C455A –Quantum Chemistry and Spectroscopy
Midterm 1 Version 2
April 21, 2006
Exams will be collected promptly at **9:20:00 am**
1 8.5x11" page of notes is allowed

-SIT IN ASSIGNED SEAT
-ALL ANSWERS MUST BE IN THE ANSWER BOXES
-CROSSED OUT/PARTIALLY ERASED WORK WILL BE IGNORED
-NO PARTIAL CREDIT ON NUMERICAL PROBLEMS WITHOUT A FORMULA
-NO PARTIAL CREDIT ON "PHYSICALLY IMPLAUSIBLE" ANSWERS UNLESS THE ERROR IS RECOGNIZED BY THE STUDENT
-SHOW ALL WORK

Your name: Key

Student ID#: ____________________
I have neither received not provided assistance of any kind on this exam.

Signature: ____________________

In the following, u and v are functions of x, and a and n and m are real numbers

$$\int u\,dv = uv - \int v\,du$$
$$\int x^n dx = \frac{x^{n+1}}{n+1} \text{ except } n=-1$$
$$\int \frac{dx}{x} = \ln x$$
$$\int e^{ax} dx = \frac{1}{a} e^{ax}$$
$$\int (\sin ax)\,dx = -\frac{1}{a}\cos ax$$
$$\int (\cos ax)\,dx = \frac{1}{a}\sin ax$$
$$\int (\sin^2 ax)\,dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax$$
$$\int (x\sin^2 ax)\,dx = \frac{x^2}{4} - \frac{\cos 2ax}{8a^2} - \frac{x\sin 2ax}{4a}$$
$$\int (\cos^2 ax)\,dx = \frac{1}{2}x + \frac{1}{4a}\sin 2ax$$
$$\int (x^2\sin^2 ax)\,dx = \frac{1}{6}x^3 - \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax - \frac{1}{4a^2}x\cos 2ax$$
$$\int (x^2\cos^2 ax)\,dx = \frac{1}{6}x^3 + \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax + \frac{1}{4a^2}x\cos 2ax$$
$$\int x^m e^{ax} dx = \frac{x^m e^{ax}}{a} - \frac{m}{a}\int x^{m-1}e^{ax} dx$$
$$\int \frac{e^{ax}}{x^m} dx = -\frac{1}{m-1}\frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1}\int \frac{e^{ax}}{x^{m-1}} dx$$
$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cdot\sin\left(\frac{m\pi x}{a}\right)dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cdot\cos\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{nm}$$
$$\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right]\cdot\left[\cos\left(\frac{n\pi x}{a}\right)\right]dx = 0$$
$$\int_0^\pi \sin^2 mx\,dx = \int_0^\pi \cos^2 mx\,dx = \frac{\pi}{2}$$
$$\int_0^\infty \frac{\sin x}{\sqrt{x}}dx = \int_0^\infty \frac{\cos x}{\sqrt{x}}dx = \sqrt{\frac{\pi}{2}}$$
$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (a>0, \text{ n positive integer})$$
$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}} \quad (a>0, \text{ n positive integer})$$
$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad (a>0, \text{ n positive integer})$$
$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a}\right)^{1/2}$$

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}$$
$$\frac{d}{dx}\frac{u}{v} = \frac{1}{v}\frac{du}{dx} - \frac{u}{v^2}\frac{dv}{dx}$$
$$\frac{d}{dx}(u^n) = nu^{n-1}\frac{du}{dx}$$
$$\frac{d}{dx}\left(\frac{1}{u^n}\right) = -\frac{n}{u^{n+1}}\frac{du}{dx}$$
$$\frac{d}{dx}[f(u)] = \frac{d}{du}[f(u)]\cdot\frac{du}{dx}$$

$$\frac{d}{dx}(u^n v^m) = u^{n-1}v^{m-1}\left(nv\frac{du}{dx} + mu\frac{dv}{dx}\right)$$

$$\frac{d}{dx}(e^u) = e^u\frac{du}{dx}$$
$$\frac{d\sin x}{dx} = \cos x$$
$$\frac{d\cos x}{dx} = -\sin x$$
$$\frac{d\sin u}{dx} = \frac{du}{dx}\cos u$$
$$\frac{d\cos u}{dx} = -\frac{du}{dx}\sin u$$

$$\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

Total Points: 100

Question 1:_________/21

Question 2:_________/27

Question 3:_________/28

Question 4:_________/24

Total: _____________/ 100

Potentially Useful Information:

