to the normal mode limiting case? In particular, does $x << k_{LR}$ favor the normal mode or local mode limit? Why?

C. Evaluate $[\mathbf{H}, \mathbf{a}_L^{\dagger}\mathbf{a}_L]$ and $[\mathbf{H}, \mathbf{a}_s^{\dagger}\mathbf{a}_s]$. These quantities are important in the Heisenberg equation of motion. They will reveal the terms in **H** that cause the local mode and normal mode quantum numbers not to be conserved. This is a problem in operator algebra and does not depend on which of the two sets of parameters is used to specify **H**.

D. To (eventually) examine $\langle \mathbf{q}_L \rangle_t$ and $\langle \mathbf{q}_s \rangle_t$ you will need to evaluate the commutators

$$[\mathbf{H}, 2^{-1/2}(\mathbf{a}_L + \mathbf{a}_L^{\dagger})] \qquad \text{and} \qquad [\mathbf{H}, 2^{-1/2}(\mathbf{a}_s + \mathbf{a}_s^{\dagger})].$$

These commutators will identify the terms in **H** that cause $\langle \mathbf{q}_L \rangle_t$ and $\langle \mathbf{q}_s \rangle_t$ to move. According to Newton,

$$F = ma$$
$$\frac{1}{m}\frac{dp}{dt} = \frac{d^2q}{dt^2} = -\frac{1}{m}\frac{dV(q)}{dq}$$

If $V(q) = \frac{1}{2}kq^2 \quad , \frac{1}{q}\frac{\partial V}{dq} = k.$

You should find that the "effective force constant" for the $\mathbf{q}_L$ oscillator is different from that for the $\mathbf{q}_s$ oscillator. The effective force constant may be defined as

$$k_{eff} = \frac{1}{q}\frac{\partial H}{\partial q}.$$

[HINT: $\omega_s = \omega + \lambda$ and $\omega_a = \omega - \lambda$, where λ is intimately related to k_{LR}.]

This problem involves a lot of operator algebra.

E. Let $|\Psi(0)\rangle = |n_s = 10, n_a = 0\rangle$.

Construct $|\Psi(t)\rangle$ and, from $\boldsymbol{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$, construct $\boldsymbol{\rho}(t)$.

Do this considering only the energy eigenvalues and eigenvectors of the P = 10 polyad. Do this twice, once for each of the two sets of parameters.

(i) Use $|\Psi(t)\rangle$ to compute the survival probability

$$\wp(t) = \left|\langle\Psi(\mathbf{q},t)\|\Psi(\mathbf{q},0)\rangle\right|^2.$$

(ii) Use $\boldsymbol{\rho}(t)$ to compute

$$\langle\mathbf{q}_L\rangle_t$$
$$\langle\mathbf{q}_s\rangle_t$$
$$\langle\mathbf{a}_s^\dagger\mathbf{a}_s\rangle_t$$
$$\langle\mathbf{a}_L^\dagger\mathbf{a}_L\rangle_t$$

Do you notice anything remarkable?

(iii) Compute the Fourier transform of $\langle\mathbf{q}_L\rangle_t$ and $\langle\mathbf{q}_s\rangle_t$ and discuss the result in terms of your answer to part D.

F. Now we shall use the results of part C. For a time-independent operator $\hat{A}$, a basic quantum mechanical relation is

$$i\hbar\frac{d\langle\hat{A}\rangle}{dt} = \langle[\hat{A},\hat{H}]\rangle,$$

whence we get

$$i\hbar\frac{d\langle\mathbf{a}_L^\dagger\mathbf{a}_L\rangle}{dt} = \langle[\mathbf{H},\mathbf{a}_L^\dagger\mathbf{a}_L]\rangle$$

and

$$i\hbar \frac{d\langle \mathbf{a}_s^{\dagger}\mathbf{a}_s \rangle}{dt} = \langle [\mathbf{H}, \mathbf{a}_s^{\dagger}\mathbf{a}_s] \rangle .$$

These are expressions for the rate of change of n_L and n_s, or the energy flow in or out of mode L or s, respectively.

Using the same state $|\Psi(t)\rangle$ as in part D, plot $d\langle \mathbf{a}_L^{\dagger}\mathbf{a}_L \rangle / dt$ and $d\langle \mathbf{a}_s^{\dagger}\mathbf{a}_s \rangle / dt$ as a function of time for one or both sets of parameters. is the relationship between these plots and those of $\langle \mathbf{a}_L^{\dagger}\mathbf{a}_L \rangle_t$ and $\langle \mathbf{a}_s^{\dagger}\mathbf{a}_s \rangle_t$ consistent with intuition?