5.74 Introductory Quantum Mechanics II
Spring 2009

5.74, Problem Set #1
Spring 2009
Due Date: February 19, 2009

1. Functions of operators. Let the eigenfunctions and eigenvalues of an operator $\hat{A}$ be φ_n and a_n respectively: $\hat{A}\varphi_n = a_n\varphi_n$. If $f(x)$ is a function that we can expand in powers of x, show that φ_n is an eigenfunction of $f(\hat{A})$ with eigenvalue $f(a_n)$:

$$f(\hat{A})\varphi_n = f(a_n)\varphi_n$$

2. Displacement operator. Just as $\hat{U}(t,t_0) = \exp\left[-i\hat{H}(t-t_0)/\hbar\right]$ is the time-evolution operator which displaces $\psi(\bar{r},t)$ in time, $\hat{D}(\bar{r},\bar{r}_0) = \exp\left(-i\hat{p}(\bar{r}-\bar{r}_0)/\hbar\right)$ is the spatial displacement operator that moves ψ in space.

    a) Defining $\hat{D}(\lambda) = \exp(-i\hat{p}\lambda/\hbar)$, for a one-dimensional displacement, show that

    $$\hat{D}^\dagger x \hat{D} = x + \lambda$$

    where λ is a displacement vector. The relationship you've seen in 5.73

    $$exp(i\hat{G}\lambda)\hat{A}\ exp(-i\hat{G}\lambda) = \hat{A} + i\lambda\left[\hat{G},\hat{A}\right] + \left(\frac{i^2\lambda^2}{2!}\right)\left[\hat{G},\left[\hat{G},\hat{A}\right]\right] + ...$$
    $$+ \left(\frac{i^n\lambda^n}{n!}\right)\left[\hat{G},\left[\hat{G},\left[\hat{G}...\left[\hat{G},\hat{A}\right]\right]\right]...\right] + ...$$

    will be useful here.

    b) For the ground eigenstate of the one-dimensional harmonic oscillator $|\psi_0\rangle$, show that the wavefunction

    $$|\psi_0 - \lambda\rangle = \hat{D}(\lambda)|\psi_0\rangle$$

    is the same as the wavefunction of the state $|\psi_0\rangle$, only shifted by λ.

    c) In spectroscopy the Franck-Condon factor, I, quantifies the overlap of vibronic levels in ground and excited electronic states. Let's calculate this for overlap between two displaced harmonic oscillators. Specifically, calculate the Franck Condon factor for overlap of a harmonic oscillator with eigenstates $|\psi_n\rangle$ with a displaced harmonic oscillator *in the ground state*. That is:

$$I = \left|\langle \psi_n | \psi_0 - \lambda \rangle\right|^2 = \left|\langle \psi_n | \hat{D}(\lambda) | \psi_0 \rangle\right|^2$$

Evaluate this by expressing D in terms of raising and lowering operators. You will need to make use of the identity $e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}[\hat{A},\hat{B}]}$, which we need if $\hat{A}$ and $\hat{B}$ do not commute but $\left[\hat{A},\hat{B}\right]$ commutes with $\hat{A}$ and $\hat{B}$.

3.   Time-Development of the Density Matrix

The density matrix is an alternate approach to representing the state of a quantum system. It becomes very practical for condensed phase and nonlinear spectroscopy problems. The density matrix ρ is defined as the outer product of the system wavefunction $\rho = |\psi\rangle\langle\psi|$.

a)   If you express the wavefunction as an expansion $|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$, convince yourself that the expectation value of an operator A is written as $\langle A(t)\rangle = Tr\left[A\rho(t)\right]$.

b) Using the time-dependent Schrödinger equation, show that the time-dependence of the density matrix is given by the Liouville-Von Neumann equation:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H,\rho].$$

By deriving this equation, you have also effectively demonstrated that the density matrix in the interaction picture $\rho_I = |\psi_I\rangle\langle\psi_I|$ evolves according to the following equation of motion:

$$\frac{\partial \rho_I}{\partial t} = -\frac{i}{\hbar}[V_I,\rho_I].$$

c) Time-integrate the Liouville-Von Neumann equation from 0 to t, and show that this integral solution for the time-development of ρ is equivalent to $\rho(t) = U\rho(0)U^\dagger$. Likewise in the interaction picture, the solution to the Liouville equation is $\rho_I(t) = U_0 \rho_I(0)U_0^\dagger$.

