**Supplement 7: Chemistry 6854**

**Physical Chemistry Alfred State College**

***The Path to Exact Solution of the H Atom***

**7.1. Step 1: Reduction of the Two Body Problem**

r=rp +re

me

μ

**z re**

1-body, reduced mass view of H atom

2-body view of H atom

rp

r

mp y

y c.m.

x x r1 +r2

First, the two body system represented by the proton and electron is recast as a reduced mass, one body problem as was done with the rigid rotor. In this view, the reduced mass μ, moves around the center-of-mass (c.m.) of the H atom system which is fixed, rather than having both the proton and electron move.

Since, however, mp ~1.0072 amu while the me ~0.000549 amu:

μ =0.000549\*1.0072 = 0.0005482 amu

1.0072 + 0.000549

Hence, μ ~ 0.9987 me and can effectively be thought of as just the electron itself.

Similarly, the c.m. frame places the proton rp away from the center-of-mass while the electron is re from the center-of-mass, where re +rp =r, the distance between proton and electron.

However, the center-of-mass relative to the proton taken as the initial reference Cartesian position (0,0,0) can be computed as below, where we have assumed for convenience that the system lies temporarily along just the x axis.

xcm = mp xp +me xe = mp\*0 +mer = 0.000549\*r = 0.0005448r

mp +me mp +me 1.0072 +0.000549

The distance rp the proton from the center of mass =r-0.0005448r =0.9995 r which can be approximated as just r and the proton can be effectively placed at the center of mass. Since we have already shown that μ~ me then the reduced mass can be thought of as the electron and the proton can be viewed as the center of mass with little error.

**7.2. Step 2: Write the Reduced Mass Schrodinger Equation in Spherical Coordinates**

Approximating re=r, μ=me=m, and 1/4πεo =K, the Schrodinger equation in 3 dimensions using Cartesian coordinates is written as below where the `del ’ squared operator ∇2 =

**1** {-ħ 2∇ -Ke2 } ψ(x,y,z) =E ψ(x,y,z) ***Schrodinger equation***

2m r ***in Cartesian coordinates***

The above is the quantum translation of the classical expression of total energy E (see table 4.1

Page 119 of text.)

KE + PE = total E

p2 -Ke2 =E

2m r

As noted in class, the use of Cartesian coordinates in **1** is incompatible with the physical situation since:

1 = 1

r √ (x2 +y2 +z2)

The presence of the radical in the denominator is intractable to separation of variables methods, a technique critical to any successful solution. It is thus necessary to convert ∇2 to an equivalent form in spherical coordinates. The results of this (horribly tedious) conversion is captured in equation 6.3 of your text and is reproduced below:

∇2 = 1 ∂ r2 ∂ + 1 ∂ sin θ ∂ + 1 ∂2

r2 ∂r ∂r r2 sin θ ∂θ ∂θ r2sin2 θ ∂φ2

Plugging in this version of the ∇2 we arrive at equation 6.4 of your text:

***Schrodinger equation for H atom***

**2** -ħ 2 {1 ∂ r2 ∂ + 1 ∂ sin θ ∂ + 1 ∂2 }ψ(x,y,z) -Ke2ψ(x,y,z) =Eψ(x,y,z)

2m r2 ∂r ∂r r2 sin θ ∂θ ∂θ r2sin2 θ ∂φ2 r

***in spherical coordinates***

**7.3. Step 3: The Spherical Expression, 2, Is Massaged to Allow Separation Of Variables**

We multiply 2 through by mr2 , subtract mr2Eψ(x,y,z) from the right hand side and isolate the r and (θ, φ) pieces of the ∇2 part of the expression to produce essentially equation 6.5 of your text:

**3** ***Spherical Schrodinger Equation Manipulated into a `Separated’ Form***

{-ħ 2∂ **r2** ∂ **- 2mr2 [ Ke2 – E ]}** ψ(**r,**θ**,**φ**)** - ħ 2{ **1** ∂ **sin** θ∂ **+ 1** ∂**2}** ψ(**r,**θ**,**φ**) =0**

