CHEM 550/475 2005
Homework 2. Due Monday Oct 10 at 5pm in Prof. Ginger's mailbox.
CIRCLE YOUR ANSWERS AND KEY RESULTS
STAPLE YOUR PAPERS TOGETHER

Levine
2.17 – time dependent wave function for a free particle
2.29 – probability concept review
3.5 – basic operator practice
3.15 – commutator identity
3.42 – operator concept review – provide counter-examples for false cases!

Additional Problems:

1) *Why is simple harmonic motion so common in classical mechanics?*
We solved the ODE for the simple harmonic oscillator (mass on a spring) in class last week, we will solve the quantum version next week. In the meantime, why do you think so many classical systems exhibit simple harmonic motion? We derived the equation of motion based on a Hooke's law restoring force (i.e. F=-k*x), however, we can also see this results from any harmonic potential.

a) Since $F = -\nabla \cdot V$ for any conservative force, what kind of potential function leads to a Hooke's law like restoring force and resulting simple harmonic motion?
b) Take any arbitrary potential that we will call *U(x)*. Write out the Taylor expansion for U(x) about a local minimum x_0.
c) Thus, from b) what kind of motion can be expected for sufficiently small displacements from the local potential minimum? *What do we mean by "sufficiently small displacements"?*

2) *Do Levine problem 2.15 for a longer molecule and compare with the butadiene result from Levine 2.15 (you don't need to work the butadiene problem if you are familiar with it):*

a) γ-Carotene, one of the precursors of vitamin A, is a conjugated system containing 11-double bonds (you will need to calculate the total bond length). Calculate the wavelength of light needed to excite the HOMO-LUMO transition of the pi electrons for carotene using the simple free electron model. Compare the calculated value with the observed transition at 460 nm.

b) Explain why the 'free electron model' gives an error for butadiene?
Hint: do electrons attract or repel one another?

3) ***Nonstationary states for a particle in a box***

Consider a particle in an infinite square well of width *L*. Initially, (at *t*=0) the system is described by a wavefunction that is equal parts a ***superposition*** of the ground and first excited states. In other words, the time zero wavefunction is:

$$\Psi(x,0) = C[y_1(x) + y_2(x)]$$

a) Find *C* so that the wavefunction is normalized.

b) Write the time-dependent wave function $\Psi(x,t)$ for any later time *t*

c) Show that this superposition is *not* a stationary state (i.e. show that $|\psi|^2$ evolves in time). Then use Maple to animate a plot of $|\psi|^2$ as a function of *t*

d) If many systems are prepared in this state and their energies are measured, what will the result be? ***Discuss both the average of these measurements, and discuss the statistics of the specific results of a series of individual measurements.***

e) Find <x> and <p> as a function of *t* for this superposition state

4) ***Particle in the FINITE box:*** *(read the handout first)*

As promised, move from the idealized INFINITE walled box, to the FINITE walled box. Consider a box of width ***a***, *centered at the origin*. Instead of rising to infinity outside the box, the potential is now V_0.

a) Given a=1.0 nm, and $V_0=1.2\text{x}10^{-18}$ J Determine the lowest 5 energy levels for an electron placed into this box. What is the wavelength of the electron in each of these 5 states. Compare this electron wavelength with the wavelengths of an electron placed in the lowest 5 energy levels of an infinite box of the same width.

b) Repeat the calculation for a box of width 0.9 nm and depth $5\text{x}10^{-19}$ J. For these parameters will there be fewer or more bound states than for those in part a? How many allowed energy levels are there and what are their energies?

5) Free-particle wave packets:

The wave-functions for the free particle with well-defined momentum (momentum operator eigenfunctions) tell us nothing about the position of the particle. We would like to construct wave-functions for a free particle which also contain some position information. We know we can create new wavefunctions from a linear superposition of any set eigenfunctions, we use momentum eigenfunctions as our basis below. We consider a "free" electron that has kinetic energy of roughly ~ 100 eV traveling in towards the right.

a) Write down the wave function, and Plot Re(ψ) and $|\psi|^2$ over the range x=-5 to +5 Angstroms for an electron with KE=100 eV traveling to the right.

b) Plot Re(ψ) and $|\psi|^2$ over the range x=-5 to +5 Angstroms for the linear superposition of 3 free-particle momentum eigenfunctions with different discrete values of p, p=.95*p0, p=p0, and p=1.05*p0. You should choose the values of the coefficients so that <p> is still p0 (i.e. for a 100 eV electron).

c) Expand the graph axis from 5b to cover –10 to 10 Angstroms. **Comment**.

You may have noticed that this approach will only get us so far, even if you take an infinite sum. You see the free particle wavefunctions do not have discrete eigenvalues—*any* value of *k* is allowed. Our Fourier series expansions dealt with sums of *discrete* eigenvalues (say finite multiples of sin(n*Pi*x/L) for the classical wave on a string). However, we can still use a version of a Fourier series when dealing with a continuum spectrum of eigenvalues. As you may have guessed, the Fourier series sum then has to go over to an integral as the sum becomes one over an infinite number of eigenfunctions with infinitesimal differences between each.

We DEFINE G(k) as the complex Fourier transform of the function f(x) as (note the "normalization" constant for the FT and its inverse are different in many textbooks, but the product is always 1/2Pi):

$$G(k) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} f(x)e^{ikx}dx$$

We can then represent the function f(x) as an integral over possible e^{ikx} functions, with the *G(k)* carrying the "weights" just as the An and Bn coefficients carried the weights in the Fourier sine and cosine series.

$$f(x) = \int_{-\infty}^{\infty} G(k)e^{ikx}dk$$

(Another way to think about a Fourier transform is as an operation that converts a function from one basis (domain) to another conjugate domain. Position and wavenumber (x,k) form one conjugate pair, time and frequency form another conjugate pair). Fourier transform methods are ubiquitous in the sciences. A Fourier transform is exactly what your FTIR spectrometer performs when it converts its interferometer data (intensity versus interferometer path length [position]) to wavenumber to display your IR spectrum). FT-NMR is also a routine technique.

d) Assume the wavefunction for our particle is given by a Gaussian wavepacket the form $\psi(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-x^2/2\sigma^2}$ with a width σ=1 Angstrom. Plot this wave function for x=-10 to x=+10 Angstroms. (from this point on, we will let the particle have <p>=0 and <x>=0 for simplicity).

e) Use the Fourier Transform relationships given in part *c* to compute the distribution of wavevectors *k* needed to create this wavefunction. Plot G(k) for k=-10E10 to 10E10 reciprocal meters (1/10 angstroms to 1/10 Angstroms).

f) Repeat d and e for a width sigma of 0.25 Angstroms. Compare the result with that in d and e. Interpret this result in the context of your understanding of the postulates and of Heisenberg’s uncertainty principle.

g) Though they exist, we haven’t yet introduced a position eigenfunction. What do you think are the properties of a “position eigenfunction”? Do you know of any functions with such properties?