Chemistry 331 **Assignment #4** (due Thursday, 31 October, in class)

1. For a free electron with 50 keV kinetic energy, calculate the:

a) the electron speed

[3] **b)** the electron momentum

c) the de Broglie wavelength of the electron

2. A free electron is described by the wave function

$$\psi(x) = Ae^{-i2\pi x/\lambda}$$

a) Show that it is equally probable to find the electron at any position x.

b) Show that $\psi(x)$ is an eigenfunction of the linear momentum operator $-\frac{ih}{2\pi}\frac{\mathrm{d}}{\mathrm{d}x}$ with eigenvalue $p_x = -h/\lambda$.

[4] **c)** Show that $\psi(x)$ is an eigenfunction of the kinetic energy operator $-\frac{h^2}{8\pi^2 m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$ with eigenvalue $E = p_x^2/2m$.

d) Is the electron moving the positive x-direction? Explain.

3. **a)** An electron with 10.0 eV kinetic energy hits a 10.1 eV potential energy barrier. Calculate the penetration depth.

[3] **b)** A 10.0 eV proton encountering a 10.1 eV potential energy barrier has a much smaller penetration depth than the value calculated in **a**. Why?

c) Give the classical penetration depth for a 10.0 eV particle hitting a 10.1 eV barrier.

4. A free electron with 40.0 eV electron moving the positive x-direction encounters a 30.0 eV potential energy barrier at $x \geq 0$.

a) Calculate the probability the electron is reflected at $x = 0$.

[3] **b)** Calculate the classical probability the electron is reflected at $x = 0$.

c) Calculate the speed of the electron in the $x \geq 0$ region.

... page 2

5. Optical microscopes use visible light (wavelengths from 400 to 800 nm) to image materials. The highest resolution that can be achieved ($\approx$ one half wavelength) is about 200 nm.

[1] **Electron microscopes** use beams of high energy electrons (40 to 400 keV) to take images samples. Estimate the highest resolution of an electron microscope.

6. **Scanning tunneling microscopes** are widely used to take high resolution (0.01 to 0.1 nm) images of surfaces. In a scanning tunneling microscope, what is doing the tunneling? What are

[2] they tunneling through?

7. A free electron moving in the positive x-direction encountering a potential energy barrier in the region $x \geq 0$ is described by

$$\psi_{\mathrm{I}}(x) = A\exp(-i2\pi x/\lambda_{\mathrm{I}}) + B\exp(-i2\pi x/\lambda_{\mathrm{I}}) \qquad x < 0 \quad \text{(zone I)}$$

$$\psi_{\mathrm{II}}(x) = C\exp(i2\pi x/\lambda_{\mathrm{II}}) \qquad x \geq 0 \quad \text{(zone II)}$$

with $A = 0.80\ \mathrm{m}^{-1/2}$, $B = 0.20\ \mathrm{m}^{-1/2}$ and $C = 1.00\ \mathrm{m}^{-1/2}$.

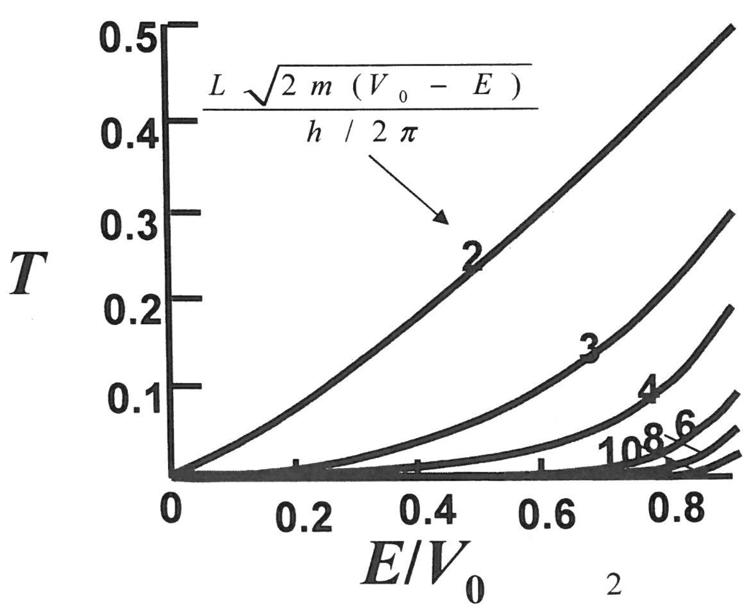
a) Show that the wave function is continuous at $x = 0$.

