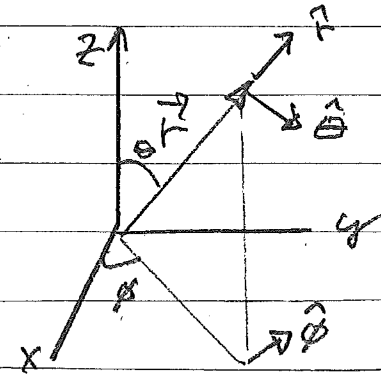
Lecture 4: Spherical Harmonics

Compute $\hat{L}^2$

$$\hat{r}\times\hat{\theta}=\hat{\phi}$$



$$\hat{r} = \sin\theta\left(\cos\phi\,\hat{x}+\sin\phi\,\hat{y}\right)+\cos\theta\,\hat{z}$$
$$\hat{\theta} = \cos\theta\left(\cos\phi\,\hat{x}+\sin\phi\,\hat{y}\right)-\sin\theta\,\hat{z}$$
$$\hat{\phi} = -\sin\phi\,\hat{x}+\cos\phi\,\hat{y}$$

and $$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r}+\hat{\theta}\,\frac{1}{r}\frac{\partial}{\partial\theta}+\hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}$$

$$\vec{L} = \vec{r}\times\left(\frac{\hbar}{i}\vec{\nabla}\right)=\frac{\hbar}{i}\left(\hat{\phi}\frac{\partial}{\partial\theta}-\hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$
$$\hat{L}_x = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta}-\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

and eventually

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

spherical harmonics : eigenfunctions

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

normalized as:

$$\int d\Omega \, |Y_{\ell m}|^2 = \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi \, |Y_{\ell m}|^2 = 1$$

Solve by separation of variables and powerseries or raising and lowering operators.

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y = \frac{\hbar}{i}(-\sin\phi \pm i\cos\phi)\frac{\partial}{\partial\theta}$$
$$- \frac{\hbar}{i}\cot\theta(\cos\phi \pm i\sin\phi)\frac{\partial}{\partial\phi}$$
$$= \frac{\hbar}{i} e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_+ Y_{\ell\ell} = 0 = \frac{\hbar}{i} e^{i\phi}\left(i\frac{\partial}{\partial\theta} - \cot\frac{\partial}{\partial\phi}\right) Y_{\ell\ell}$$

$$Y_{\ell\ell} = e^{i\ell\phi}\,\Theta_{\ell\ell}(\theta)$$

$$\left(\frac{\partial}{\partial\Theta} - \ell\cot\theta\right)\Theta_{\ell\ell} = 0$$

$$\boxed{Y_{\ell\ell} = C_\ell \, e^{i\ell\phi} \sin^\ell\theta}$$

normalization gives

$$C_\ell = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}$$

Next use $\hat{L}_- Y_{\ell,m} = \hbar\sqrt{\ell(\ell+1)-m(m\mp1)}\; Y_{\ell,m-1}$

$$Y_{\ell m}(\theta,\phi) = \frac{(-1)^\ell}{2^\ell \ell!}\sqrt{\left(\frac{2\ell+1}{4\pi}\right)\frac{(\ell-m)!}{(\ell+m)!}}\, e^{im\phi}$$

$$\times \frac{1}{\sin^m\theta}\left(\frac{d^{\ell-m}}{d(\cos\theta)^{\ell-m}}\sin^{2\ell}\theta\right)$$

Comments

1. $\hat{L}_z Y_{\ell m} = \frac{\hbar}{i}\frac{\partial}{\partial\phi} Y_{\ell m} = \hbar m Y_{\ell m}$

2. Single valued $Y_{\ell m}(\theta,\phi) = Y_{\ell m}(\theta,\phi+2\pi)$

$$e^{im(\phi+2\pi)} = e^{im\phi} \quad \text{for } m \text{ integer}$$

3. $Y_{\ell,-m} = (-1)^m Y^*_{\ell,m}$

4. Orthonormality

$$\int d\Omega\, Y^*_{\ell m} Y_{\ell' m'} = \delta_{\ell\ell'}\delta_{mm'}$$

or $\langle \ell,m|\ell',m'\rangle = \delta_{\ell\ell'}\delta_{mm'}$

5. $Y_{\ell m}$ in any spherically symmetric ∇^2 problem

Spherical harmonics

https://en.wikipedia.org/wiki/Table_of_spherical_harmonics

l = 0[1]