Workfunctions of Metals:

Al	4.28 eV
Au	5.1 eV
Ca	2.87 eV
Li	2.3 eV
Na	2.28 eV

Spin Operators and Eigenfunctions:

$$S_z\alpha = \tfrac{\hbar}{2}\alpha$$

$$S_z\beta = \tfrac{\hbar}{2}\beta$$

$$S_y\alpha = i\tfrac{\hbar}{2}\beta$$

$$S_y\beta = -i\tfrac{\hbar}{2}\alpha$$

$$S_x\alpha = \tfrac{\hbar}{2}\beta$$

$$S_x\beta = \tfrac{\hbar}{2}\alpha$$

$$S^2\alpha = \tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2\alpha$$

$$S^2\beta = \tfrac{1}{2}(1+\tfrac{1}{2})\hbar^2\beta$$

Values of Some Physical Constants

Constant	Symbol	Value
Atomic mass constant	*amu*	$1.660\,5402 \times 10^{-27}$ kg
Avogadro constant	N_A	$6.022\,1367 \times 10^{23}$ mol^{-1}
Bohr magneton	$\mu B = eh/2m_e$	$9.274\,0154 \times 10^{-24}$ J · T^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0^2/r_e e^2$	$5.291\,772\,49 \times 10^{-11}$ m
Boltzmann constant	k_B	$1.380\,658 \times 10^{-23}$ J · K^{-1}
		0.695 038 cm^{-1}
Electron rest mass	m_e	$9.109\,3897 \times 10^{-31}$ kg
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ · m^3 · kg^{-1} · s^{-2}
Molar gas constant	R	8.3145101 J · K^{-1} · mol^{-1}
		0.083 1451 dm^3 · bar K^{-1} · mol^{-1}
		0.082 0578 dm^3 · atm K^{-1} · mol^{-1}
Molar volume, ideal gas		
(one bar, 0^0C)		22.711 08L · mol^{-1}
(one atm, 0^0C)		22.414 09 L · mol^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,7866 \times 10^{-27}$ J · T^{-1}
Permittivity of vacuum	ε_0	$8.854\,187\,816 \times 10^{-12}$ C^2 · J^{-1} · m^{-1}
	$4\pi\varepsilon_0$	$1.112\,650\,056 \times 10^{-10}$ C^2 · J^{-1} · m^{-1}
Planck constant	h	$6.626\,0755 \times 10^{-34}$ J · s
	$\hbar$	$1.054\,572\,66 \times 10^{-34}$ J · s
Proton charge	e	$1.602\,177\,33 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\,221\,28 \times 10^{8}$ s^{-1} · T^{-1}
Proton rest mass	m_p	$1.672\,6231 \times 10^{-27}$kg
Rydberg constant (Bohr)	$R_\infty = m_e e^4/8\varepsilon_0^2 h^2$	$2.179\,8736 \times 10^{-23}$ J
		109 737.31534 cm^{-1}
Rydberg constant for H	R_H	109677.581 cm^{-1}
Speed of light in vacuum	c	299 792 458 m · s^{-1} (defined)
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4/15h^3c^2$	$5.670\,51 \times 10^{-8}$ J · m^{-2} : K^{-4} · s^{-1}

1) Back to Basics (21 points)

A) The European Union has developed the "Teramobil" system, a terawatt laser mounted in a mobile truck platform. This laser has a peak power of 5×10^{12} W at a wavelength of 800 nm. How many photons are contained in a short 70×10^{-12} s burst from the Teramobil laser?

