**Chem 6854: Physical Chemistry**

**Homework Assignment #3**

40 points total

Show all work !

Due Friday 15 February

3.1 Problem 3.1a, b and d page 96 (1 pt each/3 pts total)

3.1 a) SQRT(x4) **= ±x2** b)(d3/dx3 +x3)e-αx = d3/dx3(e-ax) + x3e-ax = -a3e-ax +x3e-ax =**e-ax(x3-a3)**

∂2 + ∂2 + ∂2 (x3y2z4) = y2z4∂2x3 + x3z4∂ 2(y2) + x3y2∂2 (z4)

∂x2 ∂y2  ∂z2  ∂x2 ∂y2  ∂z2

= y2z4(3\*2x) + x3z4(2) + x3y2(4\*3z2)

**6xy2z4 + 2x3z4 + 12x3y2z2**

3.2 Problem 3.2 a,c,f page 96 ( 1 pt each/3 pts total)

The operator **A** is linear if **A(f1 +f2) = Af1  + Af2e.g. we can distribute A of a sum of functions A (∑akfk) into a sum of Afk=∑ak Afk**

**3.2a)√(f1 + f2) ≠√f1 + √f2  A= SQR not linear operator**

**Example √(3+6) =±3 ≠ √3 +√6 ~4.18**

**3.2c)0\*(f1+f2) = 0\*f1 + 0\*f2 =0 either way A = 0 is a linear operator**

**3.2 f) ln (f1+f2) ≠ ln (f1) +ln (f2) A= ln not linear operator**

**Example: ln (e+ e) = 1.69 ≠ ln e + ln e= 2**

3.3 Problem 3.5 a,b,c pg 96 (1 pt each/ 3 pts total)

1. **A =d2/dx2=> A2 = (d2/dx2)2 = d4/dx4**

**For b and c it is convenient to write D=d/dx**

1. **A = d/dx +x => A2 f =(D + x)(D+x)(f)=(D+x)(Df +xf) = D2f +D(xf) +xDf +x2f where D=d/dx**

**D2f + xDf + fDx +xDf +x2f=**

**D2f +2xDf + f + x2f = (D2 +2xD +x2 +1)f**

1. **A = d2/dx2 -2xd/dx +1=> A2 f = (D2 -2xD +1)(D2-2xD +1)f= (D2 -2xD +1)(D2f -2xDf +f)**

**=D4f –D2(2xD)f+D2f -2xD3f -2xD[-2xDf] -2xDf + D2f-2xDf +f**

**= D4f –D(D)(2xD) +D2f -2xD3f +2xD[2xDf] -2xDf + D2f-2xDf +f**

**= D4f –D(2xD2+2D)+D2f -2xD3f +2x[2xD2f + 2Df] -2xDf + D2f-2xDf +f**

**=D4f –2xD3f-2D2f-2D2f+D2f -2xD3f +4x2D2f +4xDf -2xDf + D2f-2xDf +f**

**Gathering like terms: D4f -4xD3f +(4x2D2f -3Df2 +D2f) +~~4xDf -4xDf~~ +f = [(D4 -4xD3 +(4x2-2)D2 +1)]f**

**(Note D2 (xD) ≠D3x !)**

**3.4. Unit-free particle-in-a-box analysis (2 pts for a,b,c and d/8 pts total)**

Given that: d2f(x) + Ef=0, with the boundary conditions: f(0) =F(L) =0, with E assumed to be a constant.

dx2

1. Derive a general statement for the allowed eigenvalues of E

*a=1, b=0, c=E => r1,r2 = ±i√(E) => f= C1cos(√E x) +C2sin√E x*

*f(0)=0 means C1 = 0 since cos(0)=1*

*f(L)=0 means √E L = nπ since sin(nπ) = 0 for any n=1,2,3…*

*=>***√E =nπ/L or E=n2π2/L2**

1. Derive an expression for f(x) wherein ∫(f(x))2 dx = 1 when integrated over the range x= 0🡪 x= L.

*From above: f(x) = C2 sin(nπx/L)*

*L*

*C22 ∫ sin2(nπx/L)dx =1 = C22(L/2) for any n (using Maple result for integration)*

*0*

*1= C22( L/2)=> C22=2/L=> C2 = √2/L*

**f=** **√2/L** sin(**nπx/L)**

(You can use reference table integrals, Maple or your calculator to assist in integration)

1. If a constant Vo is inserted into the equation to yield:

d2f(x) + (E-Vo) f=0,

dx2

Re-derive an expression for the eigen values of E which includes the effect of a `constant potential’ =Vo.

We can treat ‘E-Vo’ as a constant analogous to E in 3.4a in which case *=>***√(E-Vo) =nπ/L=> E-Vo = (nπ/L)2 => E=(nπ/L)2 +Vo**

1. Briefly explain in your own words what part of the above problem in 3.4a(and c) force `discrete integer’ states (n=1,2,3…) onto E and why.

*The source of the integers arises from the boundary condition for f(L)=0 which forces the argument (√E L ) of the remaining sine term, C2sin (√E L) to be such that the sin (√E L) =0. This means (√E L) = nπ since sin (nπ) = 0 if n= 1,2,3…*

Aside on Probability average calculations (see also pp 63-70, Math Chapter B)

The average value of any quantity x can be seen through the lens of the `probability distribution’ of x. We illustrate the basic nature of this approach with a simple example.

