Chem 542
Homework for Part 3: Time-dependent QM

1. Consider in more detail time-dependent perturbation theory to calculate the transition probability from state |i> of a diatomic molecule to state |j>, induced by a Gaussian light pulse of frequency ω interacting with the molecular dipole μ. Assume that the molecular energy levels are known and that the interaction Hamiltonian is given by

$$V(t) = \hat{\mu}\mathcal{E}\cos(\omega t + \varphi)e^{-(t/\Delta t)^2} \quad ,$$

   where $\mathcal{E}$ is the field strength, φ the phase and Δt the duration of the pulse.

   a. Compute the matrix element of $\cos\theta$ "explicitly" to show that only $\Delta J = \pm 1$ transitions are allowed. $\Delta J = 0$ transitions are allowed in nonlinear molecules (Q-branch). Give a physical reason for why they are not allowed in diatomic molecules. [Hints: can a diatomic 'rotate' about the internuclear axis? Also, "explicitly" means you can use integral formulas for spherical harmonics, Clebsch-Gordan coefficients, 3-j symbols or the like as known quantities.]

   b. Evaluate the integral B.3.7.8 explicitly by rewriting the cosine in terms of complex exponentials to get the two integrals depending on the sum and difference of frequencies ω_{fi} and ω; as in the lecture notes, assume that all phase-dependent terms average out (incoherent light) in the final answer.

   c. As stated in the notes, the normalized lineshape of the transition look like a delta function as $\Delta t \rightarrow \infty$. Why would such a lineshape not be observed in a real molecule, even with a perfect high resolution light source?

2. Derive the equation for <A(t)> in terms of eigenstate overlaps <0|i> and eigenenergies E_i discussed after equation B.3.1.18. As a special case, consider the operator $U^*(t)$ and show that the autocorrelation-squared of the wavefunction, $P(t) = |<0|t>|^2 = \Sigma\, I_i + \Sigma\, I_i\, I_j \cos(\omega_{ij}t)$, where $I_i = |<0|i>|^2$. (Note: be careful to specify the range of is and js you sum over!)

3. Let us calculate what the vibrational dipole autocorrelation function C(t) of a collection of vibrating diatomic molecules at temperature T looks like. The relevant dipole matrix elements in eq. B-73 in this case are

   <v|μ' Δr |v±1><v±1|μ' Δr |v>,

   where Δr is the deviation of the bond distance from equilibrium. Here we have expanded μ in a first-order Taylor series $\mu = \mu_0 + \mu'\,\Delta r$, and used the harmonic oscillator approximation for the vibrational wavefunction |v> such that Δr only has matrix elements off-diagonal by ±1.

   a. Rather than performing the full quantum-mechanical trace over $\exp[-E_0/kT]\mu(0)\mu(t)$, consider a classical approximation where we replace the matrix elements of Δr in B-74 by

$$\Delta r(t) = \Delta r_{max}(E) \cos(\omega_0 t).$$

Here ω_0 is the vibrational frequency of the molecule, and $\Delta r_{max}(E)$ is the energy-dependent maximum deviation. Compute C(t) by replacing the summation by an integral over the action variable I=hv and the quantum energy by E=hv(v+1/2)≈vI; e.g. you may approximate the partition function by

$$Q = \Sigma_v \exp[-E(v)/kT] \approx \int_0^\infty dv \exp[-E(v)/kT] = \frac{1}{h}\int_0^\infty \exp[-E(I)/kT]dI$$

and make similar approximations in the numerator of B.3.8.5 to obtain C(t). Keep in mind that Δr_{max}, the maximum deviation from equilibrium, is a function of E (and hence I) which needs to be evaluated using the harmonic oscillator approximation.

b. Calculate the line shape $\Gamma(\omega)$ by inverse Fourier transform.

4. Show that the commutation relationship $[x(t),p(t)] = i\hbar$ holds at all times. (Do it by explicitly introducing x_0 and p_0, for which you know it holds, and applying the time evolution operators.

5. Show that the overlap of two states $|\Psi\rangle$ and $|\chi\rangle$ is preserved under the same unitary time evolution.