$$5\times10^{12}\ \mathrm{J/s} \times 70\times10^{-12}\ \mathrm{s} = 350\ \mathrm{J} \times \frac{1\ \text{photon}}{2.48\times10^{-19}\ \mathrm{J}} = 1.41\times10^{21}\ \text{photons}$$

$$E_{photon} = \frac{hc}{\lambda} = \frac{1240\ \mathrm{eV\,nm}}{800\ \mathrm{nm}} \times 1.6\times10^{-19}\ \mathrm{J/eV} = 2.48\times10^{-19}\ \mathrm{J/photon}$$

+7

Photons/burst:
1.41×10^{21} photons

1B) A frequency tripled YAG laser with a wavelength of 354.7 nm and a power of 3 mW is directed at a clean sodium surface in a vacuum. What is the maximum speed of an ejected photoelectron?

$$KE = \tfrac{1}{2}mv^2 = E_{photon} - \phi_{metal} = \left(\frac{1240\ \mathrm{nm\text{-}eV}}{354.7\ \mathrm{nm}} - 2.28\,\mathrm{eV}\right) 1.6\times10^{-19}\ \mathrm{J/eV}$$

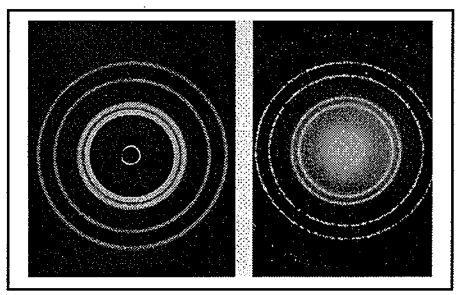
$$= 1.94\times10^{-19}\ \mathrm{J}$$

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{1.94\times10^{-19}\ \mathrm{J}\times 2}{9.11\times10^{-31}\ \mathrm{kg}}} = 6.53\times10^{5}\ \mathrm{m/s}$$

+7

Speed:
6.53×10^{5} m/s

1C) Shown at right are two identical diffraction patterns taken by passing an x-ray beam (left) and an electron beam (right) through a very thin Al foil in the exact same geometry for both beams. If the x-rays have an energy of 8.04 keV, what is the kinetic energy of the electrons used to make the diffraction pattern (in eV)?



Same diffraction pattern $\Rightarrow$ same wavelength

$$\lambda_{x\text{-ray}} = \frac{hc}{E} = \frac{1240\ \mathrm{eV\text{-}nm}}{8040\ \mathrm{eV}} = 0.154\ \mathrm{nm}$$

+7

$$\lambda_{e^-} = \frac{h}{p} = 0.154\times10^{-9}\ \mathrm{m} = \frac{6.626\times10^{-34}\ \mathrm{J\text{-}s}}{p} \Rightarrow p = 4.30\times10^{-24}\ \mathrm{kg\ m/s}$$

$$E = \frac{p^2}{2m} = \frac{(4.3\times10^{-24}\ \mathrm{kg\ m/s})^2}{2\cdot 9.11\times10^{-31}} = 1.01\times10^{-17}\ \mathrm{J}\times\frac{1\,\mathrm{eV}}{1.6\times10^{-19}} =$$

Energy:
63.5 eV

2) Particle in a box (~~28~~ 27 Pts). An electron confined to an infinitely deep 1-dimensional box 2 nm long has the following wave function:

$$\psi(x) = C[\phi_2(x) + 2i\phi_4(x) - 3\phi_6(x)]$$

Where, as usual, ϕ_n denotes the n[th] normalized energy eigenfunction for the particle in a box with energy E_n.

A) Is this wave function normalized? If not, find the normalization constant C that normalizes this wave function.

$$\underbrace{\int \psi^* \psi = 1}_{+1} = c^2(1^2 + 2^2 + 3^2)$$

sum of squared coeff must = 1

$$c^2 = \frac{1}{14}$$

+6

$$C = \frac{1}{\sqrt{14}}$$

Normalized (yes/no)?: NO +1
C= (if not normalized)?: $C = \frac{1}{\sqrt{14}}$

B) What is the probability of measuring the electron energy to be *E=0.85 eV* for the electron with this wave function?

