Diatomic Molecules

$$E_{vib} = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad m = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass}$$

Energy eigenvalues:

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar w} \qquad w = \sqrt{\frac{k}{m}} \qquad n = 0,1,2,\ldots$$

n = 0 gives the ground state
n = 1 is the 1st excited state

In 2D:

$$V(x,y) = \frac{1}{2}k\left(x^2 + y^2\right) = \frac{1}{2}mw^2\left(x^2 + y^2\right)$$

$$\hat{T} = \frac{\hat{p}_x^2 + \hat{p}_y^2}{2m}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

Hence, the TISE becomes:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)y + \frac{1}{2}mw^2\left(x^2 + y^2\right)y = Ey$$

Where:

$$y = y(x,y)$$

Now: $\hat{H}y = Ey$

Where:

$$\boxed{\begin{aligned} \hat{H} &= \hat{H}_x + \hat{H}_y \\ \hat{H}_x &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}mw^2x^2 \\ \hat{H}_y &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}mw^2y^2 \end{aligned}}$$

For the 1D SHO:

$$\hat{H}_x y_{n_x}(x) = \left(n_x + \frac{1}{2}\right)\hbar w y_{n_x}(x)$$

Thus:

$$\boxed{E_{n_x,n_y} = \left(n_x + n_y + 1\right)\hbar w}$$

Hence, get degeneracy of energy states… where more than one state has the same energy.
If two or more states have the same energy, any linear superposition of them is another energy eigenfunction with the same energy.

Angular Momentum:

$$\underline{L} = \underline{r} \times \underline{p}$$

$$\therefore$$

$$\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}} = \begin{vmatrix} \underline{i} & \underline{j} & \underline{k} \\ x & y & z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

Thus, the *z*-component of angular momentum is:

$$\begin{aligned} \hat{L}_z &= x\hat{p}_y - y\hat{p}_x \\ &= -xi\hbar\frac{\partial}{\partial y} + yi\hbar\frac{\partial}{\partial x} \end{aligned}$$

Thus:

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

Or, in plane polars:

$$\boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial f}}$$

Postulate:

$$y\,(r,f) = R(r)\Phi(f)$$

Which should satisfy the eigenproblem:

$$-i\hbar\frac{\partial}{\partial f}y = L_z y \qquad \{\leftrightarrow \hat{L}_z y = L_z y\}$$

Thus:

$$-i\hbar\frac{\partial\Phi}{\partial f} = L_z\Phi$$

Which has solutions:

$$\Phi(f) = Ae^{\frac{iL_z f}{\hbar}}$$

Now: $\Phi(f) = \Phi(f + 2p)$

Thus:

$$e^{\frac{iL_z(f+2p)}{\hbar}} = e^{\frac{iL_x f}{\hbar}}$$

Hence:

$$e^{\frac{iL_x 2p}{\hbar}} = 1$$

Hence:

$$\boxed{L_z = m\hbar} \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Thus:

$$y(r,f) = R(r)e^{imf}$$

"Quantised angular momentum in units of $\hbar$"

Thus, energy eigenfunctions are of the form: $R(r)e^{imf}$.
Notice that;

$$\left[\hat{H}, \hat{L}_z\right] = 0$$

Which means that they commute.
In 3D we get:

$$\underline{\hat{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x$$

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

Which means that two components of $\underline{L}$ cannot have simultaneously definite values. Only one component can have a definite value.

$$\left[\underline{\hat{L}}^2, \hat{L}_x\right] = \left[\underline{\hat{L}}^2, \hat{L}_y\right] = \left[\underline{\hat{L}}^2, \hat{L}_z\right] = 0$$

Thus can have simultaneously definite values of $\hat{L}^2$ and $\hat{L}_x / \hat{L}_y / \hat{L}_z$.
Now:

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial q^2} + \cot q \frac{\partial}{\partial q} + \frac{1}{\sin^2 q}\frac{\partial^2}{\partial f^2}\right)$$

Which is the angular part of the Laplacian ∇^2, in spherical polars.

Now, consider the TISE in 3D, for motion in a central potential:

$$V(r,q,f) \rightarrow V(r)$$

Hence:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]y = Ey$$

Now, in spherical polars, the Laplacian is:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin q}\frac{\partial}{\partial q}\left(\sin q \frac{\partial}{\partial q}\right) + \frac{1}{r^2 \sin^2 q}\frac{\partial^2}{\partial f^2}$$

Thus the TISE becomes:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2 y}{\partial r^2} + \frac{2}{r}\frac{\partial y}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2 y}{\partial q^2} + \cot q \frac{\partial y}{\partial q} + \frac{1}{\sin^2 q}\frac{\partial^2 y}{\partial f^2}\right]\right] + V(r)y = Ey$$

Now, from before:

$$\left(\frac{\partial^2 y}{\partial q^2} + \cot q \frac{\partial y}{\partial q} + \frac{1}{\sin^2 q}\frac{\partial^2 y}{\partial f^2}\right) = -\left(\frac{\hat{L}^2}{\hbar^2}\right)y$$

Hence, the TISE reduces to:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + V(r)\right]y + \frac{\hat{L}^2}{2mr^2}y = Ey$$

Which shows the radial and angular components of kinetic energy… the rotational part is:

$$T_{rot} = \frac{\hat{L}^2}{2mr^2}$$

Eigenfunctions & eigenvalues of $\hat{L}^2$:

- Simultaneously eigenfunctions of $\hat{L}^2$ & $\hat{L}_z$.

$$y(r,q,f) = R(r)F(q,f) \rightarrow y = RF$$

Thus:

$$\hat{L}^2 y = L^2 y$$

$$\hat{L}^2 RF = L^2 RF$$

$$R\hat{L}^2 F = RL^2 F$$

$$\therefore$$

$$\hat{L}^2 F = L^2 F$$

$\hat{L}_z$ must have e^{imf} as the phi-dependence. Thus:

$$F(q,f) = P(q)e^{imf}$$

Putting into $\hat{L}^2$

$$-\hbar^2\left(\frac{\partial^2 P}{\partial q^2}+\cot q\,\frac{\partial P}{\partial q}-\frac{m^2}{\sin^2 q}P\right)=L^2 P$$

Write $L^2 = l\hbar^2$. Hence:

$$\frac{d^2P}{dq^2}+\frac{\cos q}{\sin q}\frac{dP}{dq}+\left(l-\frac{m^2}{\sin^2 q}\right)P=0$$

Which has sets of solutions, with:

$$l=\ell(\ell+1) \qquad\qquad \ell=0,1,2,3,\ldots$$

$$\therefore\ l=0,2,6,12,20,30,42,\ldots$$

ℓ is thus the "orbital quantum number".
For each ℓ there is an "m":

$$m=(-\ell),(-\ell-1),\ldots,-1,0,+1,\ldots,(\ell-1),\ell$$

m is the "azimuthal quantum number".
Note:

$$\left(\hat{L}_z\right)^2 \le L^2$$
$$\Rightarrow m^2\hbar^2 \le \ell(\ell+1)\hbar^2$$

Eigenfunctions of $\hat{L}^2$ are:

$$P_{\ell,m}(\cos q)$$

Or:

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

Which is a "spherical harmonic".
Thus:

$$y(r,q,f)=R(r)Y_{\ell,m}(q,f)$$