angular Momentum

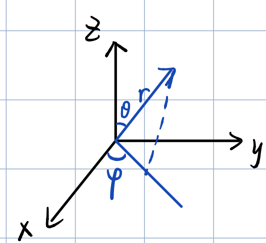
$\vec{L} = \vec{R} \times \vec{p}$ orbital AM

$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$L_x = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ $\qquad \vec{p} = -i\hbar\frac{\partial}{\partial \vec{R}}$.

$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ $\qquad$ real space representation.

spherical coordinate



$\vec{r}\,(x, y, z)$

$x = r\sin\theta\cos\varphi$

$y = r\sin\theta\sin\varphi$ $\qquad r \geq 0.\quad \theta \in [0, \pi]$

$z = r\cos\theta$ $\qquad \varphi \in [0, 2\pi)$

$r = \sqrt{x^2+y^2+z^2}$

$\theta = \arccos\frac{z}{\sqrt{x^2+y^2+z^2}}$

$\varphi = \arctan\frac{y}{x}$.

$$dr = \frac{2x}{2\sqrt{x^2+y^2+z^2}}dx + \frac{y}{r}dy + \frac{z}{r}dz$$

$$d\theta = \frac{xz}{r^2\sqrt{x^2+y^2}}dx + \frac{yz}{r^2\sqrt{x^2+y^2}}dy - \frac{x^2+y^2}{r^2\sqrt{x^2+y^2}}dz$$

$$d\varphi = \frac{y}{x^2+y^2}dx + \frac{x}{x^2+y^2}dy$$

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial \theta}\cdot\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi}\cdot\frac{\partial \varphi}{\partial x} + \frac{\partial}{\partial r}\cdot\frac{\partial r}{\partial x}$$

$$= \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{\sin\theta}{\sin\varphi}\frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\varphi\frac{\partial}{\partial \theta} + \frac{1}{r}\frac{\cos\varphi}{\sin\theta}\frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial z} = \cos\frac{\partial}{\partial r} - \frac{1}{r}\sin\varphi\frac{\partial}{\partial \theta}$$

$\therefore L_x = -i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)$

$L_y = -i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)$

$L_z = -i\hbar\frac{\partial}{\partial\varphi}$.

$L_+ = L_x + iL_y = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\cdot\frac{\partial}{\partial\varphi}\right)$

$L_- = (L_+)^+ = \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\cdot\frac{\partial}{\partial\varphi}\right)$

$L^2 = L_x^2 + L_y^2 + L_z^2 = \frac{1}{2}(L_-L_+ + L_+L_-) + L_z^2$

$= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\cdot\frac{\partial^2}{\partial\theta} + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\varphi^2}\right)$

$L^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle$

$L_z|l,m\rangle = m\hbar|l,m\rangle$

$\langle\vec{r}|l,m\rangle = \varphi_{l,m}(r,\theta,\varphi) = f(r)Y_l^m(\theta,\varphi)$

归一化?

$L^2Y_l^m = l(l+1)\hbar^2Y_l^m$

$L_zY_l^m = m\hbar Y_l^m$

$\Downarrow$

$-i\hbar\frac{\partial}{\partial\varphi}Y_l^m = m\hbar Y_l^m$

$Y_l^m = g_{l,m}(\theta)e^{im\phi}$.

$Y_l^m(\theta,\phi+2\pi) = Y_l^m(\theta,\phi)$

$e^{im\cdot2\pi} = 1$. $m=$ integer

$L_+|l,l\rangle = 0$

$L_+Y_l^l = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)g_{ll}(\theta)e^{il\phi} = 0$

$\frac{\partial}{\partial\theta}g_{ll} + i\cot(\theta)(il)g_{ll}\theta = 0$

$g_{ll} \propto \sin^l\theta$

$Y_l^l(\theta,\varphi) = C_l\sin^l\theta\, e^{im\phi}$

$$\int |\langle \vec{r} | l, m\rangle|^2 \, dx\,dy\,dz = 1$$

$$\int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi \; |f(r) Y_L^m|^2 r^2 \sin\theta = 1$$

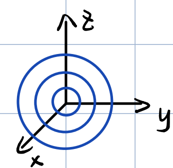
$$\int_0^\infty |f(r)|^2 r^2 dr = 1$$

$$\int_0^\pi d\theta \int_0^{2\pi} d\varphi \; |Y_L^m|^2 \sin\theta = 1$$

$$L_- Y_L^m = \hbar \sqrt{l(l+1) - m(m-1)} \; Y_L^{m-1}$$

Y_L^L.