$$E = 0.85\,eV \; (1.36\times10^{-19} J) = \frac{n^2 h^2}{8mL^2} = \frac{n^2 (6.626\times10^{-34}\ J\text{-}s)}{8(9.11\times10^{-31})(2\times10^{-9}\ nm)^2}$$

$$n^2 = 9 \qquad n=3 \quad +2$$

+7

$$n=3$$

$P(E_3) = |c_3|^2$

coefficient of ϕ_3 in $\psi(x)$ is $\emptyset$

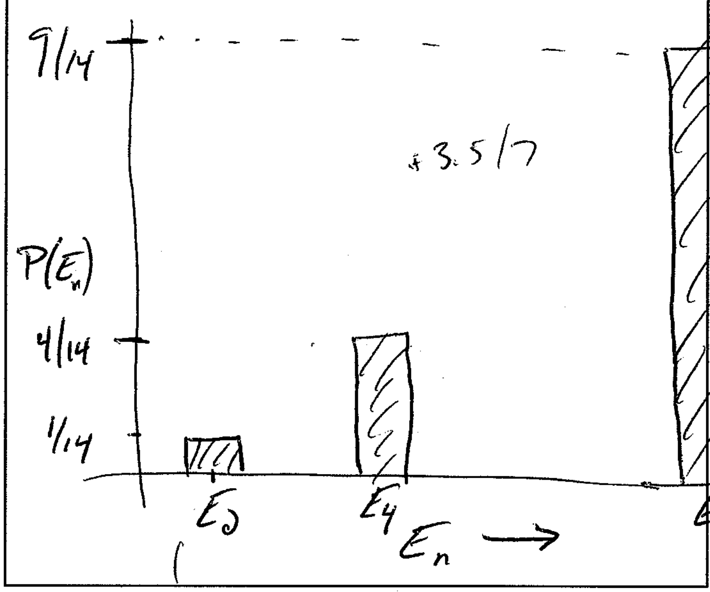
$$\Rightarrow P(E_3) = 0$$

P(E=0.85eV)=?: 0

2) Particle in a box (cont.).

2C) Draw a histogram (bar graph) with the y-axis being probability, and the x-axis being energy that summarizes the results you'd get from experimentally measuring the energy for many identical systems with above wavefunction. (In other words, graphically show—and label your graph—what the odds of measuring E_1, E_2...etc. are). What is the expectation value for the energy?

Draw graph here:



+7

$P(E_n) \propto |C_n|^2$

$\langle E\rangle =$

$\frac{1}{14} E_2 + \frac{4}{14} E_4 + \frac{9}{14} E_6 =$

$\frac{1}{14} 4E_1 + \frac{4}{14} 16E_1 + \frac{9}{14} 36E_1$

$= 28 \; E_1$ $\qquad E_1 = 0.094$ eV (from 2B)

$=$

+3.5/7

<E>= $2.64\,eV \cdot 4.23\times10^{-19}\,J$

2D) What will the average value for the position of the particle (i.e. <x>) if the ends of the box are at x=–1 nm and x=+1 nm (For credit you should set up then evaluate the appropriate integral by hand, and you must get the right answer for the right reasons).

$$\langle x\rangle = \int_{-L/2}^{+L/2} \psi^*\psi = \frac{1}{14}\int_{-L/2}^{+L/2} (\phi_2 - 2i\phi_4 - 3\phi_6)\, x\, (\phi_2 + 2i\phi_4 - 3\phi_6)\,dx$$

+1 pc

$$= \frac{1}{14}\int_{-L/2}^{L/2} \phi_2^2 x + \cancel{2i\phi_2\phi_4 x} - 3\phi_6\phi_2 x - \cancel{2i\phi_2\phi_4 x} + \cancel{6i\phi_4\phi_6 x} - 3\phi_6\phi_2 x - \cancel{6i\phi_4\phi_6 x} + 9\phi_6^2 x$$

+7

$+$

$$= \frac{1}{14}\int_{-L/2}^{L/2} \phi_2^2 x - 6\phi_6\phi_2 x + 9\phi_6^2 x + 4\phi_4^2 x\,dx$$

all ϕ_n^2 are even $\quad \phi_6\phi_2$ = even and x = odd about center of box $\Rightarrow$ even × odd =

