Angular momentum

$$\vec{L} = \hat{\vec{r}} \times \hat{\vec{p}}$$

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

The three components of $\hat{\vec{L}}$ do not commute with each other

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

Very similar to spin operators! For a good reason:

$\hat{\vec{S}}$ — spin angular momentum (intrinsic)

$\hat{\vec{L}}$ — orbital angular momentum (rotation)

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} \quad - \quad \text{total angular momentum (!)}$$

(so before $\hat{\vec{L}} = 0$ and $\hat{\vec{J}} = \hat{\vec{S}}$)

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad \rightarrow \quad \text{commutes with each } \hat{L}_i$$

Thus, as before, we can find common wave functions for $\hat{L}^2$ and $\hat{L}_z$

$$\hat{L}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle$$
$$\hat{L}_z |\ell, m\rangle = \hbar m |\ell, m\rangle$$

Moreover, $\hat{L}^2$ and $\hat{L}_i$ commute with the Hamiltonian (as long as the potential is $V(r)$)

$$[\hat{H}, \hat{L}_z] = 0 \qquad [\hat{H}, \hat{L}^2] = 0$$

Common wave-functions for all three: $\hat{H}, \hat{L}^2, \hat{L}_z$

$$\hat{H} |E, \ell, m\rangle = E |E, \ell, m\rangle$$
$$\hat{L}^2 |E, \ell, m\rangle = \hbar^2 \ell(\ell+1) |E, \ell, m\rangle$$
$$\hat{L}_z |E, \ell, m\rangle = \hbar m |E, \ell, m\rangle$$

Schrödinger equation for the central potential in position space – basis (spherical coordinates)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

can do straightforward math, but we can be clever

$$\hat{L}^2 = (\hat{\vec{r}}\times\hat{\vec{p}})(\hat{\vec{r}}\times\hat{\vec{p}}) = \hat{r}^2\hat{p}^2 - (\hat{\vec{r}}\cdot\hat{\vec{p}})^2 + i\hbar\,\hat{\vec{r}}\cdot\hat{\vec{p}}$$

$$\hat{r}^2\hat{p}^2 \;=>\; r^2(\,\hat{p}^2)$$

$$\hat{\vec{r}}\cdot\hat{\vec{p}} \;=>\; \hat{\vec{r}}\cdot p_r = r\left(-i\hbar\frac{\partial}{\partial r}\right) \qquad (\hat{\vec{r}}\cdot\hat{\vec{p}})\psi = -i\hbar\, r\,\frac{\partial\psi}{\partial r}$$

$$(\hat{\vec{r}}\cdot\hat{\vec{p}})^2\psi(r) = (\hat{\vec{r}}\cdot\hat{\vec{p}})\left[(\hat{\vec{r}}\cdot\hat{\vec{p}})\psi(r)\right] = (\hat{\vec{r}}\cdot\hat{\vec{p}})\left[-i\hbar\, r\,\frac{\partial\psi}{\partial r}\right] =$$

$$= (-\hbar^2)\, r\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right) = (-\hbar^2)\left[r\frac{\partial\psi}{\partial r} + r^2\frac{\partial^2\psi}{\partial r^2}\right]$$

$$\times\frac{1}{2\mu r^2}\quad \hat{L}^2\psi = r^2(\hat{p}^2\psi) + \hbar^2\left[r\frac{\partial\psi}{\partial r} + r^2\frac{\partial^2\psi}{\partial r^2}\right] + \hbar^2 r\frac{\partial\psi}{\partial r}$$

$$\frac{1}{2\mu}\hat{p}^2\psi = \frac{\hat{L}^2}{2\mu r^2}\psi - \frac{\hbar^2}{2\mu}\left[\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right]$$

$$\hat{H}\psi = \frac{\hat{p}^2}{2\mu}\psi + V(r)\psi = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right] + \frac{\hat{L}^2}{2\mu r^2}\psi + V(r)\psi$$

$$\hat{H}\psi = E\psi \qquad \psi_{\ell m}(r,\theta,\varphi) = \langle\vec{r}\,|E,\ell,m\rangle$$

$$\hat{L}^2\psi = \langle\vec{r}\,|\hat{L}^2|E,\ell,m\rangle = \hbar^2\ell(\ell+1)\langle\vec{r}\,|E,\ell,m\rangle = \hbar^2\ell(\ell+1)\psi_{\ell m}$$

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right] + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\psi + V(r)\psi = E\psi$$

The equation depends only on r (effectively one-dimensional)

$$\psi_{\ell m}(r, \theta, \varphi) = R(r) \, Y_{\ell m}(\theta, \varphi) \quad \leftarrow \text{spherical functions}$$

$$\hat{L}^2 \, Y_{\ell m}(\theta, \varphi) = \hbar \, \ell(\ell+1) \, Y_{\ell m}(\theta, \varphi)$$

$$\hat{L}_z \, Y_{\ell m}(\theta, \varphi) = \hbar m \, Y_{\ell m}(\theta, \varphi)$$

spatial representation of $|\ell, m\rangle$

$$\langle \vec{r} \, | \, \ell, m \rangle$$

$$R(r) = \frac{u(r)}{r} \qquad \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} = \frac{1}{r} \frac{d^2 u}{dr^2}$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) \right] u = E \cdot u(r)$$