$L=0$. $Y_0^0 = C_0$ S



$L=1$ $\quad Y_1^1 = C_1 \sin\theta \, e^{i\varphi}$ P

$$= -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\varphi}$$

$$Y_1^0 = \frac{1}{\sqrt{1\times 2 - 1\times 0}} \frac{L_- Y_1^1}{\hbar}$$

$$= \frac{1}{\sqrt{2}} e^{-i\varphi} \left(-\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\varphi}\right) Y_1^1$$

$$= \sqrt{\frac{3}{4\pi}} \cos\theta$$

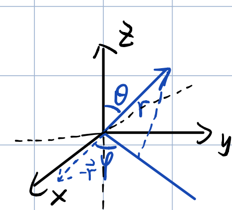
$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\varphi}.$$

$$e^{i\theta} = \cos\theta + i\sin\theta.$$

$$Y_1^1 + Y_{-1}^1 = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi \propto \frac{y}{r}$$

$$Y_1^{-1} - Y_1^1 = i\sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi \propto \frac{x}{r}.$$

$$Y_1^0 \propto \frac{z}{r}.$$



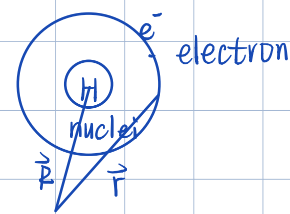
parity $\quad \hat{w}|\vec{r}\rangle = |-\vec{r}\rangle. \quad \hat{w}|r, \theta, \varphi\rangle = |r, \pi-\theta, \pi+\varphi\rangle$

$\{ \; x = r\sin\theta\cos\varphi \qquad -x$

$$\begin{cases} y = r\sin\theta\sin\varphi & \Rightarrow \quad -y \\ z = r\cos\theta & \quad\;\; -z \end{cases}$$

$$\hat{w}|l,m\rangle = (-1)^l |l,m\rangle$$

Hydrogen Atom



$$V(\vec{R}-\vec{r}) = -\frac{e^2}{|\vec{R}-\vec{r}|}$$

$$H = \frac{P_H^2}{2M} + \frac{P^2}{2m} + V(\vec{R}-\vec{r})$$

$$\vec{r}_D = \vec{R}-\vec{r} \qquad \underline{\vec{R}_D = \frac{M\vec{R}+m\vec{r}}{M+m}}$$ center of mass 质心

$$H = \frac{P_D^2}{2\mu} + \frac{P_D^2}{2M_T} + V(\vec{r}_D)$$

$$M_T = M+m \qquad \mu = \frac{Mm}{M+m}$$

$$H = H_1 + H_2$$

$$H_1|\phi_{1m}\rangle = E_{1m}|\phi_{1m}\rangle$$

$$H_2|\phi_{2m}\rangle = E_{2m}|\phi_{2m}\rangle$$

$$H|\phi_{1m}\rangle \otimes |\phi_{2m}\rangle = (H_1+H_2)|\phi_{1m}\rangle \otimes |\phi_{2m}\rangle$$

$$= (E_{1m}+E_{2m})|\phi_{1m}\rangle \otimes |\phi_{2m}\rangle$$

$$H_1 = \frac{P_D^2}{2M_T} \qquad H_2 = \frac{P_D^2}{2\mu} + V(\vec{r}_D)$$

$$\Downarrow \; \vec{r}$$

$$H_e = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}L^2\right)$$

$$L^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$\varphi = \frac{U_{nl}(r)}{r} Y_l^m(\theta,\varphi) \qquad H\varphi = E\varphi \qquad \frac{U_{nl}(r)}{r}$$ 径向函数.

$\varphi(r,\theta,\varphi)$ $\qquad U_{nl}$ 是关于r的函数.

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}U_{n,l}\cancel{Y_l^m}+\frac{\hbar^2}{2\mu r^2}l(l+1)U_{n,l}\cancel{Y_l^m}-\frac{e^2}{r}U_{n,l}\cancel{Y_l^m}=EU_{n,l}\cancel{Y_l^m}.$$

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}+\frac{l(l+1)\hbar^2}{2\mu r^2}-\frac{e^2}{r}\right)U_{n,l}=EU_{n,l}$$

a symptotic analysis　　奇异点分析. $\chi_l(r)$.

