Lecture #3 Hydrogenic Atoms (Chapter **13**)

I. Applications of QM:

B. Rigid Rotor (RR) in a plane

C. Harmonic Oscillator

II. Experimental Observation of Line Spectra

III. QM Picture of Hydrogenic Atoms (13.1-13.3)

A. Energy Levels

B. Energy Functions (s,p,d)

I. Applications of QM

B. Rigid Rotor in a Plane

Model for rotational motion in which two bodies are separated by a rigid connector (good for modeling rotational energy of diatomic molecules assuming fixed bond length).

For a particle rotating on a ring of radius r in a plane: it's angular speed is $\omega = 2\pi\nu_{rot} = v/r$. Note v = linear speed along tangent. The moment of inertia is $I = mr^2$, thus the angular momentum = $J=I\omega=mvr = p\times r$. The total **Energy = Kinetic Energy = I**w^2**/2 =** J^2**/2I =** p^2r^2**/2I.**
substituting the de Broglie relation (converts classical to QM): $p=h/\lambda$.
$E = (hr/\lambda)^2/2I$,
Imposing boundary conditions: An integral number of wavelengths must match circumfrence of path (justification seen via Fig. 12.27): $n\lambda = 2\pi r$, substituting this for λ in the above expression yields $E = (hn/2\pi)^2/2I = \dfrac{n^2\hbar^2}{2I}$ for n = 0, ±1,±2,±3,...

renaming **n** as $\mathbf{m_l}$ leads to a final expression: $E = \dfrac{m_l^2\hbar^2}{2I}$ for m_l = 0, ±1,±2,±3,...

Correspondence Between Rectilinear and Angular Quantitites

Linear	Angular
Mass (m)	Moment of Inertia ($I=mr^2$)
Speed ($v = 2\pi r\nu_{rot}$) cm/sec (r = cm/rad, ν_{rot} = rev/sec)	Angular Speed ($\omega = 2\pi\nu_{rot} = v/r$) radians/sec
Momentum (p=mv)	Angular Momentum ($L=I\omega=mvr$) Kg m^2 s^{-1} radians, usu. *radians* is excluded to have: Kg m^2 s^{-1} ($h/2\pi$ units)
Kinetic Energy $mv^2/2 = p^2/(2m)$	Rotational Kinetic Energy $I\omega^2/2 = L^2/2I$

Exercise: For HCl rotating in a plane, if the moment of inertia (I) of HCl is 2.6E-47 Kg m^2, what energy in joules is needed to excite it from m_l = 1 to m_l = 2 level. What wavelength does this correspond to?

C. Harmonic Oscillator

Energy eigenvalue = E_u **=hν_0 (u+ ?)** u **= 0,1,2,3…**

How would you write this equation in cm^{-1} ?

FUNDAMENTAL FREQUENCY « k(force constant)

ν_0 **=fundamental frequency in Hz,** $\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = fundamental\ \ frequency$ in cm^{-1},

obtained from observing u=0 to u=1 transition from this we may find value of force constant k in N m^{-1}.

$\Delta\bar{\nu}_{\upsilon=1} = \bar{\nu}_{\upsilon=1} - \bar{\nu}_{\upsilon=0} = \bar{\nu}_0(1+ ?) - \bar{\nu}_0(0+ ?) = \bar{\nu}_0$

CAUTION WHEN COMPUTING m, make sure you divide molar masses by N_A to get "molecular mass"!

$\Delta E = h\nu$ = fundamental frequency. Given the observed fundamental freq →calc k. For example, if for $H^{35}Cl$ n=0 to n=1 has a fund freq of 2.9×10^3 cm^{-1}, calculate k.

$$\bar{\nu}(cm^{-1}) = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}\left(u + \frac{1}{2}\right)$$

$$\Delta\nu_{0\to1} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} = 2.886\ x\ 10^3\ cm^{-1}$$

$$k = (2\pi\ \Delta\nu\ c)^2\ \mu$$

$$c = 2.998\times10^{10}\ cm\ s^{-1}$$

$$\mu = \left[\frac{M_H M_{Cl}}{M_H + M_{Cl}}\right]\frac{1}{N_A} = \left[\frac{1.008\ g\ mol^{-1}\times35.00\ g\ mol^{-1}}{1.008\ g\ mol^{-1} + 35.00\ g\ mol^{-1}}\right]\frac{1}{6.022\times10^{23}\ mol^{-1}}\left(\frac{1Kg}{1000\ g}\right) = 1.627\times10^{-27}\ Kg$$

$$k = 4.81x10^2\ N\ m^{-1}$$

Purpose: Historical observation of H Line spectra. 2. Solving Schrodinger Equation to determine the energy levels (E) and wavefunctions (Ψ).

II. Experimental Observation of Line Spectra

When electric current passes through H_2, it dissociates into electronically excited H atoms that emit radiation at discrete λ as they return to ground state.

The waveno. (λ & ν) fit the **Rydberg equation**: *Empirical*

$$\tilde{n} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) n_1 = 1,2,3... \qquad n_2 = n_1+1, n_1+2,... \quad \textbf{(1)}$$

n_1 = 1 (Lyman), 2 (Balmer), 3 (Paschen), 4 (Brackett) and 5 (Pfund)
R_H = Rydberg constant = 109677 cm^{-1}
What is the wavenumbers for a transition in the paschen series with n_2 = 5?
What is the frequency?

Bohr Frequency Condition: $\Delta E = h\nu$, Condition of resonance: E-diff between levels matches photon's E. These allowed E states are **stationary states**.

III. QM Picture of Hydrogenic Atoms: E Levels

Deriving Rydberg Expression from Bohr Postulates

Classical Rutherford Nuclear Model has a nucleus of charge Ze orbited by an electron, and predicts electron would fall to nucleus. But Bohr's stationary state hypothesis coupled with this presented a quantum mechanical picture with stable orbits. Solved the S.E. with Coulombic Potential to get energy eigenvalues and energy eigenfunctions (*stationary state*).

A. Energy Levels (Eigenvalues)

This was accomplished by setting boundary conditions in which the Coulombic force (V/r) balanced the centrifugal force and this result substituted into the Energy conservation equation: E = KE + Coulomic Potential E.

The Coulombic Potential Energy = V = $-Ze^2/(4\pi\varepsilon_0 r)$ (2)

The resulting Energy Levels from boundary condition:

$E = -hcZ^2R/n^2$ where R = 109677 cm^{-1} (3) n= prinicple quantum number. n = 1,2,3...

where $$hcR = \frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2} \quad (4)$$

$$\mu = \frac{m_e m_N}{m_e + m_N}$$ **Reduced mass** (5) Since $m_N >> m_e$ then $\mu \sim m_e$.

Exercise E8.12

Shortest λ = highest energy transition for n =3 $\rightarrow$ n =∞, Thus waveno = $Z^2R(1/3^2)$ where Z = 3 for Li, thus waveno = 109677 cm^{-1}, and corresponding λ = 91.2 nm.

Can compute **ionization energies** as energy from n = 1 to n = ∞.: I = E = $-hcZ^2R$

HINT: It may be much easier to just use wavenumbers, i.e: $\tilde{n} = -Z^2R/n^2$ when you ultimately want to find λ.