

**CIRCLE YOUR ANSWERS AND KEY INTERMEDIATE RESULTS**

**USE MAPLE WHENEVER POSSIBLE**

**STAPLE YOUR PAPERS TOGETHER**

**INCLUDE ALL COMPUTER PRINTOUTS (with commentary)**

**Levine Problems (5<sup>th</sup> Ed in parenthesis) 6<sup>th</sup> Ed**

**(3.31) 3.36** – Probabilities for particles in a 3D box

**(3.36) 3.42** – Degeneracy and 3D box levels

**Additional Problems**

1) Consider a particle in an infinitely deep *two-dimensional* square well with sides of length  $L$ .

- What are the five lowest allowed energy levels for this system.
- Use the computer to make 3D plots that display the probability of finding the particle as a function of position within the box.
- Compare the wave functions associated with any one pair of degenerate states.

2) Tunneling is important to many chemical processes, for instance, electrons tunnel during many redox reactions and protons can tunnel during acid/base reactions. On a relative scale (e.g. compared to electron tunneling and proton tunneling), how important do you think carbon atom tunneling is to organic reactions, on the whole? *Give a qualitative justification of your answer in writing.* Next, **justify your answer quantitatively by comparing the relative tunneling rates for an electron, proton, and carbon atom across a rectangular potential barrier 1 Angstrom wide, with height of 1 eV.** Assume that the kinetic energy of each particle is 0.5 eV. Ultimately the relative importance of different processes depends on the rate of competing processes and it is true that for some reactions (the automerization of 1,3-cyclobutadiene, the ring expansion of 1-methylcyclobutylefluorcarbene) carbon tunneling plays a central role.

3) The amount of current flowing in an electrochemical cell between a gold electrode that has been modified with a straight-chain alkanethiol self-assembled monolayer (e.g. HS-(CH<sub>2</sub>)<sub>n</sub>-CH<sub>3</sub>) and a redox-active species in solution is measured as function of the length of the aliphatic chain. It is found empirically that the current as a function of carbon chain length,  $L$ , can be given by the equation:  $I=I_0\exp(-B*L)$  where  $B$  is a constant equal to approx = 1/Angstrom. **Explain.** Assuming the electrons have the same effective mass as the free electron, **calculate the barrier height.**

4) Consider the particle in a 1D box of length  $L$  with ends at  $x=0$  and  $x=L$ . The state

function at one point in time is:  $\psi(x) = \sqrt{\frac{30}{L^5}}x(L-x)$ .

- If the energy of this particle is measured, what is the probability that the measurement will return the value  $E=h^2/(8mL^2)$ ?

b) If the energy of this particle is measured, what is the probability that the measurement will return the value  $E=49h^2/(8mL^2)$ ?

c) If the energy is measured to be  $E=49h^2/(8mL^2)$  and then *the energy of the same particle* is quickly measured a second time, what energy will the second measurement return?

### 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  $\sim 100$  eV traveling in towards the right.

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

b) Plot  $\text{Re}(\psi)$  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  $p$ ,  $p=.95*p_0$ ,  $p=p_0$ , and  $p=1.05*p_0$ . You should choose the values of the coefficients so that  $\langle p \rangle$  is still  $p_0$  (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  $\sin(n*\text{Pi}*x/L)$  for the classical wave on a string). However, we can still use a version of a Fourier series when dealing with *a continuous 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  $1/2\text{Pi}$ ):

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

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  $A_n$  and  $B_n$  coefficients carried the weights in the Fourier sine and cosine series.

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

(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 of the form  $\psi(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2}$  with a width  $\sigma=1$  Angstrom. Plot this wave function for  $x=-10$  to  $x=+10$  Angstroms. (from this point on, we will let the particle have  $\langle p \rangle = 0$  and  $\langle x \rangle = 0$  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) We haven’t yet introduced a position eigenfunction. What properties would a “position eigenfunction” have? Do you know of any functions with such properties?