[3] **b)** Is the electron showing barrier-penetration behavior? Or barrier-transmission behavior? Justify your answer.

c) Calculate the probability the electron is reflected at $x = 0$.

8. The ammonia molecule can invert its structure by having the N atom tunnel through the plane of hydrogen atoms: $H_3N\ =\ NH_3$

[2] Use $V_0 = 4.1 \times 10^{-20}$ J (the energy barrier for inversion), $L = 0.085$ nm (the barrier width), and $E = 1.8 \times 10^{-20}$ J (the ground-state vibrational energy) to calculate the tunneling probability T.



Chem 331   **Assignment #4**

Q1   A free electron has $50\ keV = 50{,}000\ eV$ kinetic energy.

a) Speed of the electron?

Ignoring small relativistic corrections:

$$E = 50{,}000\ eV = (50{,}000 \times 1.602 \times 10^{-19}\ J) = \frac{1}{2} m v^2$$

$$\text{speed } v_x = \sqrt{2E/m}$$

$$= \sqrt{(2 \times 50{,}000 \times 1.602 \times 10^{-19}\ J) / 9.110 \times 10^{-31} kg}$$

$$\boxed{v_x = 1.33 \times 10^{8}\ m\ s^{-1}}$$

b) electron momentum?

$$P_x = m v_x = (1.33 \times 10^{8}\ m\ s^{-1})(9.110 \times 10^{-31}\ kg)$$

$$\boxed{P_x = 1.21 \times 10^{-22}\ kg\ m\ s^{-1}}$$

c) de Broglie wavelength of the electron?

$$\lambda = \frac{h}{P_x} = \frac{6.626 \times 10^{-34}\ Js}{1.21 \times 10^{-22}\ kg\ m\ s^{-1}} = 5.48 \times 10^{-12}\ m$$

$$\boxed{\lambda = 0.00548\ nm}$$

Q2 A free electron is described by the wave function

$$\psi(x) = A^{-i2\pi x/\lambda}$$

a) probability distribution function for the electron

$$P(x) = \psi^*(x)\,\psi(x)$$

$$= \left(Ae^{-i2\pi x/\lambda}\right)^*\left(Ae^{-i2\pi x/\lambda}\right)$$

$$= A\,e^{i2\pi x/\lambda}\,A\,e^{-i2\pi x/\lambda} \quad = A^2 e^{i2\pi x/\lambda - i2\pi x/\lambda}$$

$$\boxed{P(x) = A^2 e^0 = A^2 = \text{a constant}}$$

(equally likely to find the electron at any x value)

b) $$\hat{p}_x\,\psi(x) = -\frac{ih}{2\pi}\,\frac{d}{dx}\,Ae^{-i2\pi x/\lambda}$$

$$= -\frac{ih}{2\pi}\,A\left(\frac{-i2\pi}{\lambda}\right)e^{-i2\pi x/\lambda}$$

$$= i^2\frac{h}{\lambda}\,Ae^{-i2\pi x/\lambda}$$

(de Broglie relation $\lambda = \frac{h}{p_x}$)

a constant

$$\hat{p}_x\,\psi(x) = \left(-\frac{h}{\lambda}\right)\psi(x)$$

$\psi(x)$ is an eigenfunction of $\hat{p}_x$ with eigenvalue $p_x = \frac{h}{\lambda}$

(Q2 cont.)

