

Homework 3. Due **Tuesday Oct 19** by **Noon** in Prof. Ginger's mailbox. *Page 1/2*

CIRCLE YOUR ANSWERS AND KEY INTERMEDIATE RESULTS

USE MAPLE WHENEVER POSSIBLE

STAPLE YOUR PAPERS TOGETHER

INCLUDE ALL COMPUTER PRINTOUTS (with commentary)

Levine Problems (5th Ed in parenthesis) 6th 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 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: $\psi(x) = \sqrt{\frac{30}{L^5}}x(L-x)$.

a) 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 that same particle* is quickly measured a second time, what energy will the second measurement return?

2) 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-(CH₂)_n-CH₃) 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 effective barrier height** (difference between the electron kinetic energy and the top of the barrier).

4) 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 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?