4. Electronic excitation by electron scattering.

An electron passes by a hydrogen (Z=1) atom with a velocity v in the y direction. At the time of closest approach ($t = 0$), the ion is separated by a distance B (the impact parameter) along the x direction. At any other time, the distance between the atom and electron is

$$R(t) = \sqrt{B^2 + (vt)^2} \qquad (1)$$

As it passes by, the Coulombic interactions with the electron will act to mix the electronic states of the atom, which we will take to be real hydrogen-like wavefunctions.
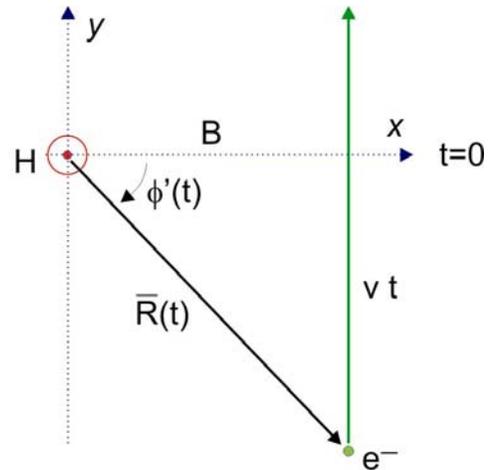
The time dependent Hamiltonian for this problem could be written in terms of the Hamiltonians for the atom and for the electron, as well as a time-dependent interaction between them $H = H_{atom} + H_{electron} + V(t)$. Let's consider how a weak interaction mixes the atomic eigenstates. This is an appropriate picture if $|V(t)| \ll |H_{atom}|$. To just consider the induced changes to the electronic wavefunction of the atom, we will write

$$H = H_{atom} + V(t) \qquad (2)$$

and treat the problem in the interaction picture. We will assume that we prepare the atom at t $= -\infty$ in the 1s orbital [$b_{1s}(-\infty) = 1$] and follow time dependent interactions that couple the 1s state to the n = 2 states. This would hold for relatively large impact parameters, so we will assume that the separation of the free electron from the hydrogen nucleus and the H electron are approximately equal: $R_{pe} \approx R_{ee} = R(t)$. We can take the frame of reference to be the atomic nucleus.

We will get this by directly numerically solving the coupled linear differential equations that describe the time-evolution of b_n, the expansion coefficients in the eigenstates of H_0:

$$\frac{\partial b_m(t)}{\partial t} = \frac{-i}{\hbar} \sum_n b_n(t) e^{-i\omega_{nm}t} V_{mn}(t) \qquad (3)$$

We will write the appropriate form of the Hamiltonian in eq. 2, calculate the matrix elements in V, and then numerically solve eqs. 3.

(a)   Write out an explicit form of the Hamiltonian in eq. 2 in terms of kinetic and potential energies involved. Assume that you can neglect the kinetic energy of the nucleus. Neglect any interactions between the particles other than the Coulomb terms (for instance spin).

(b)   To start, determine the time-dependent matrix elements in the interaction picture Hamiltonian $V_{ab}(t) = \langle a | V(t) | b \rangle$ where $|a\rangle$ and $|b\rangle$ include the n=1 and n=2 (2s, 2px, 2py, 2pz) states.

There are a few ways but the way I did this was as follows: Choose the nucleus as the frame of reference and write the problem in terms of spherical coordinates. Write the hydrogenic wavefunctions in terms of spherical harmonics $|a\rangle = R(r)|\ell m\rangle$. The matrix elements involve an integral over the wavefunctions for the bound electron position, which are described by coordinates (r, θ, ϕ). The position of the free (moving) electron is described by the coordinates $(R(t), \theta', \phi'(t))$. It will be necessary to represent the time-dependent potential in terms of an expansion in spherical harmonics, for which the following expression (from Jackson, Classical Electrodynamics) is very helpful:

$$\frac{1}{\overline{R}(t) - \overline{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{1}{R(t)} \left(\frac{r}{R(t)}\right)^{\ell} Y^*_{\ell m}(\theta', \phi') Y_{\ell m}(\theta, \phi) \qquad (4)$$

Here $\overline{R}(t)$ and $\overline{r}$ are vectors from the nucleus to the electrons, but R(t) and r are scalars.

Evaluate all of the matrix elements. Show their dependence on the impact parameter, the Bohr radius a_0, electron velocity, and time.

(c)   Solve the coupled differential equations for the time-dependent interactions between the electronic states.

This will require numerically solving the set of five coupled first-order linear differential equations that describe the time-evolution of the expansion coefficients for the n=1 and n=2 states. (You can neglect couplings to higher lying states). You will need to numerically integrate the differential equations.

If you are using MathCad, the Runga-Kutta routine for numerically solving differential equations requires real valued numbers to solve the equations. You will need to separate the real and imaginary parts of each equation, giving twice as many coupled differential equations. To see these, expand eq. 3 using $b_k = Re[b_k] + i\, Im[b_k]$, and then separate the real and imaginary variables. (See problem set 0).

Show the time-dependent probabilities of occupying the n=1 and n=2 states, from large negative times to large positive times. You can take the energy of the 1s state to be $E_{n=1}=0$ and the energies of the n=2 states to be $E_{n=2} = 82{,}000$ cm^{-1}. To start, choose B = $2a_0$. Chose what you would call relatively low or high velocities for these parameters. What time point would effectively constitute $t = -\infty$? Discuss the influence of the velocity and impact parameter on the observed time-dependence.

(d)   Make sequential contour plots of the time-dependent electron probability density in the *x-y* plane for several times from t<0 to t>0 to illustrate the behavior.