CHM 3411
First hour exam
February 8, 2019

There are 5 problems on the exam. Do all of the problems. Show your work.

1) [16 points] The light intensity of a particular light source (not an ideal blackbody) is given by the equation

$$M(\lambda,T)\, d\lambda = \frac{A}{\lambda^3} \exp(- B/\lambda T)\, d\lambda \tag{1.1}$$

where A and B are constants.

a) Find an expression for λ_{max}, the wavelength of maximum intensity, for a light source whose intensity is given by eq 1.1

b) Find an expression for $M(\lambda,T)$ that is correct for long wavelengths ($\lambda \to \infty$).

2) [18 points] Consider the momentum operator

$$p = - i\hbar \frac{d}{dx} \tag{2.1}$$

For each of the following functions determine whether the function is or is not an eigenfunction of p. Clearly indicate your answer and give work to show your answer is correct. For cases where the function is an eigenfunction, give the corresponding eigenvalue.

a) $$f(x) = \frac{1}{(2)^{1/2}} \sin(4x) \tag{2.2}$$

b) $$f(x) = \frac{1}{\pi} \exp(2ix) \tag{2.3}$$

c) $$f(x) = 2\pi\, [\, \sin(3\pi x) + i \cos(3\pi x)\,] \tag{2.4}$$

3) [12 points] What is the value for the commutator $[x^2, p]$, where x is the operator for position and $p = - i\hbar\, d/dx$ is the operator for momentum in one dimension.

4) [36 points] The n = 4 solution to the particle in a one dimensional box TISE is

$$\psi(x) = (2/L)^{1/2} \sin(4\pi x/L) \qquad 0 \le x \le L \tag{4.1}$$

$$\psi(x) = 0 \qquad x < 0 \text{ or } x > L$$

a) Find $<x>$ and $<x^2>$, the expectation values for x and x^2, for a particle in the n = 4 state of the particle in a box.

b) Is the n = 4 solution to the particle in a box orthogonal to the function

$$f(x) = A\, (x^2 – Lx) \qquad 0 \le x \le L \tag{4.2}$$

$$f(x) = 0 \qquad x < 0 \text{ or } x > L$$

c) Find the value for the constant A in eq 4.2 that makes f(x) a normalized function.

5) [18 points] The value for the vibrational constant for the molecule NaF (sodium fluoride) is ϖ = 536. cm^{-1}.

a) What is the energy of the v = 2 state of the NaF molecule? Assume the molecule is correctly described as a harmonic oscillator. Give your answer in units of cm^{-1} and J/molecule.

b) What is the value for k, the force constant, for the chemical bond in NaF? Give your answer in units of N/m (note that 1 N/m = 1 kg/s^2).

The masses of the most common isotopes of Na and F (in atomic mass units) are m(Na) = 22.9898 amu, m(F) = 18.9984 amu.

Solutions.

1) a) To find an extreme point we set $d/d\lambda M(\lambda,T) = 0$

But $$\frac{d}{d\lambda} = \frac{A}{\lambda^3}\exp(-B/\lambda T) = -\frac{3}{\lambda^4} A\exp(-B/\lambda T) + \frac{A}{\lambda^3}\exp(-B/\lambda T)\frac{B}{\lambda^2 T} = 0$$

If we multiply both sides by $\frac{\lambda^4 \exp(B/\lambda T)}{A}$ we get

$$-3 + \frac{B}{\lambda T} = 0$$

$$3 = \frac{B}{\lambda T} \quad \text{or } \lambda_{max} = \frac{B}{3T}$$

b) $$M(\lambda,T) = \frac{A}{\lambda^3}\exp(-B/\lambda T)$$

The power series expansion of the exponential is $\exp(-B/\lambda T) = 1 - \frac{B}{\lambda T} + \ldots$

If we substitute into the expression for $M(\lambda,T)$, we get

$$M(\lambda,T) = \frac{A}{\lambda^3}[1 - B/\lambda T + \ldots]$$

As $\lambda \to \infty$, all the terms in the brackets become negligibly small except the leading term, and so

$$\lim(\lambda \to \infty) M(\lambda,T) = \frac{A}{\lambda^3}$$

2) a) $-i\hbar\, d/dx [(1/2)^{1/2} \sin(4x)] = - i\hbar (4) [(1/2)^{1/2} \cos(4x)]$, so NO, not an eigenfunction

b) $-i\hbar\, d/dx [(1/\pi) \exp(2ix)] = - i\hbar (2i) [(1/\pi) \exp(2ix)] = 2\hbar [(1/\pi) \exp(2ix)]$

so YES, an eigenfunction, eigenvalue is $2\hbar$

c) $-i\hbar\, d/dx \{ 2\pi [\sin(3\pi x) + i \cos(3\pi x)] \} = - i\hbar\{ (2\pi) [(3\pi) \cos(3\pi x) - (3\pi i) \sin(3\pi x)] \}$

If we remove the common factor of 3π from inside the square brackets, we get

$= - i\hbar (3\pi) \{ (2\pi) [\cos(3\pi x) - i \sin(3\pi x)] \}$ If we move i to inside the square brackets, then

$= - \hbar (3\pi) \{ (2\pi) [i \cos(3\pi x) - i^2 \sin(3\pi x)] \}$

$= - 3\pi\hbar \{ 2\pi [\sin(3\pi x) + i \cos(3\pi x)] \}$ so YES, eigenfunction, eigenvalue is $3\pi\hbar$

