CHEM 550/475 2008

Homework 2. **Due Tues Oct 7 at 5pm** in Prof. Ginger's mailbox. *Page 1/2*

CIRCLE YOUR ANSWERS AND KEY RESULTS

STAPLE YOUR PAPERS TOGETHER

Levine 5th Ed

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 – you should provide counter-examples for false cases!
(plus 3.42(o) "Every function of x,y, and z has the form f(x)g(y)h(z)")

Levine 6th Ed

2.18 – time dependent wave function for a free particle
2.30 – probability concept review
3.8 – basic operator practice
3.13 – commutator identity
3.50 – operator concept review – you should provide counter-examples for false cases!

Additional Problems:

1) Why is simple harmonic motion so common in classical mechanics?

a) Since $F = -\nabla V$ 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 *V(x)*. Write out the Taylor expansion for V(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"?*

d) 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, explain why you think so many classical and quantum exhibit simple harmonic motion. In other words, why are harmonic potentials encountered so often? (Hint: look at a-c above!)

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 yourself). Calculate the wavelength of light needed to excite the HOMO-LUMO transition of the pi electrons for carotene using the simple 1D free electron model. Compare the calculated value with the experimental value for the observed transition at 460 nm.

b) Explain why the 'free electron model' gives such an error for carotene?
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:

$$\Psi(x,0) = C[\psi_1(x) + \psi_2(x)]$$

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 analytically that this superposition is *not* a stationary state (i.e. show that $|\psi|^2$ is a function of 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? ***Give both the average of these measurements, and the statistics of the specific results of a series of individual measurements that lead to this average.***

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. (is it longer or shorter?) (circle your answers!)*

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? (circle your answers)*

This material is taken from the CHEM 455 lecture notes on "Quantum Chemistry and Spectroscopy" by Tom Engel

We describe the potential by

$$V(x)=V_0 \quad x\leq -\frac{a}{2} \qquad \text{Region I}$$

$$V(x)=0 \quad -\frac{a}{2}<x<\frac{a}{2} \quad \text{Region II}$$

$$V(x)=V_0 \quad x\geq \frac{a}{2} \qquad \text{Region III}$$

The eigenfunctions must have the following form in these three regions

$$\psi(x)=Be^{+\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x}+B'e^{-\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x}=Be^{+\kappa x}+B'e^{-\kappa x} \qquad \text{Region I}$$

$$\psi(x)=C\sin\sqrt{\frac{2mE}{\hbar^2}}\,x+D\cos\sqrt{\frac{2mE}{\hbar^2}}\,x=C\sin k\,x+D\cos k\,x \qquad \text{Region II}$$

$$\psi(x)=A\,e^{-\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x}+A'\,e^{+\sqrt{\frac{2m(V_0-E)}{\hbar^2}}\,x}=A\,e^{-\kappa x}+A'\,e^{+\kappa x} \qquad \text{Region III}$$

Here we apply the condition that 1) the wavefunction must be normalizable 2) the wave function must be continuous, and 3) the wavefunction must have a continuous first derivative

In order that the wave functions remain finite at large positive and negative values of x, $A'=B'=0$. There is an additional condition that must be satisfied. To have physically meaningful solutions for the eigenfunctions, the wave functions in the separate regions must have the same amplitude and derivatives at the values of $x = a/2$ and $x = -a/2$ bounding the regions. This restricts the possible values for the coefficients *A*, *B*, *C*, and *D*. Show that applying these conditions gives the equations

$$Be^{-\kappa\frac{a}{2}}=-C\sin k\frac{a}{2}+D\cos k\frac{a}{2} \qquad B\kappa e^{-\kappa\frac{a}{2}}=Ck\cos k\frac{a}{2}+Dk\sin k\frac{a}{2}$$

$$Ae^{-\kappa\frac{a}{2}}=C\sin k\frac{a}{2}+D\cos k\frac{a}{2} \qquad -A\kappa e^{-\kappa\frac{a}{2}}=Ck\cos k\frac{a}{2}-Dk\sin k\frac{a}{2}$$