c) $$\hat{T}\psi(x) = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\psi(x)$$

$$= -\frac{h^2}{8\pi^2 m}\frac{d}{dx}\frac{d}{dx}Ae^{-i2\pi x/\lambda}$$

$$= -\frac{h^2}{8\pi^2 m}\frac{d}{dx}A\left(-\frac{i2\pi}{\lambda}\right)e^{-i2\pi x/\lambda}$$

$$= -\frac{h^2}{8\pi^2 m}A\left(-\frac{i2\pi}{\lambda}\right)\left(-\frac{i2\pi}{\lambda}\right)e^{-i2\pi x/\lambda}$$

$$= \left(-\frac{h^2}{8\pi^2 m}\right)\frac{4\pi^2}{\lambda^2}i^2Ae^{-i2\pi x/\lambda}$$

$$= \frac{1}{2m}\left(\frac{h}{\lambda}\right)^2\psi(x)$$

a constant

$$\hat{T}\psi(x) = \left(\frac{p_x^2}{2m}\right)\psi(x)$$

$\psi(x)$ is an eigenfunction of the kinetic energy operator with eigenvalue $\frac{p_x^2}{2m}$ = kinetic energy

$$\left(= \frac{m^2v_x^2}{2m} = \frac{1}{2}mv_x^2\right)$$

(Q2 cont.)

d) $p_x = \left(-\frac{h}{\lambda}\right) = m v_x$ negative $\qquad v_x < 0$

the electron is moving in the -ve x direction

Q3 a) an electron with $E = 10.1$ eV kinetic energy hits a $V_0 = 10.0$ potential energy barrier

penetration depth $\quad D_p = \dfrac{h/2\pi}{\sqrt{(V_0 - E)2m}}$

$$V_0 - E = (10.1 - 10.0)(eV)\left(1.602 \times 10^{-19} \frac{J}{eV}\right)$$

$$= 1.602 \times 10^{-20}\ J$$

$$D_p = \frac{6.626 \times 10^{-34}\ Js / 2\pi}{\sqrt{(1.602 \times 10^{-20}\ J)\, 2\,(9.110 \times 10^{-31}\ kg)}}$$

$$\boxed{D_p = 0.617 \times 10^{-9}\ m = 0.617\ nm}$$

b) classical penetration depth is zero $\quad (E < V_0)$

c) D_p is proportional to $\dfrac{1}{\sqrt{\text{particle mass}}}$

a proton is 1836 times heavier than an electron, proton penetration depth is $\sqrt{1836} = 42.8$ times smaller

$$\left(\frac{E}{V_0} = \frac{40.0\,eV}{30.0\,eV} = \frac{4}{3} \right)$$

Q4 An electron with $E = 40.0$ eV kinetic energy hits a $V_0 = 30.0$ eV potential energy barrier

a) probability the electron is reflected?

$$R = \frac{2\frac{E}{V_0} - 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0}-1\right)} - 1}{2\frac{E}{V_0} + 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0}-1\right)} - 1}$$

$$= \frac{2\frac{4}{3} - 2\sqrt{\frac{4}{3}\left(\frac{4}{3}-1\right)} - 1}{2\frac{4}{3} + 2\sqrt{\frac{4}{3}\left(\frac{4}{3}-1\right)} - 1}$$

$$= \frac{2\frac{4}{3} - 2\sqrt{\frac{4}{9}} - 1}{2\frac{4}{3} + 2\sqrt{\frac{4}{9}} - 1}$$

$$= \left(\frac{1}{3}\right)^2 \qquad \boxed{R = \frac{1}{9} = 0.111}$$

also $R = \left(\frac{k_I - k_{II}}{k_I + k_{II}}\right)^2$

b) Classically, the incoming particle has more than enough energy (40.0 eV) to surmount the barrier (30.0 eV), and the probability of reflection is zero

(Q4 cont.)

c) The incoming $\underbrace{\text{free}}_{\text{zero potential energy}}$ electron has 40.0 eV of kinetic energy. (x < 0, Zone I)

The transmitted electron in zone II ($x \geq 0$) has the same total energy (energy is conserved) 40.0 eV, but 30.0 eV of that energy is potential energy, leaving 10.0 eV kinetic energy

zone I ($x<0$) $\quad E_I = T_I + \cancelto{0}{V_I} = T_I = 40.0\,\text{eV}$

Zone II ($x \geq 0$) $\quad E_{II} = T_{II} + V_{II} = T_{II} + V_0 = 40.0\,\text{eV}$

$$T_{II} = 40.0\,\text{eV} - 30.0\,\text{eV} = 10.0\,\text{eV}$$

Speed of the electron in the barrier:

$$T_{II} = \frac{1}{2} m v_{II}^2 \qquad v_{II} = \sqrt{2T_{II}/m}$$

$$v_{II} = \sqrt{\frac{2\,(10.0\,\text{eV})(1.602\times10^{-19}\,\text{J/eV})}{9.110\times10^{-31}\,\text{kg}}}$$

$$\boxed{v_{II} = 1.87\times10^{6}\ \text{m s}^{-1}}$$

$\left(\text{max. kinetic energy} = \text{max. momentum} = \text{shortest de Broglie wavelength} \right)$