∂**r** ∂**r r sin** θ∂θ∂θ **sin2** θ∂φ**2**

r-only piece θ**,**φ piece

7.4**. Step 4: the General Wave Function , ψ(r,θ,φ) Recast as R(r)Y(θ,φ) and Plugged into 3**

Setting **ψ(r,θ,φ) = R(r)Y(θ,φ), equation 3 becomes:**

{-ħ 2∂ **r2** ∂ **- 2mr2 [ Ke2 – E ]}** **R(r)Y(θ,φ)** - ħ 2{ **1** ∂ **sin** θ∂ **+ 1** ∂**2} R(r)Y(θ,φ) =0**

∂**r** ∂**r r sin** θ∂θ∂θ **sin2** θ∂φ**2**

r-only piece **θ,φ-only piece**

Since the r-only piece of the operator above ignores θ,φ and the θ,φ-only piece of the operator ignores R(r), we can re-write the above so:

**Y(θ,φ)** {-ħ 2∂ **r2** ∂ **- 2mr2 [ Ke2 – E ]}** **R(r)** - ħ 2 **R(r)**{ **1** ∂ **sin** θ∂ **+ 1** ∂**2} Y(θ,φ) =0**

∂**r** ∂**r r sin** θ∂θ∂θ **sin2** θ∂φ**2**

Finally, we divide the equation by ψ(r,θ,φ) = R(r)Y(θ,φ) which produces **4 (see also 6.8 and 6.9 of text.)**

**4 -1** {ħ 2∂ **r2** ∂ **- 2mr2 [ Ke2 – E ]}** **R(r) -ħ 2** { **1** ∂ **sin** θ∂ **+ 1** ∂**2} Y(θ,φ) =0**

**R(r)** ∂**r** ∂**r r Y(θ,φ) sin** θ∂θ∂θ **sin2** θ∂φ**2**

-β (constant) +β (constant)

***Schrodinger’s equation with Separable terms in r and (θ,φ)***

Since r and (θ,φ) are independent of each other, the two halves of the equation above must sum to zero and each half must equal a constant with magnitude β, but which are opposite in sign. The result is very similar to the solution form for the classical wave equation of chapter 2.

7.5**. Step 5: First Solve the Y(θ,φ) Piece, the Spherical Harmonic Function**

**-ħ 2** {∂ **sin** θ∂ **+ 1** ∂**2} Y(θ,φ) =βY(θ,φ)**

**sin** θ∂θ∂θ **sin2** θ∂φ**2**

This is done by further separating Y(θ,φ)= P(θ)Φ(φ). Substituting this into the θ,φ piece of the equation above allows a relatively simple determination of Φ(φ) which is done in detail on pp. 193-194 of the text. The result is:

Φ(φ)= (1/2π)1/2eimφ, m=0, ±1, ±2…

The remaining differential equation left after this piece is extracted looks so (eq. 6.22 of text)

**Legendre’s equation**

Where x= cos θ and the β and m are defined above. The differential equation is known as Legendre’s equation for the mathematician who first proposed and solved it. The solutions for P(x) end up depending on integers L= 0,1,2 and m=0, ±1, ±2…±L. That is, for each value of L, there are a family of solutions m=0, ±1, ±2…±L, which mean for L, there are 2L +1 possible family members.

7.5**. Step 6: Solve the R( r) Piece Last**

**-1** {ħ 2∂ **r2** ∂ **- 2mr2 [ Ke2 – E ]}** **R(r) = -β**

**R(r)** ∂**r** ∂**r r**

The above problem is rarely explored in any detail in undergraduate (or graduate) quantum chemistry courses since it is exceedingly tedious to solve. The results yield, however, a lovely eigen solution for E and complete expressions for R(r ) called Laguerre polynomials found in Table 6.4, page 207.

E ends up being exactly the original Bohr solution:

n=1,2,3…

Where ***a*** is the Bohr radius which has the familiar form:

**a**= ħ 2/mKe2

It is also noted that because the sum of the r and (θ,φ) halves of equation **4** must sum to zero, that if the quantum number n is specified, so is L since:

L = 0,1,2..(n-1)

The complete wave functions for n=1-3 are found in Tables 6.5 and 6.6 (pages 208 and 218) of your text. The consequences and properties of the solutions found therein are explored in lecture.