<x>= 0 +1

6 5 5 6 6
A B C D E 28

3) Uncertainty, Operators, Eigenfunctions (~~30~~ pts)

3A) Explicitly evaluate the commutator $[\hat{x}, \hat{p}_x]$

$$[\hat{x}, \hat{p}_x]f = \underbrace{(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})}_{+1}f = \underbrace{x\left(-i\hbar\frac{d}{dx}\right)f - \left(-i\hbar\frac{d}{dx}\right)(xf)}_{+1 \text{ for correct operators}}$$

$$= \cancel{-i\hbar x\frac{df}{dx}} + \cancel{i\hbar x\frac{df}{dx}} + i\hbar f$$

+6

$$[x, p_x]f = i\hbar f$$

$$[x, p_x] = i\hbar$$

$\boxed{[\hat{x}, \hat{p}_x] = i\hbar}$

3B) Why does your result from A suggest that you can never know both the position and momentum of a particle exactly at the same time? (don't restate the uncertainty principle—explain WHY 3A implies there must be an uncertainty principle in a 1-3 sentences).

To know an observable exactly ψ must be an eigenfunction of the corresponding operator. However, two operators $\hat{A}$ + $\hat{B}$ have simultaneous eigen functions IFF $[A, B] = 0$, since $[x, p_x] \neq 0$ you can't have ψ that is an eigenfunction of both

+5

3C) Is the ground state wave function for a particle in an infinite depth box of length L an eigenfunction of the momentum operator? If yes, what is the eigenvalue. *Verify by explicit application of the momentum operator to the wave function..*

+5

$$-i\hbar\frac{d}{dx}\left(\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\right) \stackrel{?}{=} c\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

$$-i\hbar\sqrt{\frac{2}{L}}\left(\frac{\pi}{L}\right)\cos\left(\frac{\pi x}{L}\right) \neq c\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

$\Rightarrow$ Not an eigenfxn

Yes/No=?	NO
Eigenvalue if yes=	N/A

3D) Find the momentum eigenfunctions by solving the momentum eigenvalue equation, $\hat{p}_x\psi(x) = C\psi(x)$.

$$-i\hbar \frac{d\psi}{dx} = C\psi$$

$$\int \frac{d\psi}{\psi} = \int \frac{Ci}{\hbar}\, dx$$

+6

$$\ln \psi = \frac{Ci}{\hbar} x$$

$$\psi = e^{iC/\hbar x}$$

C is eigenvalue (can be + or -)

p_x eigenfunctions= $e^{iC/\hbar x}$ (eigenval C)

$= e^{ikx}$ = eigenval $\hbar k$

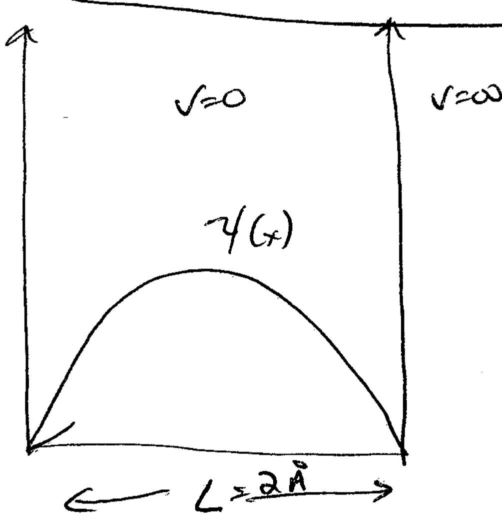
3E) One electron is placed in an infinitely deep box, and another electron in a box of depth V=5 eV. If each box is 2 Angstroms wide, for which electron will we have more uncertainty about its momentum if both are in the ground state (lowest energy eigenstate)? You should draw both potentials and both wave functions as part of your answer.

