

## Hermitian Operators:

An operator  $\hat{A}$  is Hermitian if:

$$\int \mathbf{f}^* \hat{A} \mathbf{y} dx = \int (\hat{A} \mathbf{f})^* \mathbf{y} dx$$

For all normalisable functions  $\mathbf{f}$  and  $\mathbf{y}$ .

All eigenvalues of a Hermitian operator are real.

The eigenfunctions of  $\hat{A}$  with different eigenvalues are orthogonal.

All operators used thus far are Hermitian.

## Rotational States of Diatomic Molecules:

Model as “rigid rotors”:

$$E_{rot} = \frac{1}{2} I \omega^2$$

And:  $L = I \omega$ .

Hence:

$$E_{rot} = T_{rot} = \frac{L^2}{2I}$$

And:

$$\hat{T}_{rot} = \frac{\hat{L}^2}{2I}$$

Thus, using the eigenvalue for angular momentum:

$$E_{\ell} = \frac{\ell(\ell+1)\hbar^2}{2I}$$

For a given  $\ell$ , there are  $(2\ell + 1)$  possible values of  $m$ . Hence degeneracy.

For a rotor with two masses  $m_1$  &  $m_2$ , separated by a distance  $r_0$ , by a rigid rod:

$$I = m_0^2 \Rightarrow E_{\ell} = \frac{\ell(\ell+1)\hbar^2}{2m_0^2} \quad m = \frac{m_1 m_2}{m_1 + m_2}$$

## Central Force Problems:

TDSE:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x, y, z, t) \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Which gives the time evolution.

TISE:

$$-\frac{\hbar^2}{2m}\nabla^2\mathbf{y} + V(\underline{r})\mathbf{y} = E\mathbf{y}$$

Which gives the stationary states.

In polars, this becomes:

$$\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\mathbf{y}}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2}\mathbf{y} + V(r)\mathbf{y} = E\mathbf{y}$$

Hydrogen Atom:

Here:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

We want solutions of the form:

$$\begin{aligned}\mathbf{y}(r, \mathbf{q}, \mathbf{f}) &= R(r)Y_{\ell, m}(\mathbf{q}, \mathbf{f}) \\ \hat{L}^2 Y_{\ell, m}(\mathbf{q}, \mathbf{f}) &= \ell(\ell+1)\hbar^2 Y_{\ell, m}(\mathbf{q}, \mathbf{f})\end{aligned}$$

Putting into the TISE, gives – after a lot of algebra:

$$-\frac{d^2u}{dr^2} + \frac{\ell(\ell+1)}{r^2}u - \frac{2}{r}u = eu$$

Where:

$$\begin{aligned}r &= \frac{r}{a_0} & a_0 &= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.53\text{\AA} = \text{Bohr radius} \\ e &= \frac{E}{E_R} & E_R &= \frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2} = 13.6\text{eV} = \text{Rydberg energy} \\ u(r) &= \frac{R(r)}{r}\end{aligned}$$

Giving solutions:

$$u(\mathbf{r}) = r^{\ell+1} e^{-br} f(\mathbf{r})$$

$$E = -b^2 E_R$$

Eventually, get:

$$E_n = -\frac{E_R}{n^2}$$

$n^2$  is the principle quantum number.

$$n = 1, 2, 3, \dots$$

This model assumes single proton, of infinite mass with respect to the electron.

### Quantum Numbers:

$$\ell = 0, 1, 2, 3, \dots$$

$$n = \ell + 1, \ell + 2, \ell + 3, \dots$$

Thus:

$$\ell = 0, 1, 2, 3, \dots$$

$$n = 1, 2, 3, 4, \dots$$

$$m = -\ell, (-\ell - 1), \dots, 0, \dots, (\ell - 1), \ell$$

Hence, degeneracy of  $2\ell + 1$  values of  $m$ .

Quantum numbers  $n, \ell, m$  specify values of  $E, L^2, L_z$ :

$$E = -\frac{E_R}{n^2} \quad L^2 = \ell(\ell + 1)\hbar^2 \quad L_z = m\hbar$$

$$n = 1, 2, 3, 4, \dots \quad \ell = 0, 1, 2, \dots, (n - 1) \quad m = -\ell, \dots, 0, \dots, +\ell$$

For example, the quantum numbers can be deduced from wavefunctions:

$n$	$\ell = 0$	$\ell = 1$	$\ell = 2$
1	$e^{-r/a_0}$	---	---
2	$\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$	$\frac{r}{a_0}e^{-r/a_0}$	---
3	$\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$	$\frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/3a_0}$	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

This table is for the radial parts of the wavefunctions only.

They are given, generally, by:

$$R_{n,\ell}(r) = A \left(\frac{r}{a_0}\right) e^{-r/na_0} \sum_{k=0}^{n-\ell-1} (-1)^k c_k \left(\frac{r}{a_0}\right)$$

Hence, the total wavefunction is given by:

$$y_{n\ell m}(r, \mathbf{q}, \mathbf{f}) = R_{n\ell}(r) Y_{\ell m}(\mathbf{q}, \mathbf{f})$$

Where:

$$Y_{\ell m}(\mathbf{q}, \mathbf{f}) = P_{\ell m}(\mathbf{q}) e^{imf}$$

Thus:

$$Y_{\ell m}(\mathbf{q}, \mathbf{f}) \quad \text{a spherical harmonic}$$

$$P_{\ell m}(\mathbf{q}) \quad \text{an associated Legendre polynomial}$$

Normalisation:

Require:

$$\iiint |\mathbf{y}_{n\ell m}(r, \mathbf{q}, \mathbf{f})|^2 dV = 1$$

Or, with limits and the volume element:

$$\int_{r=0}^{\infty} \int_{\mathbf{q}=0}^{\mathbf{p}} \int_{\mathbf{f}=0}^{2\mathbf{p}} |\mathbf{y}_{n\ell m}|^2 r^2 \sin \mathbf{q} dr d\mathbf{q} d\mathbf{f}$$

However, the  $Y_{\ell m}$  terms are already normalised. Hence, just require:

$$\int_0^{\infty} r^2 R_{n\ell}^2(r) dr = 1$$

The effective potential term is:

$$V_{eff} = -\frac{\ell(\ell+1)\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Notice which term dominates for  $\ell \geq 1$ .

i.e, for  $\ell = 0$ , the coulomb potential term dominates... but as  $\ell$  increases, the angular part becomes more dominant.

In other single-electroned atoms, with  $Z$  protons:

$$E_n = -\frac{Z^2}{n^2} E_R$$

The reduced mass correction looks like:

$$\mathbf{m} = \frac{m_e m_N}{m_e + m_N} \Rightarrow E_n = -\frac{Z^2}{n^2} E_R \frac{m_N}{m_e + m_N} \quad \text{for a nucleus mass } m_N$$

## Transitions:

For an electron transition from a high  $n$ , to a lower  $m$  state, the energy of the emitted photon  $E_g = h\nu$  is given by:

$$h\nu = E_R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)$$

Lyman series:                      Transitions into  $m = 1$  state:

$$h\nu = E_R \left( \frac{1}{1^2} - \frac{1}{n^2} \right) \qquad \text{UV frequencies}$$

Balmer series:                      Transitions into  $m = 2$  state:

$$h\nu = E_R \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \qquad \text{Optical/UV}$$

Pashcen series:                      Transitions into  $m = 3$  state:

$$h\nu = E_R \left( \frac{1}{3^2} - \frac{1}{n^2} \right) \qquad \text{IR}$$