CIRCLE YOUR ANSWERS AND KEY INTERMEDIATE RESULTS
USE MAPLE WHENEVER POSSIBLE
STAPLE YOUR PAPERS TOGETHER
INCLUDE ALL COMPUTER PRINTOUTS (with commentary)

Levine Problems

3.31 – Probabilities for particles in a 3D box

3.36 – Degeneracy and 3D box levels

4.29 Morse Potential – also: **c)** Given that D_e = 7.31E-19 J/molecule, and a=1.82E10 m^{-1} for HCl, calculate the force constant *k* for the HCl bond. Plot the Morse Potential for HCl and the corresponding Harmonic oscillator potential on the same graph.
d) for what displacements from equilibrium is the harmonic oscillator (HO) potential a good approximation (say within 90%) of the Morse potential?
e) For what physical situations would the HO potential yield a poor approximation to the actual potential?

Additional Problems

1) Consider a particle in an infinitely deep *two-dimensional* square well with sides of length *L*.
a) What are the five lowest allowed energy levels for this system.
b) Use the computer to make 3D plots that display the probability of finding the particle as a function of position within the box.
c) 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, 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) In lecture we derived the density of states for particle in a 3D box as:

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$, *starting with an approximation for the number of states with*

$nx^2 + ny^2 + nz^2 \leq n^2$ *as a function of n.* Test this starting approximation by writing a program or routine in Maple (or C or Fortran or Basic or Labview or whatever) to calculate the ACTUAL number of levels below the energy corresponding to a given n

and it to the formula (and calculate % error of the formula) for values of n from n=1 to n=200 (i.e. n^2=1 to 400000).

4) The amount of current flowing in an electrochemical cell between a gold electrode that has been modified with a straight-chain alkylthiol self-assembled monolayer (e.g. HS-$(CH_2)_n$-CH_3) 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**.

5) 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: $\psi(x) = \sqrt{\dfrac{30}{L^5}}x(L-x)$.

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

6) According to Bohr's Correspondence principle, our quantum calculation and a classical calculation must give the same answer when predicting the probability of finding the end of the spring-mass harmonic oscillator at a certain point. Test this. Plot $|\psi|^2$ for the first few levels of the H.O. Use your favorite computer package [Maple] to plot $|\psi|^2$ for large values of n. Compare this with the classical 'probability distribution' for the position of the harmonic oscillator (e.g. the fraction of time a particle oscillating with amplitude A spends at given point x is $f(t)dt = \dfrac{dx}{2\pi\sqrt{A^2 - x^2}}$