Q5 for a 400 keV (400,000 eV) electron,

the de Broglie wavelength (see Q1) is

$$\lambda = \frac{h}{\text{momentum}} = \frac{h}{mv_x}$$

$$= \frac{h}{m\sqrt{2E/m}} = \frac{h}{\sqrt{2mE}}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s}}{\sqrt{2\,(9.110 \times 10^{-31}\ \text{kg})\ 400{,}000 \times 1.602 \times 10^{-19}\ \text{J eV}^{-1}}}$$

$$\boxed{\lambda = 1.94 \times 10^{-12}\ \text{m}} = 0.00194\ \text{nm}$$

Q6 Scanning Tunneling Microscopy

electrons tunnel through the gap between the sample and the electrode tip, a high energy barrier where the electrons are not bound to atoms or molecules (lower energy)

Q7 a) at $x = 0$;

$$\psi_I(0) = A\exp(0) + B\exp(0)$$
$$= A + B$$
$$= 0.80\ m^{-1} + 0.20\ m^{-1}$$
$$= 1.00\ m^{-1}$$

$$\psi_{II}(0) = C\exp(0)$$
$$= C$$
$$= 1.00\ m^{-1}$$

$$\psi_I(0) = \psi_{II}(0)$$

b) in zone II ($x \geq 0$), the probability distribution

is $P_{II}(x) = \psi_{II}^* \psi_{II} = Ce^{-i2\pi x/\lambda_{II}}\, Ce^{i2\pi x/\lambda_{II}}$

$= C^2 e^0 = C^2$ a constant

$\therefore$ transmission (the electron "keeps on going" in zone II)

in barrier penetration $P(x) \to 0$ as $x \to \infty$ (not a constant)

c) reflection probability = reflection coefficient R

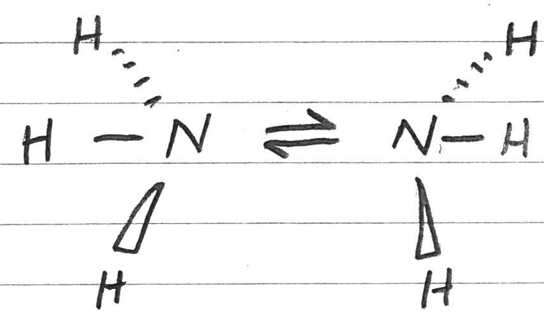
$$R = \frac{B^2}{A^2}$$

$$= \frac{(0.20\ m^{-1})^2}{(0.80\ m^{-1})^2}$$

$$\boxed{R = 0.0625}$$

Q8 barrier tunneling coefficient:

$$\beta = \frac{L\sqrt{2m(V_0 - E)}}{h/2\pi}$$



$L = 0.085$ nm

$V_0 = 4.1 \times 10^{-20}$ J

$E = 1.8 \times 10^{-20}$ J

$$m = \frac{0.014 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.32 \times 10^{-26} \text{ kg}$$

(mass of N atom)

calculate $\boxed{\beta = 26.4}$

at $E/V_0 = 0.439$ and $\beta = 26.4$

read $\boxed{T \simeq 0.00}$ (from the graph in the course notes)

but T is large enough for NH_3 molecules to invert about 30 billion times per second!

(Q8 cont.)

$\frac{E}{V_0} = 0.4390$

$\beta = 26.4$

Tunneling probability calculated:

$$T = \left[1 + \frac{V_0^2}{16E(V_0 - E)}(e^{\beta} - e^{-\beta})^2\right]^{-1}$$

$$= \left[1 + \frac{1}{16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)}(e^{\beta} - e^{-\beta})^2\right]^{-1}$$

$$= \left[1 + \frac{1}{16(0.439)(1 - 0.439)}(e^{26.4} - e^{-26.4})^2\right]^{-1}$$

$$= 8.43 \times 10^{-13}$$