3) The easiest way to find the value for a commutator is to let it operate on some arbitrary function f(x) So

$[x^2,p] f(x) = (x^2 p - p x^2) f(x) = x^2 (- i\hbar\, d/dx) f(x) - (- i\hbar\, d/dx) x^2 f(x)$

$= - i\hbar x^2 (df(x)/dx) + i\hbar x^2 (df(x)/dx) + i\hbar (2x) f(x) = 2i\hbar x f(x)$

Therefore $[x^2,p] = 2i\hbar x$

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

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

The general form for this integral is

$$\int x\, [\sin(ax)]^2\, dx = \frac{x^2}{4} - \frac{x \sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}$$

If we let $a = 4\pi/L$, then we get

$= (2/L)\ \{ (x^2/4) – (L/16\pi)\, x \sin(8\pi x/L) – (L^2/128\pi^2) \cos(8\pi x/L\}_0^L$

Since $\sin(0) = \sin(8\pi) = 0$, and $\cos(0) = \cos(8\pi) = 1$, this gives us

$= (2/L)\ (L^2/4) = L/2$

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

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

The general form for this integral is

$$\int x^2\, [\sin(ax)]^2\, dx = (x^3/6) - [\, (x^2/4a) – (1/8a^3)\,] \sin(2ax) - (x/4a^2) \cos(2ax)\,]$$

If we let $a = 4\pi/L$, then we get

$= (2/L)\ \{ (x^3/6) – [\, (Lx^2/16\pi) – (L^3/512\pi^3)\,] \sin(8\pi x/L) – (xL^2/64\pi^2) \cos(8\pi x)\ \}_0^L$

Since $\sin(0) = \sin(8\pi) = 0$, and $\cos(0) = \cos(8\pi) = 1$, this gives us

$= (2/L)\ \{ (L^3/6) – (L^3/64\pi^2)\ \} = L^2\ \{ (1/3) – (1/32\pi^2)\ \}$

b) To check for orthonormality we need to find the value for the integral

$\int_0^L [(2/L)^{1/2} \sin(4\pi x/L)]\ [\ A\, (x^2 – Lx)\ ]\, dx$

$= A(2/L)^{1/2} \int_0^L \sin(4\pi x/L)]\ [\ (x^2 – Lx)\ ]\, dx$

$= A(2/L)^{1/2}\ \{ \int_0^L x^2 \sin(4\pi x/L)\, dx – L \int_0^L x \sin(4\pi x/L)\, dx\ \}$

There are two integrals we need here

$\int x^2 \sin(ax)\, dx = (2x/a^2) \sin(ax) – (x^2/a) \cos(ax) + (2/a^3) \cos(ax)$

$\int x \sin(ax)\, dx = (1/a^2) \sin(ax) – (x/a) \cos(ax)$

If we let $a = 4\pi/L$, then we get

$= A(2/L)^{1/2}\ \{ (xL^2/8\pi^2) \sin(4\pi x/L) – (x^2L/4\pi) \cos(4\pi x/L) + (L^3/32\pi^3) \cos(4\pi x/L)\ ]$

$- L\ [\ (L^2/16\pi^2 \sin(4\pi x/L) – (xL/4\pi) \cos(4\pi x/L)\ ]\ \}_0^L$

Since sin(0) = sin(4π) = 0 , and cos(0) = cos(4π) = 1, this gives us

$= A(2/L)^{1/2} \{ - (L^3/4\pi) + L (L^2/4\pi) \} = 0$

So the two functions are orthonormal.

Note that there is an easier way of showing these two functions are orthogonal based on symmetry.

c) Normalization is the condition

$1 = \int_0^L [A (x^2 - xL)] [A (x^2 - xL)] dx$

$= A^2 \int_0^L [x^4 - 2x^3L + x^2L^2] dx$

$= A^2 [(x^5/5) - (2x^4/4) + (x^3/3)]_0^L$

$= A^2 L^5 [(1/5) - (1/2) + (1/3)] = \frac{A^2 L^5}{30}$

Solving for A gives $A = (30/L^5)^{1/2}$

5) a) E(in cm^{-1}) = $(v + ½) \varpi = (2.5) (536.\ cm^{-1}) = 1340.\ cm^{-1}$

Using the conversion between cm^{-1} and J, we get

E(in J) = $(1340.\ cm^{-1}) (1.986 \times 10\text{-}23\ J/cm^{-1}) = 2.661 \times 10^{-20}$ J/molecule

b) $\varpi = (1/2\pi c) (k/\mu)^{1/2}$

If we square both sides of this equation and solve for k, we get

$k = 4\pi^2\varpi^2c^2\mu$

$\varpi = (536.\ cm^{-1}) (100\ cm/m) = 53600.\ m^{-1}$

$\mu = \frac{m_{N}am_{F}}{(m_{Na} + m_F)} = \frac{(22.9898\ amu)(18.9984\ amu)}{(22.9898 + 18.9994)\ amu} = 10.402\ amu\ (1.661 \times 10^{-27}\ kg/amu) = 1.728 \times 10^{-26}\ kg$

So $k = (4\pi^2) (53600.\ m^{-1})^2 (2.998 \times 10^8\ m/s)^2 (1.728 \times 10^{-26}\ kg) = 176.\ kg/s^2 = 176.\ N/m$