CHM 3411 - Physical Chemistry 2
First Hour Exam
February 13, 2015

There are five problems on the exam. Do all of the problems. Show your work.

$N_A = 6.022 \times 10^{23}$	$m_e = 9.109 \times 10^{-31}$ kg	1 eV = 1.602×10^{-19} J
$c = 2.998 \times 10^{8}$ m/s	$k = 1.381 \times 10^{-23}$ J/K	1 cm^{-1} = 1.986×10^{-23} J
$h = 6.626 \times 10^{-34}$ J·s	1 kg = 6.022×10^{26} amu	

1. (12 points) The experimental value for the work function for nickel metal is Φ = 5.01 eV. If light of wavelength λ = 400.0 nm strikes a nickel surface in a photoelectric effect experiment, will electrons be produced? If so, what will be the maximum kinetic energy of the ejected electrons? Justify your answer.

2. (18 points) Consider an ideal black body emitter at T = 4500. K.

   a) What is the total intensity of light emitted by the blackbody?

   b) What is the intensity of light emitted by the blackbody in the range 580. nm $< \lambda <$ 620. nm?

In both of these problems give your final answer in units of $J/m^2 \cdot s$.

3. (16 points) For each of the following operators and functions, determine under what conditions (if any) the function is an eigenfunction of the operator. For those functions that are eigenfunctions, find the corresponding eigenvalues. Justify your answers.

   a) $\hat{O} = d/dx$, $f(x) = ax^2$, where a is a positive constant

   b) $\hat{O} = d^2/dx^2$, $f(x) = \sin(ax) + \cos(ax)$, where a is a positive constant

   c) $\hat{O} = (d^2/dx^2 - ax^2)$, $f(x) = \exp(x^2)$, where a is a positive constant

4. (26 points) The following question concerns the particle in a one dimensional box, where

$V = 0 \quad 0 < x < L$

$V = \infty \quad x \leq 0$ or $x \geq L$

The normalized solution (wavefunction) for the $n = 3$ state for this system is

$\psi_3(x) = (2/L)^{1/2} \sin(3\pi x/L)$ inside the box

$\psi_3(x) = 0$ outside of the box.

a) Find the probability of a particle in the $n = 3$ state of the above system being found in the region $0 < x < (L/4)$.

b) Find $\langle x^2 \rangle$, the expectation value for x^2, for a particle in the $n = 3$ state of the above system.

c) An electron is trapped inside a one dimensional box. Light of wavelength $\lambda = 774.$ nm is absorbed by the system and moves the electron from the $n = 3$ to the $n = 4$ state. Based on this information find L, the size of the box containing the electron. Give your final answer in units of nm.

5. (28 points) The time independent Schrodinger equation (TISE) for a particle on a ring is

$[(- \hbar^2/2m) (d^2/d\phi^2)] \psi(\phi) = E \psi(\phi)$

Consider the function $\psi(\phi) = A [\sin(\phi) - \cos(\phi)]$

a) Find the value of A that makes $\psi(\phi)$ a normalized function.

b) Is $\psi(\phi)$ an eigenfunction of the TISE for a particle on a ring? If your answer is yes, give the corresponding eigenvalues. Justify your answers.

c) How many nodes are there in the function $\psi(\phi)$, and where are they located?

d) Is $\psi(\phi)$ orthogonal to the following function over the range of the particle on a ring?

$f(\phi) = [\sin(\phi) + \cos(\phi)]$

Justify your answer.

Solutions.

1) We first find the critical wavelength

$$\frac{hc}{\lambda_0} = \Phi$$

and so $\lambda_0 = \dfrac{hc}{\Phi} = \dfrac{(6.626 \times 10^{-34}\ J{\cdot}s)(2.998 \times 10^{8}\ m/s)}{(5.01\ eV)(1.602 \times 10^{-19}\ J/eV)} = 2.475 \times 10^{-7}\ m = 247.5\ nm$

Since the light being used is longer wavelength than this, the photons do not have sufficient energy to eject electrons from the metal, so no electrons are produced.

2) a) $M(T) = \sigma T^4 = (5.67 \times 10^{-8}\ J/m^2{\cdot}s{\cdot}K^4)(4500.\ K)^4 = 2.33 \times 10^{7}\ J/m^2{\cdot}s$

b) $M = M(580.\ nm < \lambda < 620.\ nm, T) = \int_{580}^{620} M(\lambda,T)\, d\lambda$

$\cong M(\lambda_{ave},T)\,(\Delta\lambda)$ where $\lambda_{ave} = (580.\ nm + 620.\ nm)/2 = 600.\ nm$
$\Delta\lambda = (620.\ nm - 580.\ nm) = 40.\ nm = 40. \times 10^{-9}\ m$