6. Qualitative wavepacket analysis: consider a repulsive potential of the form V = a/x.
    a. Sketch the potential and four of the continuum eigenfunctions, choosing the conventional phase so the lobe at the turning point is positive.
    b. Take four of these eigenstates and add them: draw the resulting wavepacket at t=0. [Of course, a real wavepacket would also contain all the in-between eigenstates.]
    c. Sketch the wavepacket at t > 0 when the eigenfunctions at the lowest and highest energy have acquired a relative phase of π.
    d. The wavepacket at t=0 has average momentum ≈ 0. As it evolves, it acquires momentum and a momentum spread. Based on the energy spread ΔE of the four eigenstates at t=0, the particle mass m, and the fact that at long time V ≈ 0, how will the width of the wavepacket change at long times?

7. Consider a traveling Gaussian wavepacket

$$\Psi(x,t=0) = \frac{1}{\sqrt[4]{2\pi\Delta x_0^2}} e^{ip_0 x/\hbar} e^{-(x-x_0)^2/4\Delta x_0^2}$$

    a. Show that the root mean square Δp_0 about the average momentum p_0 satisfies
    $\Delta x_0 \Delta p_0 = \hbar/2$. (The root mean square of operator A is $\{\langle\Psi|A^2|\Psi\rangle - \langle\Psi|A|\Psi\rangle^2\}^{1/2}$)
    b. Let Ψ evolve as a free particle. Show that at some later time, the square of Ψ evolved as

$$|\Psi(x,t)|^2 = \frac{1}{\sqrt[4]{2\pi\Delta x_t^2}} e^{-(x-x_t)^2/2\Delta x_t^2}$$

where $x_t = x_0 + p_0 t/m$ and $\Delta x_t^2 = \Delta x_t^2 + (\Delta p_0 t/m)^2$; in words, the center of the wavepacket follows the classical trajectory of a free particle, and the width increases in accordance with the spread in momentum governed by the Heisenberg principle.

[Hint: there are several ways to do this; probably the least laborious is to insert a complete set of momentum eigenstates, i.e. $|\Psi(t)|^2 = |<x|t>|^2 = |\int dp<x|p><p|t>|^2 = |\int dp<x|p><p|U(t)|0>|^2$. U(t) is the free particle propagator $\exp[-itp^2/2m\hbar]$, which is easily handled in the momentum representation; $<x|p>$ is the plane wave in the momentum representation. Now the Gaussian integral can be done by completing the square.

8. A two-level system Hamiltonian H_0 with energies $E_0 = 0$ and E_1 and eigenstates $|0>$ and $|1>$ is subject to a square EMP (electromagnetic pulse) $\varepsilon(t) = \varepsilon$ (when $0 \leq t \leq t_{pulse}$, $\varepsilon(t) = 0$ otherwise). The interaction Hamiltonian is $H_{Pulse} = \hat{\mu}\varepsilon(t)$, where the transition dipole operator is $\hat{\mu} = |0>\mu<1| + |1>\mu<0|$.

   a. Write the Hamiltonian H_0 and the transition dipole operator $\hat{\mu}$ as a 2x2 matrices. Are both hermitian as they should be?

   b. Compute the transition probability $P_{01}(t) = |c_{01}(t)|^2$ at $t = t_{Pulse}$ as a function of $\omega = (E_1 - E_0)/\hbar$ and μ, using first order time-dependent perturbation theory.

9. a. Solve problem 9 exactly, starting in state $|\Psi(t=0)> = |0>$, using the eigenstates $|0>$ and $|1>$ of H_0 as your basis set. At $t=0$, $P_{00} = |<\Psi(t)|0>|^2 = 1$ and $P_{01} = |<\Psi(t)|1>|^2 = 0$, but later these probabilities will change.

   b. The approximation in 9 says that $P_{01}(t_{Pulse})$ keeps increasing with pulse duration. Based on your exact solution, when does first order time-dependent perturbation theory break down?

   [Hint: The total Hamiltonian $H_0 + H_{Pulse}$ is actually time-independent between $t=0$ and t_{Pulse}. It has its own eigenfunctions $|0'>$ and $|1'>$ which can be expressed in terms of $|0>$ and $|1>$ by unitary transformation. Such eigenfunctions are known as 'dressed states' or 'Floquet states' because they are eigenfunctions in the presence of the external field.]