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}} \quad = 1/\mathrm{sqrt}(4\pi)$$

l = 1[1]

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta \quad = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$

$$Y_1^{0}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta \quad = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$

$$Y_1^{1}(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta \quad = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

l = 2[1]

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{-2i\varphi}\cdot\sin^2\theta \quad = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)^2}{r^2}$$

$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta\cdot\cos\theta \quad = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x-iy)z}{r^2}$$

$$Y_2^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot(3\cos^2\theta-1) \quad = \frac{1}{4}\sqrt{\frac{5}{\pi}}\cdot\frac{(2z^2-x^2-y^2)}{r^2}$$

$$Y_2^{1}(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta \quad = \frac{-1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$

$$Y_2^{2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot e^{2i\varphi}\cdot\sin^2\theta \quad = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)^2}{r^2}$$

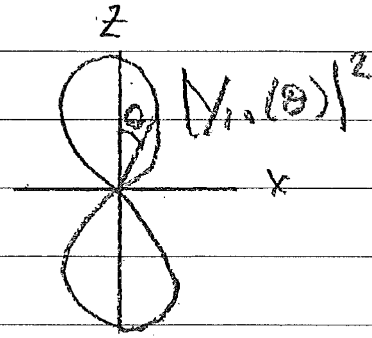
e.g. $\nabla^2 = -4\pi\rho(r)$ electrostatics with spherically symmetric ρ, boundary conditions.

P orbitals ($\ell = 1$)

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\left(\frac{z}{r}\right)$$

In X-Z plane:

"P_z orbital"



linear combinations of $Y_{1,\pm 1}$ give "P_x, P_y orbitals"

$$\frac{Y_{1,-1} - Y_{11}}{\sqrt{2}} = \sqrt{\frac{3}{4\pi}}\left(\frac{x}{r}\right)$$

$$\frac{i(Y_{11} + Y_{1-1})}{\sqrt{2}} = \sqrt{\frac{3}{4\pi}}\left(\frac{y}{r}\right)$$

P-orbitals and Molecular Structure

notation - chemical shell

$$n\,L^{\alpha}_{\text{spin}}$$

$2(2\ell+1) \leftarrow$ subshell multiplicity

α spin

$n \uparrow$ shell

$L \leftarrow \ell = 0, 1, 2, 3, \ldots$ subshell

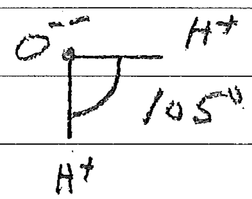
$s, p, d, f, \ldots$

Atomic configuration (more later)

$O:\ 1s^2 2s^2 2p^4$ valence -2

p-orbitals minimize Coulomb repulsion

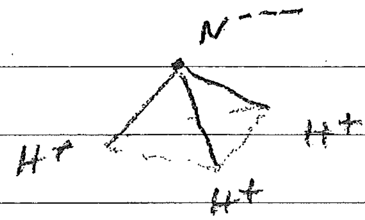
H_2O



polar

$N:\ 1s^2 2s^2 2p^3$ valence -3

NH_3



non-planar

Uncertainty Principle

$$[\phi, \hat{L}_z] \underset{\vec{r}}{\rightarrow} \left[\phi, \frac{\hbar}{i}\frac{\partial}{\partial\phi}\right] = i\hbar$$

naively expect $\Delta\phi \Delta L_z \geq \hbar/2$

however, $0 < \phi < 2\pi$

consider $f(\theta) = \frac{1}{\sqrt{2\pi}}$

$$\langle\phi\rangle = \int_{-\pi}^{\pi} d\phi \left(\frac{\phi}{2\pi}\right) = 0$$

$$\langle\phi^2\rangle = \int_{-\pi}^{\pi} d\phi \left(\frac{\phi^2}{2\pi}\right) = \frac{1}{2\pi}\left(\frac{1}{3}\right)\phi^3 \Big|_{-\pi}^{+\pi} = \frac{\pi^2}{3}$$

$$\Delta\phi = \pi/\sqrt{3}$$

$$\langle L_z\rangle = \int_{-\pi}^{\pi} d\phi \frac{1}{\sqrt{2\pi}} \frac{\hbar}{i}\left(\frac{\partial}{\partial\phi}\right)\frac{1}{\sqrt{2\pi}} = 0$$

$$\langle L_z^2\rangle = 0$$

There is no such uncertainty relation for ϕ, L_z because of limited range of ϕ.

