5.74 Introductory Quantum Mechanics II
Spring 2009

5.74, Problem Set #3
Spring 2009
Due Date: Mar. 10, 2003

1. Relaxation from a Prepared State

The linear response function $R(\tau)$ describes the time-dependent behavior of a system subject to an impulsive perturbation from equilibrium. You can also imagine applying a force that holds the system away from isolated equilibrium state, and then suddenly releasing this force. The relaxation back to equilibrium is dictated by the step response function $S(\tau)$, which we will investigate.

The Hamiltonian for the system will reflect an applied constant force prior to time zero:

$$H = H_0 - f(t)A \qquad\qquad f(t) = \left\{ \begin{matrix} f_0 & t<0 \\ 0 & t \geq 0 \end{matrix} \right\} = f_0\,\Theta(-t)$$

$\Theta(t)$ is the unit step function. We have applied the force at a time in the distant past, so that the system at $t = 0$ has come to equilibrium under the Hamiltonian H. At long times, $t = +\infty$, the system is at equilibrium under H_0. We will use the eigenstates of H_0 as the basis to solve this problem.

a) Give expressions for the expectation value of A at time $t = 0$, $\langle A \rangle_0$, and at time $t = +\infty$, $\langle A \rangle_\infty$. To help evaluate ensemble averages such as $\langle e^{-\beta H} A \rangle$, you can make use of the *classical* linear response approximation:

$$e^{-\beta(H_0 - fA)} \approx e^{-\beta H_0}\left(1 + \beta f A\right) \qquad\qquad (fA << H_0)$$

Explain why a quantum evaluation is more complicated.

b) Given that the system initiates at $\langle A \rangle_0$ at $t = 0$, what is the time-development of A for $t > 0$, where the system evolves only under H_0? To solve this, first prepare the system in the state $H = H_0 - f_0 A$ at $t = 0$. To do this imagine starting with the equilibrium system under H_0 at $t = -\infty$, gradually ramping up the extra force at a rate η, and then abruptly shutting it off at $t = 0$:

$$f(t) = f_0\,\mathrm{e}^{\eta t}\,\Theta(-t).$$

Obtain an expression describing the time-evolution of the internal variable A for $t > 0$ for the limit that $\eta \to 0$. It may be helpful to make use of the Fourier transform relationship that relates the response function to the susceptibility.

c) Given that the time correlation function for the fluctuations in A are given by

$$C_{AA}(t) = \langle A_I(t) A_I(0) \rangle = \sum_{n,m} p_n \left|A_{mn}\right|^2 e^{-i\omega_{mn} t}$$

Show that the step response in (b) can be differentiated to give the impulse response and that the step response can be expressed as an expansion in cosines, i.e., functions that are even in time.

2. Harmonic Oscillators

The following questions refer to harmonic oscillators with a Hamiltonian

$$H_0 = \frac{1}{2m} p^2 + \frac{1}{2} m\omega_0^2 q^2 = \hbar\omega_0 \left(a^\dagger a + \tfrac{1}{2}\right)$$

a) Show that the thermally averaged occupation number $\langle n \rangle$ for a harmonic oscillator of frequency ω_0 is given by $\langle n \rangle = \left(\exp(\beta\hbar\omega_0) - 1\right)^{-1}$.

b) Obtain expressions for the time evolution of the operators $p(t)$ and $q(t)$ in terms of raising and lowering operators.

c) Calculate the correlation function for the harmonic oscillator coordinate: $C_{qq} = \langle q(t) q(0) \rangle$.

3. Displaced Harmonic Oscillator Model

Work through the correlation function description of the electronic absorption spectrum for a transition coupled to nuclear motion, using the displaced harmonic oscillator model discussed in class.

$$H_0 = |G\rangle H_G \langle G| + |E\rangle H_E \langle E|$$

$$H_G = H_g + E_g = \hbar\omega_0 \left(a^\dagger a + \tfrac{1}{2}\right) + E_g$$

$$H_E = H_e + E_e = e^{-ipd/\hbar} H_g e^{ipd/\hbar} + E_e$$

a) Assuming that the system is in the ground electronic state at equilibrium, and making the Condon approximation, show that $\langle \overline{\mu}(t) \overline{\mu}(0) \rangle = |\mu_{eg}|^2 \; e^{-i\omega_{eg} t} F(t)$, where $F(t) = \left\langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right\rangle$.

b) If the system is only in the ground state of the nuclear potential at equilibrium, show $F(t) = exp\left[\underset{\sim}{d}^2 \left(e^{-i\omega_0 t} - 1\right)\right]$ where $\underset{\sim}{d} = d\sqrt{\dfrac{m\omega_0}{2\hbar}}$.

4. Transformation between Hamiltonians.

Motivated by the previous problem, imagine that you wish to express the time-evolution of a wavefunction under one Hamiltonian H_e in terms of another H_g. We also define the difference Hamiltonian: $H_{eg} = H_e - H_g$. This suggests that we find a way of expressing the time evolution under H_e as:

$$H_e = H_g + H_{eg}$$
$$U_e = U_g U_{eg}$$

Show that we can obtain a transformation between U_e and U_g analogous to what we did with the interaction picture Hamiltonian:

$$U_{eg} = exp_+\left[\frac{-i}{\hbar}\int_0^t d\tau\, H_{eg}(\tau)\right] \qquad H_{eg}(\tau) = U_g^\dagger H_{eg} U_g$$

This also means that $U_{eg} = U_g^\dagger U_e$.