These two pairs of equations differ on the right side only by the sign of one term. We can obtain a set of equations that contain fewer coefficients by adding and subtracting each pair of equations to give

$$(A+B)e^{-\kappa\frac{a}{2}}=2D\cos\left(k\frac{a}{2}\right) \qquad (A-B)e^{-\kappa\frac{a}{2}}=2C\sin\left(k\frac{a}{2}\right)$$

$$(A+B)\kappa e^{-\kappa\frac{a}{2}}=2Dk\sin\left(k\frac{a}{2}\right) \qquad -(A-B)\kappa e^{-\kappa\frac{a}{2}}=2Ck\cos\left(k\frac{a}{2}\right)$$

At this point we notice that by dividing the equations in each pair, we can eliminate the coefficients to give

$$\kappa=k\tan\left(k\frac{a}{2}\right) \quad \text{or} \quad \sqrt{\frac{2m(V_0-E)}{\hbar^2}}=\sqrt{\frac{2mE}{\hbar^2}}\tan\left(\sqrt{\frac{2mE}{\hbar^2}}\frac{a}{2}\right) \text{ and}$$

) continued

Notice that we don't get E as a nice function of anything. If fact, this is a *transcendental* equation – one that does not have an analytical solution for E. *In general you will find that most 'real' potentials don't have analytical solutions.*

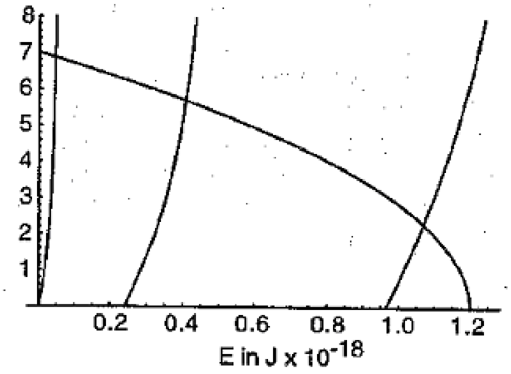
$$-\kappa = k \operatorname{cotan}\left(k\frac{a}{2}\right) \quad \text{or} \quad -\sqrt{\frac{2m(V_0-E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}}\cot\left(\sqrt{\frac{2mE}{\hbar^2}}\frac{a}{2}\right)$$

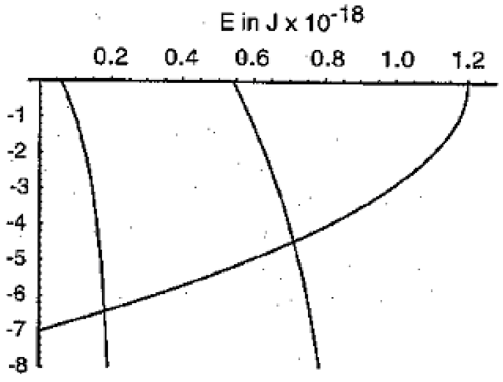
Multiplying these equations on both sides by $a/2$ gives us dimensionless parameters and our final equations are

$$\sqrt{\frac{m(V_0-E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}}\tan\sqrt{\frac{mEa^2}{2\hbar^2}} \quad \text{and}$$

$$-\sqrt{\frac{m(V_0-E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}}\cot\sqrt{\frac{mEa^2}{2\hbar^2}}$$

The allowed energy values E must satisfy these equations. They can be obtained by graphing the two sides of each equation against E. The intersections of the two curves are the allowed energy eigenvalues. For the parameters in the caption of figure 5.1, $V_0 = 1.20 \times 10^{-18}$ J and $a = 1.00 \times 10^{-9}$ m, we obtain the two graphs shown below.





There are five allowed energy levels at 4.61×10^{-20} J, 4.09×10^{-19} J, and 1.07×10^{-18} J (left figure), and 1.84×10^{-19} J and 7.13×10^{-19} J (right figure).

a) Given these values, calculate λ for each energy level. Is the relation $\lambda = \frac{2a}{n}$ (for n an integer) that arose from the calculations on the infinitely deep box still valid? Compare the λ values with the corresponding energy level in the infinitely deep box. Explain why the differences arise.

b) Repeat this calculation for $V_0 = 5.00 \times 10^{-19}$ J and $a = 0.900 \times 10^{-9}$ m. Do you think that there will be fewer or more bound states than for the problem we just worked out? How many allowed energy levels are there for this well depth and what is the energy corresponding to each level?