Suppose we have 10 students who have taken a test whose maximum score is 100. The individual scores (x) enumerated for all 10 might be:

Student # 1 2 3 4 5 6 7 8 9 10

x= test score= 59 72 59 72 80 90 90 80 80 80

To find the `class average’ it is common to add up all the scores (x) and divide by the number of students (10) e.g.

class average = (59+72+59+72+80+90+90+80+80+80) = 762 = 76.2

10 10

We can, however, group terms of like score as below to do the same average:

class average = (59 + 59)+ (72 +72) + (80+80+80+80) + (90 +90)

10

= 2(59) + 2 (72) + 4(80) + 2(90)

10 10 10 10

=0.2(59) + 0.2(72) + 0.4(80) +0.2(90) = ∑ pi xi

The fractional terms (pi= 0.2, 0.4…) can be thought of as the probability of a given score xi to occur in the population of student. For example, since 2 out of 10 students score 59, then we can say that 20% (0.2=2/10) of the students received that score (at least for the population sampled.) Note that all the pi add up to unity (1) which is interpreted to mean the entire population has been sampled. (See also : pp 63-65 of text)

Extending the example, suppose a continuous range of values x is being sampled with a continuous set of probability (densities) associated with x= ρ(x). The average of x, 〈x〉 is now computed using calculus where max and min represent the maximum and minimum values possible for x as below:

max

average of continuous x= 〈x〉 = ∫ρ (x)\*x dx equation **1**

min

Emulating the fact that in the simple case of ten students, the sum of pi = 1, a requirement for ρ(x) is that:

max

∫ρ(x)dx = 1

Min

This is often referred to as requiring `normalization’ of the probability density (see p. 66 of text). In quantum mechanics, averages of physical quantities like x, p and v are computed in very similar fashion.

**Practice with simplified `particle-in-the box’ probability density calculations**

**3.5** Suppose the probability ρ(x) of an electron to occur at x in the range from 0🡪2π varies with the general form ρ(x)=C\*sin2x

where C is a constant. (2 pts/answer; 4 pts total)

1. `normalize’ ρ(x) over the range of x , e.g. find C.

2π

∫C\*sin2x dx = 1 = C\*π =1 => C=1/π

0

b) compute the average x, 〈x〉 using the normalized expression for ρ(x)

2π

1/π∫xsin2x dx = 1/π \* π2= π =<x>

0

[Set both problems up symbolically but use your calculator or Maple to do the integrations)

**3.6a.** The variance, σx2 of an averaged value represents a measure of the statistical `spread’ of possibilities around the average value of x (see also, p. 65 of text). It is computed using the following general form, where ρ is the normalized expression of probability density.

max

σx 2 = ∫(x-〈x〉)2 ρ(x) dx

Min

Use this expression and the numerical result for <x> in 3.6.b to find the variance in x for the electron problem 3.5. (2 pts)

2π

σx 2 =1/ π∫(x-π)2 sin2 x dx= -1/2 +1/3 π2

0

3.6b. McQuarrie demonstrates in general on page 6 (eq. B.8) that:

σx2 = <x2> - <x>2 where the use of the <x2 > is shorthand for ∫x2 ρ(x)dx and <x>2 =[ ∫ x\*ρ(x) dx]2.

Compute <x2> - <x>2 for x=0🡪2π with the help of Maple or your calculator and see if your answer is the same as with 3.6a. (2 pts)

We have already computed <x>= π so <x>2 = π2

<x2>= 1/ π∫x2 sin2 x dx= -1/2 +4/3 π2 => <x2> - <x>2= -1/2 +4/3 π2 -π2 =-1/2 +1/3 π2 Same as in 3.6a

3.7. Suppose the momentum of the electron has the mathematical form: p= sin(x)cos(x). Compute the average momentum <p>

from 0->1 given your normalized expression for ρ(x), e.g. compute : (2 pts)

2π

<p> = ∫ρ(x) sin(x) cos(x) dx

0

2π

<p> = 1/π∫sin2x \* sin(x) cos(x) dx =0

0

3.8 If we substitute ρ(x)=C\*sin2x with ρ(x)=C\*cos2x, provide a simple proof that the same value for C should result.

(Hint: sin2x + cos2x =1) (3 pts)

2π

∫C\*cos2x dx =

0

2π 2π

∫C\*(1-sin2x) dx = C(2π) -C∫sin2xdx =1

0 0

=C\*2π -C\*π = C\*π=1 => C =1/π as with assuming ρ(x) = C sin2x

**Particle-in-the box probability density calculations**

3.9 Problem 3-11 page 97 3 pts

<x> = =L/2 from Maple…sensible since it puts particle on average at center of box

0 Problem 3-12 page 97 3 pts

<p>=<x> = = 0 from Maple…sensible. Particle has equal chance to move left or right

3.11 Problem 3-13, page 98 3 pts

= L2/3 –L2/2n2π2 from Maple = <x2>

{<x2> - <x>2 }1/2 ={ (L2/3 +L2/2n2π2)-L2/4 }1/2

L( 1/3 + 1/2n2π2-1/4)1/2 =L(1/12 +1/2n2π2)1/2 > 0