**Supplement 6: Chemistry 6854**

**Physical Chemistry Alfred State College**

**The Quantum Rigid Rotor Summarized**

**6.1 Simple 2D (1 variable) Rigid Rotor case: (not in text)**

Recall that the Hamiltonian operator for linear motion

**H**op= -ħ 2  d2 + V(x)

2m dx2

In 2D, the equivalent **rotational** Hamiltonian replaces

m with I =μr2 and x with φ (the angle of rotation in

the 2D plane of motion).

r

c.m.(center- of- mass)

r1 r2

**Linear form**

**H**op= -ħ 2  d2 + V(x)

2m dx2

**Rotational form**

Hop= -ħ 2  d2 + V(φ) = -ħ 2  d2 + V(φ)

2I dφ2  2μr2 dφ2

It is assumed that no retarding potential exists for the rotation, e.g. it is spinning in a vacuum and far from gravity, so V(φ)=0. Invoking quantum postulate 3, we now attempt to find a solution to the eigen value problem below, where Y(φ) is the wave function

**-ħ 2  d2 Y(φ) = EY or d2Y(φ) + 2μr2 E Y = 0**

**2μr2 dφ2 dφ2 ħ 2**

In the above, since the differential equation is 2nd order with constant coefficients

a= 1, b=0 and c= 2IE/ħ 2 = 2μr2E/ħ 2

roots = ± ik where k = (2μr2E/ħ 2)1/2

Thus:

Y(φ) = A1e+ikφ + A2e-ikφ (first is clockwise rotation, second is counterclockwise rotation)

Now the conditions are that Y(φ) = Y(φ + 2π) and <Y\* |Y> = 1

2π

Normalization => ∫ (A1e+ikφ + A2e-ikφ )\* (A1e+ikφ + A2e-ikφ )dφ =1

0

2π

∫ (A1e-ikφ + A2e+ikφ )\* (A1e+ikφ + A2e-ikφ )dφ =1

0

1 =(A12 + A22)2π + 1/ik A1A2 e+ikφ|2π -1/ik A1A2 eikφ|2π

1 =(A12 + A22)2π + (1-1) -(1-1)

√1/2π =√(A12 + A22)

If we assume A2 = 0 (i.e. the rotor is moving clockwise only) then A1 = √1/2π

Boundary condition Y(φ) = Y(φ + 2π) means (if we assume for simplicity just a clockwise rotation), i.e :

eik(φ+2π) = eikφ

dividing through, this becomes the same as :

eik(φ+2π) = e2iπk = 1 = cos 2πk +i sin 2πk

eikφ

this can only be so if k = 0, ± 1, ±2…= **±j**

(Note: McQuarrie uses **m** not **j** as the rotational quantum integer. I’ve avoided this practice **m** can easily be confused with mass=m. The tradition, however, is to use m for the 1 variable rotation problem.)

* (2μr2E/ħ 2)1/2 = ±**j**
* (2μr2E/ħ 2) = **j2**

Rotational energy of 2D rigid rotor

* E = ħ 2 j2/2μr2, j = 0,± 1, ± 2…

Wave function =Y(φ) = √1/2π e+ikφ

**6.2 General 3D (2 variable) Rigid Rotor case (pp 175-179 of text)**

The 2D rotor assumes motion only in the plane for angle φ. In reality, even if r is fixed, rotation occurs in both φ and θ necessitating consideration of a much more complex differential equation. Specifically, it is asserted that the quantum Hamiltonian for a rigid rotor spinning in 3 dimensions takes the form:

**Hspherical = -** ħ 2 /2μr2 **{**1/sin θ ∂/∂θ {sin θ ∂/∂θ} + 1/sin2θ ∂2/∂φ2 } + V(θ,φ)

The Hamilitonian above is the spherical coordinate version at constant r and is a transformation of the more usual Cartesian quantum Hamiltonian in Table 4.1 on page 119 of your text

Hcartesian = - ħ 2 /2m {d2/dx2 + d2/dy2 +d2/dz2) +V(x,y,z)

The relevant eigen value problem, where V(θφ) = 0 has the form:

**Hspherical Y(θ,φ)= -** ħ 2 /2μr2 **{**1/sin θ ∂/∂θ {sin θ ∂/∂θ} + 1/sin2θ ∂2/∂φ2 }Y(θ,φ) = EY(θ,φ)

The resulting wave function,Y(θ,φ) is refered to as the spherical harmonic Y(θ,φ))

Some examples of Y(θ,φ) are found in table 6.3, page 198 of your text.

Rotational energy of 3D rigid rotor (what HCl will follow)

E= ħ2 J(J+1) J=0 ±1,±2…

2μr2

Rotational Selection rule for transition = ΔJ= ±1

ΔE(J🡪J+1) = υ(m-1) = 2Be(J+1) where Be = h/8π2Ic the rotational constant