Quazi – one dimensional motion in an effective 1D potential

$$V_{eff}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}$$

Let's get back to a molecule

Vibration $\longrightarrow$ change in relative distance b/w two atoms, need full hamiltonian

$V_{eff}(r)$

Van-der-Vaal attraction

maybe Coulumb attraction (ionic bond)

Strong repulsion

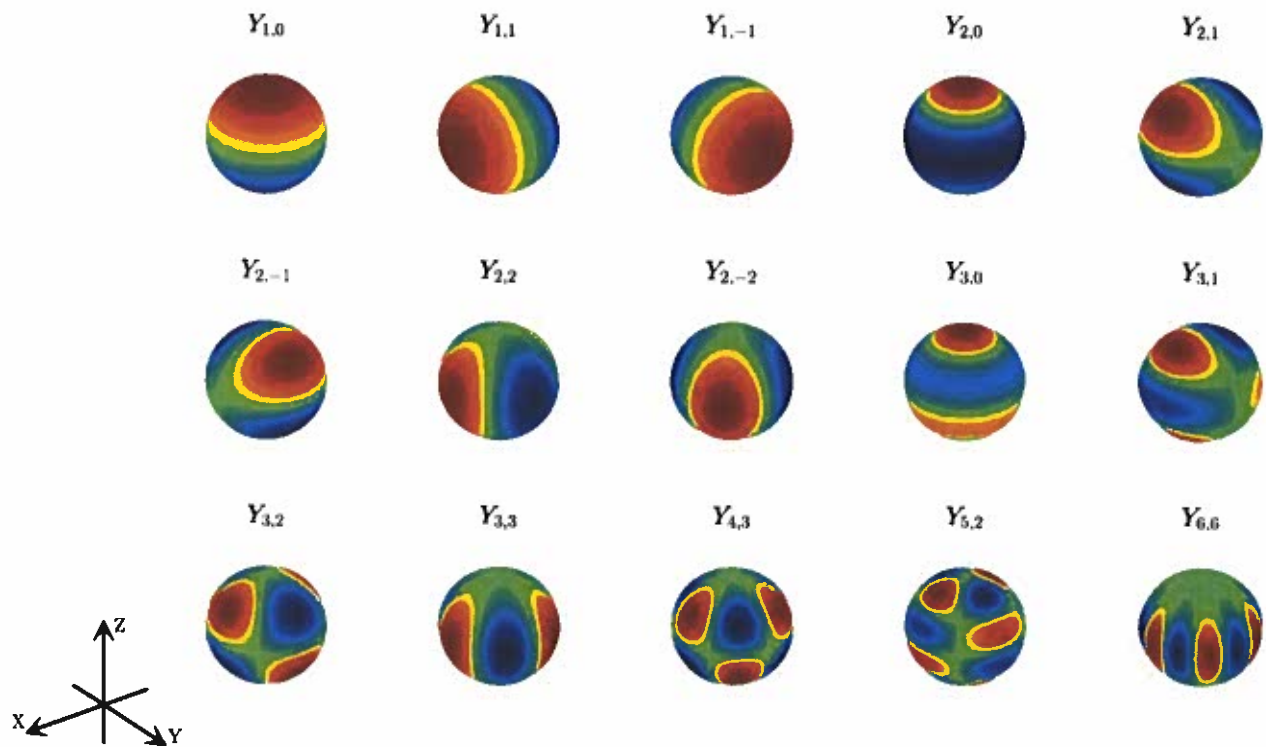$$V_{eff}(r) \approx V_{eff}(r_0) + \frac{1}{2} \frac{d^2 V_{eff}}{dr^2}\bigg|_{r=r_0} (r - r_0)^2$$

set as zero energy

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \frac{1}{2} \mu \omega_0^2 (r-r_0)^2 u = (E - V_{eff}(r_0)) u$$

SHO

$$E_{n_v} = \hbar \omega \left(n_v + \frac{1}{2} \right) \qquad \hbar \nu \rightarrow \text{vibrational levels}$$

$$Y_l^m (\theta, \phi) \equiv \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} \, P_l^m (\cos\theta) \, e^{im\phi},$$

$$P_n^m (x) = \frac{(1-x^2)^{\frac{m}{2}}}{2^n n!} \frac{d^{n+m}}{dx^{n+m}} (x^2-1)^n.$$

$$Y_0^0(\theta, \phi) = \frac{1}{2} \frac{1}{\sqrt{\pi}}$$

$$Y_1^{-1}(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \, \sin\theta \, e^{-i\phi}$$

$$Y_1^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \, \cos\theta$$

$$Y_1^1(\theta, \phi) = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \, \sin\theta \, e^{i\phi}$$

$$Y_2^{-2}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \, \sin^2\theta \, e^{-2i\phi}$$