<u>Diatomic molecule with magnetic moment</u>

external field $\vec{B} = B\hat{z}$

$$\hat{H} = \frac{\hat{L}^2}{2I} + \omega_0 \hat{L}_z$$

take $\psi(0) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi = \frac{i}{\sqrt{2}}\left(Y_{11} + Y_{1-1}\right)$

To find $\psi(t)$, we still have $[\hat{H}, \hat{L}^2] = 0$
and $[\hat{H}, \hat{L}_z] = 0$ and $\hat{H}$ has no explicit
time dependence

$$|\psi(t)\rangle = e^{-it\hat{L}^2/2I\hbar} e^{-i\omega_0 t \hat{L}_z/\hbar} |\psi(0)\rangle$$

$$= e^{-it\hbar/I} \frac{1}{\sqrt{2}}\left(e^{-i\omega_0 t}|1,1\rangle + e^{i\omega_0 t}|1,-1\rangle\right)$$

with $\langle\theta,\phi|1,\pm 1\rangle = \mp\sqrt{\frac{3}{4\pi}} \sin\theta \, e^{\pm i\phi}$

$$\psi(t) = \frac{e^{-it\hbar/I}}{\sqrt{2}} \sqrt{\frac{3}{4\pi}} \sin\theta \left(-e^{i(\phi-\omega_0 t)} + e^{-i(\phi-\omega_0 t)}\right)$$

$$= -i\sqrt{2}\, e^{-it\hbar/I} \sqrt{\frac{3}{4\pi}} \sin\theta \sin(\phi - \omega_0 t)$$

what is $\langle \hat{L}_x \rangle$?

$$\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$$

$$\langle \hat{L}_x \rangle = \left(\frac{1}{2}\right)^2 \left(\langle 1,1| + \langle 1,-1|\right)\left(\hat{L}_+ + \hat{L}_-\right)\left(|1,1\rangle + |1,-1\rangle\right)$$

$$\hat{L}_\pm |1,\pm 1\rangle = 0$$

$$\hat{L}_\pm |1,\mp 1\rangle = \sqrt{2}\hbar\, |1,0\rangle$$

so $\langle \hat{L}_x \rangle = 0$ and $\langle \hat{L}_y \rangle = 0$

At time t, we still have $\langle \psi(t)| \hat{L}_x |\psi(t)\rangle = 0$

Or $\quad [\hat{H}, \hat{L}_x] = \omega_0 [\hat{L}_z, \hat{L}_x] = i\hbar\omega_0 \hat{L}_y$

$$\frac{d}{dt}\langle \hat{L}_x \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{L}_x] \rangle = -\omega_0 \langle \hat{L}_y \rangle = 0$$

Addition theorem

Only spherically symmetric $Y_{00} = \frac{1}{\sqrt{4\pi}}$

Spherical symmetry guarantees states with same l are degenerate:

$$\hat{H}|E,l,m\rangle = E_l|E,l,m\rangle \quad (2l+1)\text{-fold degenerate}$$

Consider ensemble of atoms in thermal equilibrium at temperature T, States with same E_l are equally populated. Probability of measuring e^- at given θ,ϕ in ensemble

$$P_l(\theta,\phi) = \frac{1}{2l+1}\sum_m |Y_{lm}(\theta,\phi)|^2$$

$l=0 \qquad P_0 = \frac{1}{4\pi}$

$l=1 \qquad P_1 = \frac{1}{3}\left[|Y_{11}|^2 + |Y_{10}|^2 + |Y_{1-1}|^2\right]$

$$= \frac{1}{3}\left[2\left(\frac{3}{8\pi}\right)S^2 + \frac{3}{4\pi}C^2\right] = \frac{1}{4\pi}$$

Addition theorem

$$\frac{1}{2l+1}\sum_{m=-l}^{+l}|Y_{lm}(\theta,\phi)|^2 = \frac{1}{4\pi}$$