$r\to\infty$. $-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}u=Eu$.　　$u\propto e^{-\alpha r}$. $\alpha=\sqrt{-\frac{2\mu E}{\hbar^2}}$

$$u=e^{-\alpha r}y(r)$$

$r\to\infty$. $u\to e^{-\alpha r}$. $y(r)\to c$.

$$-\frac{\hbar^2}{2\mu}(y''-2\alpha y')+\left(\frac{l(l+1)}{2\mu r^2}-\frac{\hbar^2\alpha^2}{2\mu}-\frac{e^2}{r}-E\right)y=0$$

$r\to 0$. $-\frac{\hbar^2}{2\mu}y''+\frac{l(l+1)}{2\mu r^2}y=0$.　$y\propto r^{l+1}$　　作业. 用计算机解.

$$y=r^{l+1}w(r)$$

$$w''+\left(\frac{2(l+1)}{r}-2\alpha\right)w'+\left[\frac{2\mu e^2}{\hbar^2}-2\alpha(l+1)\right]\frac{w}{r}=0$$

假设:

$w=C$. $\frac{2\mu e^2}{\hbar^2}=2\alpha(l+1)$

$$E=-\frac{\hbar^2\alpha^2}{2\mu}=-\frac{\mu e^4}{2\hbar^2(l+1)^2}=-\frac{E_0}{(l+1)^2}.\quad E_0=\frac{\mu e^4}{2\hbar^2}.$$

$l=0$. $E=-E_0$　1s　$\varphi\propto r^0e^{-\alpha r}$

$l=1$. $E=-\frac{1}{4}E_0$　2p　$\varphi\propto r^1e^{-\alpha r}$

$l=2$. $E=-\frac{1}{9}E_0$　3d　$\varphi\propto r^2e^{-\alpha r}$

假设

$W=C_1x+C_0$.

$$\left(\frac{2(l+1)}{r}-2\alpha\right)C_1+\left(\frac{2\mu e^2}{\hbar^2}-2\alpha(l+1)\right)\left(\frac{C_0}{r}+C_1\right)=0$$

$$\frac{2(l+1)}{r}C_1=\left[\frac{2\mu e^2}{\hbar^2}-2\alpha(l+1)\right]\frac{C_0}{r}$$

$$2\alpha C_1=\left[\frac{2\mu e^2}{\hbar^2}-2\alpha(l+1)\right]C_1.$$

$C_0 = 1.$

$$C_1 = \frac{\frac{2\mu e^2}{\hbar^2} - 2\alpha(l+1)}{2(l+1)} \qquad \alpha = \frac{2\mu e^2}{\hbar^2(l+2)}$$

$$E = -\frac{E_0}{(l+2)^2}.$$

$l=0$	$E=-\frac{1}{4}E_0$	2s
$l=1$	$E=-\frac{1}{9}E_0$	3p
$l=2$	$E=-\frac{1}{16}E_0$	4d

$$\alpha = \frac{2\mu e^2}{\hbar^2(l+p+1)}. \qquad E = -\frac{E_0}{(l+p+1)^2} \qquad w = \alpha r^p.$$

$n = l+p+1$ 厄米多项式.

$$E = -\frac{E_0}{n^2}.$$

l \ p	0	1	2
1	(1s) -1	(2s) $-\frac{1}{4}$	$-\frac{1}{9}$
2	(2p) $-\frac{1}{4}$	(3p) $-\frac{1}{9}$	$-\frac{1}{16}$
3	(3d) $-\frac{1}{9}$	(4d) $-\frac{1}{16}$	$-\frac{1}{25}$

E_0

$n = l+p+1$

	s	p	d	f
l	0	1	2	3

e.g. 4d $\Rightarrow$ $n=4$. $l=2$.

ψ_{nlm}

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

$l = 0, 1, \cdots, n-1$

$-l \le m \le l.$

$$\psi_{100} \overset{p=0,\ l=0}{=\!=} e^{-\alpha r}. \qquad a_0 = \frac{1}{\alpha} = \frac{\hbar^2}{\mu e^2}.$$

Bohr Length radias.

$$= \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}.$$

$$\psi_{200} = \left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}} \cdot \frac{1}{\sqrt{8\pi a_0^3}}$$

$$\psi_{211} = -\frac{1}{8\sqrt{\pi a_0^3}} \cdot \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin\theta\, e^{i\varphi}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta$$

$$\psi_{21,-1} = \frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{\frac{-r}{2a_0}} \sin\theta e^{i\varphi}$$