Using the expression for $M(\lambda,T)$ from the handout, we get

$$M = \frac{2\pi\,(6.626 \times 10^{-34}\ J{\cdot}s)(2.998 \times 10^{8}\ m/s)^2}{(600. \times 10^{-9}\ nm)^5}$$

$$\{ \exp [(6.626 \times 10^{-34}\ J{\cdot}s)(2.998 \times 10^{8}\ m/s) / (600. \times 10^{-9}\ m)(1.381 \times 10^{-23}\ J/K)(4500.\ K)] -1 \}^{-1}$$

$$(40. \times 10^{-9}\ m)$$

$= (4.81 \times 10^{15}\ J/m^3{\cdot}s)\,(4.88 \times 10^{-3})\,(40. \times 10^{-9}\ m) = 9.39 \times 10^{5}\ J/m^2{\cdot}s$

3) a) $d/dx\,(ax^2) = 2ax$ NOT an eigenfunction

b) $d^2/dx^2\,(\sin(ax) + \cos(ax)) = - a^2\,(\sin(ax) + \cos(ax))$

Eigenfunction, eigenvalue is $- a^2$

c) $(d^2/dx^2) - ax^2) \exp(x^2) = 2 \exp(x^2) + 4x^2 \exp(x^2) - ax^2 \exp(x^2)$

$= (2 + 4x^2 - ax^2) \exp(x^2)$

If a = 4, the term in the brackets is a constant, and $\exp(x^2)$ is an eigenfunction. For that case, the corresponding eigenvalue is 2.

4) a) $P = \int_0^{L/4} [(2/L)^{1/2} \sin(3\pi x/L)]^2\, dx$

$= (2/L) \int_0^{L/4} [(\sin(3\pi x/L)]^2\, dx$

Using the table of integrals, this is

$= (2/L) [(x/2) - (L/12\pi) \sin(6\pi x/L)]_0^{L/4}$

$= (2/L) [(L/8) - (L/12\pi) \sin(3\pi/2)] = (1/4) + (1/6\pi)$

b) $\langle x^2 \rangle = \int_0^L [(2/L)^{1/2} \sin(3\pi x/L)] x^2 [(2/L)^{1/2} \sin(3\pi x/L)] dx$

$= (2/L) \int_0^L x^2 [(2/L)^{1/2} \sin(3\pi x/L)]^2 dx$

Using the table of integrals, this is

$= (2/L) \{ (x^3/6) - [(x^2L/12\pi) - (L^3/216\pi^3)] \sin(6\pi x/L) - (xL^2/36\pi^2) \cos(6\pi x/L) \}_0^L$

$= (2/L) \{ (L^3/6) - (L^3/36\pi^2) \} = L^2 \{ (1/3) - (1/18\pi^2) \} \cong 0.3277 L^2$

c) For the n = 3 $\rightarrow$ n = 4 transition

$$\Delta E = (4^2 - 3^2) (h^2/8mL^2) = \frac{7h^2}{8mL^2} = \frac{hc}{\lambda}$$

so $$L^2 = \frac{7h^2\lambda}{8mhc} = \frac{7h\lambda}{8mc} = \frac{7(6.626 \times 10^{-34} \text{ J·s})(774. \times 10^{-9} \text{ nm})}{8(9.109 \times 10^{-31} \text{ kg})(2.998 \times 10^8 \text{ m/s})} = 1.643 \times 10^{-18} \text{ m}^2$$

$L = (1.643 \times 10^{-18} \text{ m}^2)^{1/2} = 1.28 \times 10^{-9} \text{ m} = 1.28 \text{ nm}$

5) a) For normalization

$1 = \int_0^{2\pi} A^2 [\sin(\phi) - \cos(\phi)]^2 d\phi$

$= A^2 \int_0^{2\pi} \{ (\sin(\phi))^2 - 2 \sin(\phi)\cos(\phi) + (\cos(\phi))^2 \} d\phi$

But $(\sin(\phi))^2 + (\cos(\phi))^2 = 1$, so

$= A^2 \int_0^{2\pi} \{ 1 - 2 \sin(\phi)\cos(\phi) \} d\phi$

$= 2\pi A^2$, and so $A = 1/(2\pi)^{1/2}$

b) $[(- \hbar^2/2m) (d^2/d\phi^2)] \{A [\sin(\phi) - \cos(\phi)]\}$

$= (- \hbar^2/2m) (-1) \{A [\sin(\phi) - \cos(\phi)]\} = (\hbar^2/2m)\{A [\sin(\phi) - \cos(\phi)]\}$

So an eigenfunction, with eigenvalue (energy) = $(\hbar^2/2m)$

c) Nodes will occur when the wavefunction is equal to zero, which occurs when $\sin(\phi) = \cos(\phi)$

The unique nodes are therefore $\phi = \pi/4$ and $\phi = 5\pi/4$

d) To test for orthogonality we must evaluate the following integral

$\int_0^{2\pi} A [\sin(\phi) - \cos(\phi)] [\sin(\phi) + \cos(\phi)] d\phi =$

$= A \int_0^{2\pi} (\sin(\phi))^2 - (\cos(\phi))^2 d\phi$

Using the table of integrals, this is

$A \{ (x/2) - (1/4)\sin(2\phi)) - (x/2) - (1/4)\sin(2\phi)) \}_0^{2\pi} = \{ - A (1/2) \sin(2\phi) \}_0^{2\pi} = 0$

Since the integral is equal to zero the two functions are orthogonal.