infinite box has bigger Δp_x

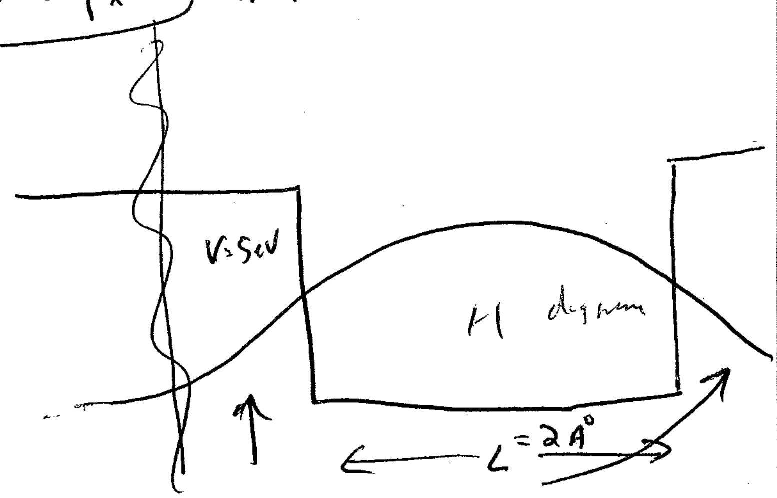
finite box

+6

$V = \infty$



+1 diagram



e- leaks out of finite box

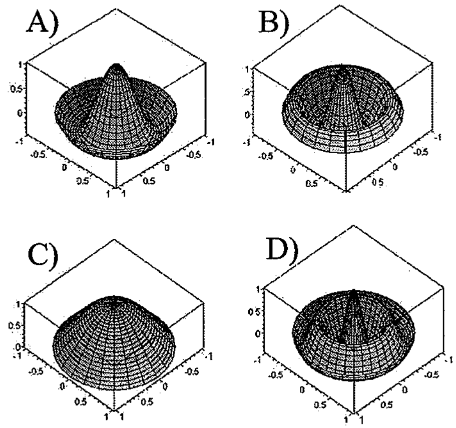
$\Rightarrow \Delta x$ is bigger

$$\Delta x\, \Delta p_x \geq \hbar/2$$

bigger Δx allows smaller Δp_x (indeed finite box has lower E)

4) Short Answer Concept Questions (24):

4A) Below are four wave functions for a particle in a 2D *circular* box. Rank them from LOW to HIGH energy. EXPLAIN.



+6

fewest nodes most nodes

C < A < B < D

more nodes = higher energy

3/6 for right ans no expl.

4B) Circle which of the following pairs is more likely to cross the barrier (unless specificed otherwise, the barrier is 1 eV high, and 0.1 nm wide). EXPLAIN EACH CHOICE WITH ONE SENTENCE **OR LESS**

i) 0.5 eV electron -or- 0.5 eV proton $T \propto e^{-\sqrt{m}}$

ii) 0.9 eV electron -or- 0.5 eV electron $T \propto e^{-\sqrt{V-E}}$

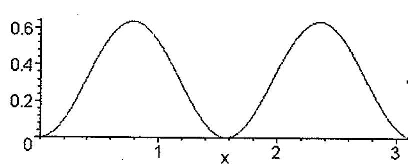
+6

iii) 2 eV Carbon atom -or- 0.9 eV electron Energy is greater than barrier height $\Rightarrow$ no tunneling required

iv) 0.9 eV electron and 0.1 nm barrier -or- 0.9 eV electron and a 0.2 nm barrier

$T \propto e^{-\sqrt{L}}$

4C) Below is plotted $|\psi(x)|^2$ for the first excited state for the particle in the box. How can the particle move from the left side of the box to the right side of the box if there is no chance of finding it in the middle of the box?



+6

The particle is not "moving" back and forth in the classical sense but is best described as a standing wave occupying the whole box – $|\psi(x)|^2$ gives us the probability of finding it somewhere if we look but does not describe motion

4D) Will the infrared absorption bands of D_2O be at higher or lower energies than for H_2O? Explain using an equation

$\Delta E_{IR} = \hbar\omega = \hbar\sqrt{\frac{K}{\mu}}$ ← increase mass increases

+6

$\mu \Rightarrow$ $\boxed{\text{lower Energy for } D_2O}$