

Due Tuesday Oct 13 by noon in Ginger's mailbox

CIRCLE YOUR ANSWERS AND KEY RESULTS

STAPLE YOUR PAPERS TOGETHER

Levine 6th Ed

2.15 – crude free electron model of butadiene

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?

- 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?
- Take any arbitrary potential that we will call $V(x)$. Write out the Taylor expansion for $V(x)$ about a local minimum x_0 .
- 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"?*
- 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) 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:

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

- Find C so that the wavefunction is normalized.
- Write down the time-dependent wave function $\Psi(x, t)$ for any later time t
- 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
- 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.***
- Find $\langle x \rangle$ and $\langle p \rangle$ as a function of t for this superposition state

4) **Particle in the FINITE box:** (read Levine and the Maple worksheet first—see the attached handout for an additional approach)

The conceptual approach is almost identical to the infinite box case, but the algebra is a bit more tedious so use a computer if you can. Consider a box of width a . Instead of rising to infinity outside the box, the potential of the “walls” is now V_0 .

a) Given the width of the box $a=1.0$ nm, and the height of the box $V_0=1.2 \times 10^{-18}$ 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) If instead the box width was 0.9 nm and depth of the well was 5×10^{-19} J, answer (qualitatively only, no calculation needed): *will there be fewer or more bound states than for those in part a?*

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

We describe the potential by

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

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

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

The eigenfunctions must have the following form in these three regions

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

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

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

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

$$\begin{aligned} B e^{-\kappa \frac{a}{2}} &= -C \sin k \frac{a}{2} + D \cos k \frac{a}{2} & B \kappa e^{-\kappa \frac{a}{2}} &= C k \cos k \frac{a}{2} + D k \sin k \frac{a}{2} \\ A e^{-\kappa \frac{a}{2}} &= C \sin k \frac{a}{2} + D \cos k \frac{a}{2} & -A \kappa e^{-\kappa \frac{a}{2}} &= C k \cos k \frac{a}{2} - D k \sin k \frac{a}{2} \end{aligned}$$

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

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

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

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

) continued

Notice that we don't get E as a nice function of anything. In 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.

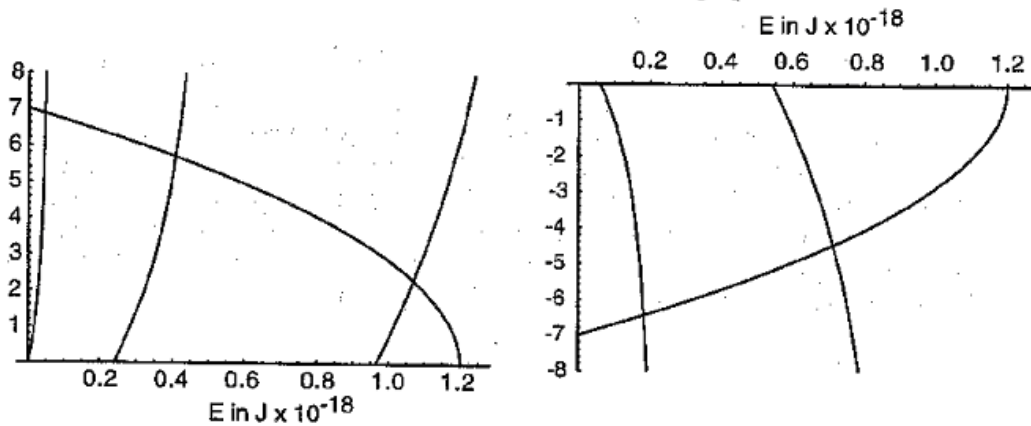
$$-\kappa = k \cotan\left(k \frac{a}{2}\right) \quad \text{or} \quad -\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} \cot\left(\sqrt{\frac{2mE}{\hbar^2}} \frac{a}{2}\right)$$

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?