$$Y_2^{-1}(\theta, \phi) = \frac{1}{2} \sqrt{\frac{15}{2\pi}} \, \sin\theta \cos\theta \, e^{-i\phi}$$

$$Y_2^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} \, (3\cos^2\theta - 1)$$

$$Y_2^1(\theta, \phi) = -\frac{1}{2} \sqrt{\frac{15}{2\pi}} \, \sin\theta \cos\theta \, e^{i\phi}$$

$$Y_2^2(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \, \sin^2\theta \, e^{2i\phi}$$

$$Y_3^{-3}(\theta, \phi) = \frac{1}{8} \sqrt{\frac{35}{\pi}} \, \sin^3\theta \, e^{-3i\phi}$$

$$Y_3^{-2}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{105}{2\pi}} \, \sin^2\theta \cos\theta \, e^{-2i\phi}$$

$$Y_3^{-1}(\theta, \phi) = \frac{1}{8} \sqrt{\frac{21}{\pi}} \, \sin\theta(5\cos^2\theta - 1) \, e^{-i\phi}$$

$$Y_3^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{7}{\pi}} \, (5\cos^3\theta - 3\cos\theta)$$
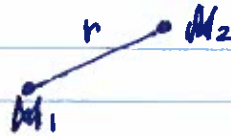
$$Y_3^1(\theta, \phi) = -\frac{1}{8} \sqrt{\frac{21}{\pi}} \, \sin\theta(5\cos^2\theta - 1) \, e^{i\phi}$$

$$Y_3^2(\theta, \phi) = \frac{1}{4} \sqrt{\frac{105}{2\pi}} \, \sin^2\theta \cos\theta \, e^{2i\phi}$$

$$Y_3^3(\theta, \phi) = -\frac{1}{8} \sqrt{\frac{35}{\pi}} \, \sin^3\theta \, e^{3i\phi}.$$

Molecular spectra

Diatomic molecules

$V_{12}(\vec{r_1}, \vec{r_2}) = V(r)$
$r = |\vec{r_1} - \vec{r_2}|$

Centrally - symmetric potential

$$\hat{H} = \frac{\hat{P}^2}{2\mu} + V(\hat{r})$$

no explicit angular dependence in Hamiltonian
$\Rightarrow$ angular momentum is conserves

$\hat{L}^2 Y_{\ell m} = \hbar^2 \ell(\ell+1) Y_{\ell m}$
$\hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m}$

$$\psi(\vec{r}) = \underbrace{\frac{u(r)}{r}}_{\text{radial component}} \cdot Y_{\ell m}(\theta, \varphi)$$

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

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u(r)}{dr^2} + \left[\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) \right] u(r) = E(r)$$

one can use this simplified equation to find possible energy states

Various possible energy-related processes

1. Motion of a molecule as a whole → neglect for now

2. Rotation
3. Vibration
4. Electron excitation (internal energy for a molecule, motion of an electron around a nucleus)

How the energy scales of these motions relate to each other ?

We can use the uncertainty principle to do the estimation.

Vibrational   spectrum

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[\underbrace{\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r)}\right] u(r) = E \cdot u(r)$$
$$\text{Veff}(r)$$
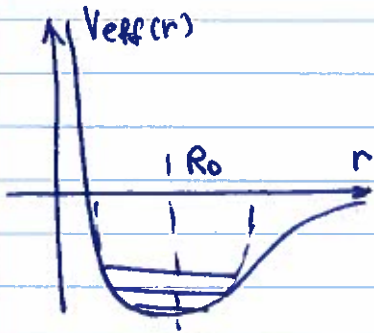
Near the equilibrium

$$\text{Veff}(r) \approx \text{Veff}(R_0) + \underbrace{\frac{dVeff}{dr}}_{=0}(r-R_0) + \frac{1}{2}\frac{d^2 Veff}{dr^2}\Big|_{R_0}$$
$$\times (r-R_0)^2$$

$$\text{Veff}(r) \approx \text{Veff}(R_0) + \frac{1}{2}\frac{d^2 Veff}{dr^2}\Big|_{R_0}(r-R_0)^2$$
$$\underbrace{\qquad\qquad\qquad}$$
$$+\frac{1}{2}\mu\omega^2 (r-R_0)^2$$

For   lower - energy   vibrational   state — SHO spectrum

$$E_{n_v} = \hbar\omega_v(n_v+\tfrac{1}{2}) \qquad n_v = 0,1,2\ldots$$
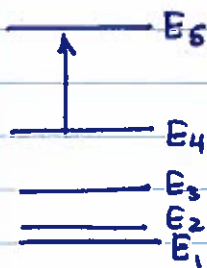 Absorption   Spectrum — a single line @ ω_v
Rotational spectrum

$$\hat{H}_{rot} = \frac{\hat{L}^2}{2I} \qquad\qquad \hat{H}_{rot}|\ell,m\rangle = \frac{\hbar^2\ell(\ell+1)}{2I}|\ell,m\rangle$$

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

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

Absorption   spectrum — equidistant
frequency   comb

$$\omega_\ell - \omega_{\ell-1} = \frac{\hbar}{I}$$