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

\[ H = \begin{pmatrix} E_B^{(0)} & V \\ V & E_D^{(0)} \end{pmatrix} = E^{(0)} \mathbb{1} + \begin{pmatrix} \Delta & V \\ V & -\Delta \end{pmatrix} \]
\[ E^{(0)} = \frac{E_B^{(0)} + E_D^{(0)}}{2}, \quad \Delta = \frac{E_B^{(0)} - E_D^{(0)}}{2} \]

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

\( E_+, \psi_+ \), and \( E_-, \psi_- \)

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

\[ \begin{align*}
| \psi_+ \rangle &= \cos(\theta / 2)|\psi_B^{(0)}\rangle + \sin(\theta / 2)|\psi_D^{(0)}\rangle \\
| \psi_- \rangle &= -\sin(\theta / 2)|\psi_B^{(0)}\rangle + \cos(\theta / 2)|\psi_D^{(0)}\rangle
\end{align*} \]

where

\[ \tan \theta = \frac{V}{\Delta}. \]

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 \( 2 \times 2 \) density matrix, \( \rho(t) \), that corresponds to \( \Psi(x,t) \) in the \( \psi_B^{(0)}, \psi_D^{(0)} \) basis set.
D. The detection operator, \( \hat{D} = \frac{|\psi_B(0)\rangle\langle\psi_B(0)|}{\langle\psi_B(0)|\psi_B(0)\rangle} \), is a projection operator, which projects out the bright state character. Write the matrix representation of \( \hat{D} \), in the \( \psi_B(0) \), \( \psi_D(0) \) basis set.

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

\[ \langle \hat{D} \rangle = \text{Trace}(\rho \hat{D}). \]

You have just re-discovered “Quantum Beats”!

F. Plot the (time-independent) fractional modulation, \( \frac{\langle \hat{D} \rangle_{\text{MAX}} - \langle \hat{D} \rangle_{\text{MIN}}}{\langle \hat{D} \rangle_{\text{MAX}}} \), vs. \( \frac{V}{E_{B}^{(0)} - E_{D}^{(0)}} \).

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 \( \hat{D} \) and \( \langle \hat{D} \rangle \) 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:

\[
\begin{align*}
H &= H_L + H_R + \hbar k_{LR}q_Lq_R \\
H_L &= \frac{1}{2} \hbar \omega_L [a_L^\dagger a_L + a_L a_L^\dagger] + \frac{1}{4} \hbar x [a_L^\dagger a_L^\dagger + a_L a_L]^2 \\
H_R &= \frac{1}{2} \hbar \omega_R [a_R^\dagger a_R + a_R a_R^\dagger] + \frac{1}{4} \hbar x [a_R^\dagger a_R^\dagger + a_R a_R]^2 \\
H^{(0)} &= H_L + H_R \\
H^{(1)} &= \frac{1}{2} \hbar k_{LR} (a_L + a_L^\dagger)(a_R + a_R^\dagger)
\end{align*}
\]

Note that \( [a_L, a_L^\dagger] = [a_R, a_R^\dagger] = 1 \)

\[ 0 = [a_L, a_R] = [a_L^\dagger, a_R^\dagger] = \text{etc.} \]

All basis states may be derived from

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

Since \( \omega_L = \omega_R = 0 \) and \( x_{LR} = x_{RR} = x \) 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
\[ P = a^+_L a_L + a^+_R a_R. \]

The selection rule for \( H^{(1)} \) 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 \( q_L \) and \( q_R \) as dimensionless, then \( \omega, x, \) and \( k_{LR} \) all have the same units. All parts of the following problem are to be based on \( [\omega = 1000, m = 1, x = 10, \text{and} k_{LR} = 1] \) 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 \( 11 \times 11 \) \( P = 10 \) 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

\[
\begin{align*}
a_s &= 2^{-1/2}(a_L + a_R), \\
a^+_s &= 2^{-1/2}(a^+_L + a^+_R), \\
a_a &= 2^{-1/2}(a_L - a_R), \\
a^+_a &= 2^{-1/2}(a^+_L + a^+_R),
\end{align*}
\]

and the normal mode basis states are

\[ |n_n_s⟩ = (a^+_s)^n (a_a)^n |00⟩[n_s^1 n_a^1]^{-1/2}. \]

The subscripts \( s \) and \( a \) stand for symmetric and antisymmetric. Calculate the expectation values of \( a_s a_a \) and \( a^+_s a^+_a \) 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 \( x \ll k_{LR} \) favor the normal mode or local mode limit? Why?

C. Evaluate \( [H, a^+_s a_L] \) and \( [H, a^+_a a_L] \). 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 \( \langle q_L \rangle_t \) and \( \langle q_s \rangle_t \) you will need to evaluate the commutators

\[ [H, 2^{-1/2}(a_L + a^+_L)] \quad \text{and} \quad [H, 2^{-1/2}(a_s + a^+_s)]. \]

These commutators will identify the terms in \( H \) that cause \( \langle q_L \rangle_t \) and \( \langle q_s \rangle_t \) 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 \( V(q) = \frac{1}{2} k q^2 \), \( \frac{1}{q} \frac{\partial V}{\partial q} = k \).

You should find that the “effective force constant” for the \( q_L \) oscillator is different from that for the \( q_s \) oscillator. The effective force constant may be defined as

\[
 k_{\text{eff}} = \frac{1}{q} \frac{\partial H}{\partial q}.
\]

[HINT: \( \omega_s = \omega + \lambda \) and \( \omega_s = \omega - \lambda \), where \( \lambda \) 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 \(\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|\), construct \(\rho(t)\).

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

\[
\rho(t) = \left|\langle\Psi(q,t)|\Psi(q,0)\rangle\right|^2.
\]

(ii) Use \(\rho(t)\) to compute

\[
\langle q_L \rangle_t,
\langle q_s \rangle_t,
\langle a_+^\dagger a_+ \rangle_t,
\langle a_+^\dagger a_- \rangle_t.
\]

Do you notice anything remarkable?

(iii) Compute the Fourier transform of \(\langle q_L \rangle_t\) and \(\langle q_s \rangle_t\) 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 \( A \), a basic quantum mechanical relation is

\[
y \hbar \frac{d\langle A \rangle}{dt} = \langle [A, H] \rangle,
\]

whence we get

\[
y \hbar \frac{d\langle a_+^\dagger a_+ \rangle}{dt} = \langle [H, a_+^\dagger a_+] \rangle
\]

and
\[ \frac{i\hbar}{\partial t} \langle a_s^\dag a_s \rangle = \langle [H, a_s^\dag a_s] \rangle. \]

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 \( \frac{\partial \langle a_s^\dag a_L \rangle}{\partial t} \) and \( \frac{\partial \langle a_s^\dag a_s \rangle}{\partial t} \) as a function of time for one or both sets of parameters. Is the relationship between these plots and those of \( \langle a_s^\dag a_L \rangle \) and \( \langle a_s^\dag a_s \rangle \) consistent with intuition?