5.72 Problem set #4 (spring 2012) Cao

I. Harmonic Oscillator

1) For a harmonic oscillator, show that $C(t) = \langle x(t)x(0)\rangle$ satisfies $\ddot{C} + \omega_0^2 C = 0$.
2) Solve for $C(t)$ and its Fourier transform $\tilde{C}(\omega) = \int C(t)e^{i\omega t}dt$.
3) The forced oscillator obeys the equation of motion
$$m\ddot{x} + m\omega_0^2 x = f(\omega)e^{-i\omega t}.$$
Derive the expression for $\chi(\omega)$ from the above equation.
4) Write the formula for $K(t)$.
5) Verify $K(t) = -\beta\dot{C}(t)$ [i.e. $\chi'' = \frac{\beta\omega}{2}\tilde{C}(\omega)$].
6) *Verify the Kramers-Kronig relations.

II. The relaxation of rotational motions can be described by the rotational diffusion equation $\frac{\partial p}{\partial t} = D_R\nabla^2 p$, where ∇^2 is the angular part of the Laplacian operator
$$\nabla^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

1) Show that the average orientation $u(t) = \langle\cos\theta(t)\rangle$ satisfies
$$\dot{u}(t) = -2D_R u(t).$$
2) Show that the orientational correlation function is given by
$$C(t) = \langle\cos\theta(t)\cos\theta(0)\rangle = \frac{1}{3}e^{-2D_R t}.$$
3) Write down $K(t)$, χ', and χ''.
4) Calculate the response to a monochromatic force $F(t) = F_0\cos\omega_0 t$, which couples to the system according to $H' = -F(t)\cos\theta(t)$.
5) Calculate the average absorption rate.

(Ref: McQuarrie, p. 398, prob. 17-19)

III. Repeat the steps in Problem I for a damped oscillator described by
$$m\ddot{x} + m\gamma\dot{x} + m\omega_0^2 x = f(t) + F(t),$$
where $f(t)$ is the random force and $F(t)$ is the external driving force.

1) Show the position correlation function satisfies
$$m\ddot{C} + m\gamma\dot{C} + m\omega_0^2 C = 0$$
with the initial condition $C(0) = (\beta m\omega_0^2)^{-1}$.
2) Derive explicit expressions for $C(t)$ and its Fourier transform $\tilde{C}(\omega)$.
3) Show that under the external force the average position $\bar{x}$ satisfies
$$\ddot{\bar{x}} + \gamma\dot{\bar{x}} + \omega_0^2\bar{x} = \frac{F(t)}{m}.$$
4) Solve $\chi(\omega)$ from the above equation.
5) Derive $K(t)$ using the expression for $\chi(\omega)$ found above.

6) Verify $K(t) = -\beta \dot{C}(t)$.

IV. *Derivation of quantum response theory (Ref: McQuarrie, Berne, Kubo, Reichl).

1) Define the quantum Liouville operator as $\mathcal{L}A = \frac{1}{\hbar}[H, A]$. Show that $\dot{A}(t) = i\mathcal{L}(t)A(t)$ and $\dot{\rho} = -i\mathcal{L}\rho$, where ρ is the density matrix and $A(t)$ is a Heisenberg operator.
2) Given $H = H_0 - AF(t)$, use perturbation theory to show
$$\langle A(t)\rangle = \int_{-\infty}^{t} K(t-t')F(t')dt',$$
where $K(t-t') = \frac{i}{\hbar}\langle [A(t), A(t')]\rangle$.
3) Show that the classical limit of the quantum commutator is: $\frac{1}{i\hbar}[A, B] = \{A, B\}$, where $\{\,,\}$ is the Poisson bracket.
4) Show that the classical limit of $K(t)$ is $-\beta \dot{C}(t)$.

V. Spectroscopic measurements are expressed as polarization responses. We calculate the response function of a linear harmonic oscillator as an example.

1) The linear response function is defined as
$$R(t) = \frac{i}{\hbar}\langle 0|[\alpha(t), \alpha(0)]|0\rangle = \frac{i}{\hbar}[\langle 0|\alpha(t)\alpha(0)|0\rangle - \langle 0|\alpha(0)\alpha(t)|0\rangle],$$
where the transition dipole is assumed to be linear in coordinate $\alpha(t) = \alpha_0 x(t)$.
Show $R(t) = \frac{\sin \omega t}{m\omega}\alpha_0^2$.
Useful expressions:
$$x(t) = \sqrt{\frac{\hbar}{2m\omega}}\left(a e^{-i\omega t} + a^\dagger e^{i\omega t}\right),\ \langle 0|aa^\dagger|0\rangle = 1, \langle 0|a^\dagger a|0\rangle = 0.$$
2) Show that the same result can be obtained classically by replacing the quantum commutation with the Poisson bracket,
$$\frac{1}{i\hbar}[\alpha(t), \alpha(0)] \to \{\alpha(t), \alpha(0)\} = \frac{\partial \alpha(t)}{\partial x(0)}\frac{\partial \alpha(0)}{\partial p(0)} - \frac{\partial \alpha(t)}{\partial p(0)}\frac{\partial \alpha(0)}{\partial x(0)}$$
Useful expression: $x(t) = x(0)\cos \omega t + \frac{p(0)}{m\omega}\sin \omega t$
3) The non-linear response function is defined as
$$R(t_1, t_2) = \left(\frac{i}{\hbar}\right)^2 \langle 0|[[\alpha(t_1 + t_2), \alpha(t_1)], \alpha(0)]|0\rangle,$$
If $\alpha = \alpha_0 x$, show $R(t_1, t_2) = 0$ from the balance of a and $a^\dagger$ operators.
4) *To obtain non-vanishing non-linear response for the harmonic oscillator, we introduce a non-linear coordinate dependence,
$$\alpha = \alpha_0 x + \alpha' x^2 + \cdots$$
Show that the leading order term in α' is proportional to $\alpha_0^2 \alpha'$.