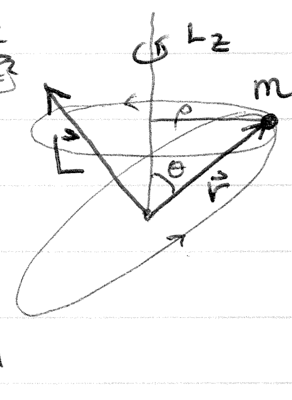
Schrödinger Equation for the Hydrogen Atom



Laplacian operator:

$$\nabla^2 = \nabla\cdot\nabla = \underbrace{\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}}_{\text{cartesian}} = \underbrace{\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2}{\partial z^2}}_{\text{cylindrical.}}$$

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Bigg(\underbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\underbrace{\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{\sim L_z^2}}_{\sim L^2}\Bigg)$$

Angular momentum:

$\vec L = \vec r\times\vec p \sim mvr$

$T=\frac{p^2}{2m}$ $\quad T_\Omega = \frac{L^2}{2I} = \frac{p_r^2\cdot r^2}{2mr^2}$ $\quad I=mr^2$ moment of inertia.

Sample equations with ∇^2

heat eq: $\frac{\partial u}{\partial t} = k\nabla^2 u$ $\quad u$=temp $\quad k$=conductivity $\quad \vec q = -k\nabla u$ heat flow

diffusion eq: $\frac{\partial u}{\partial t} = D\nabla^2 u$ $\quad u$=density. D=Fick's const. $\quad -D\nabla u$ particle flux.

Laplace eq: $\nabla^2\varphi = 0$ $\quad \varphi$=electric potential $\quad \vec E = -\nabla\varphi$ electric field

Poisson eq: $\varepsilon\nabla^2\varphi = \rho$ $\quad \varepsilon$=dielectric const $\quad \rho$=charge density.

Maxwell (wave): $\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\varphi - \nabla^2\varphi = \rho/\varepsilon$ $\quad \mu$=permeability $\quad J$=current density.

$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec A - \nabla^2\vec A = \mu\vec J$ $\quad A$=vector potential $\quad B=\nabla\times A$ magnetic field.

Schrödinger equation:

$\hat T\Psi + \hat V\Psi = \hat E\Psi$ $\qquad$ hydrogen atom: $V = \frac{-Ze^2}{4\pi\epsilon_0 r}$

$$\hat T\Psi = \frac{\hat p^2}{2\mu}\Psi = \frac{-\hbar^2}{2\mu}\nabla^2\Psi = \frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r\Psi + \frac{1}{2\mu r^2}\underbrace{\Bigg(\frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Psi}{\partial\theta} + \frac{1}{\sin^2\theta}\cdot\underbrace{\frac{-\hbar^2\partial^2}{\partial\phi^2}\Psi}_{L_z^2\Psi = \hbar^2 m^2\Psi}\Bigg)}_{L^2\Psi = \hbar^2 l(l+1)\Psi}$$

let $\Psi = R_{nl}(r)\cdot Y_{lm}(\theta,\phi)$ $\qquad Y_{lm} = \Theta(\theta)\cdot\Phi(\phi)$

1) $L_z\Phi_m(\phi) = -i\hbar\frac{\partial}{\partial\phi}\cdot e^{im\phi} = \hbar m\cdot\Phi_m$

2) $L^2 Y_{lm} = \left(\frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\hbar^2 m^2}{\sin^2\theta}\right)Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)\,Y_{lm}$ $\quad \boxed{\text{spherical harmonics}}$

$$\frac{d}{dx}\left[(1-x^2)\frac{dP_{lm}}{dx}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P_{lm}(x) = 0 \qquad P_{lm}(\cos\theta) \quad \boxed{\text{Legendre polynomials}}$$

3) $\frac{-\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}rR - \frac{l(l+1)}{r^2}R\right) - \frac{Ze^2}{4\pi\epsilon_0 r}R = E_{nl}\cdot R$

$$\frac{d^2H}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{dH}{d\rho} + \frac{n-l-1}{\rho}H = 0$$

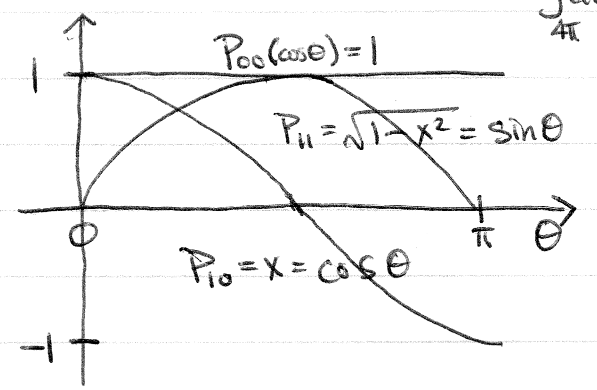
$$R(r) = e^{-\rho/2}\rho^l\, H^{2l+1}_{n+l}(\rho) \qquad \rho = \frac{2Zr}{na_0} \qquad \boxed{\text{Laguerre polynomials}}$$

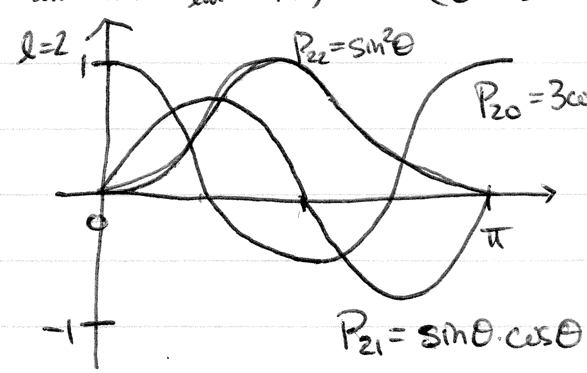
conserved	coordinate		operator/eig. func/val	quantum #		range
energy	radial	r	$\hat{H}\,\Psi_{nlm} = E_n\,\Psi_{nlm}$	principal	$n>l$	$1, 2, 3, \ldots$
angular momentum	polar	θ	$\hat{L}^2\,Y_{lm} = \hbar\,l(l+1)\,Y_{lm}$	orbital	$l \geq \lvert m \rvert$	$0, 1, \ldots (n-1)$
z-component "	azimuthal	ϕ	$\hat{L}_z\,\Phi_m = \hbar m\,\Phi_m$	magnetic	$m \in \mathbb{Z}$	$0, \pm1, \pm2, \ldots \pm l$

Spherical Harmonics: $Y_{lm} = A \cdot P_{lm}(\cos\theta) \cdot e^{im\phi}$

$$\int_{4\pi} d\Omega\; Y^*_{lm}(\theta,\phi) \cdot Y_{l'm'}(\theta,\phi) = \begin{cases} 1 & \text{if } l=l',\ m=m' \\ 0 & \text{otherwise} \end{cases}$$

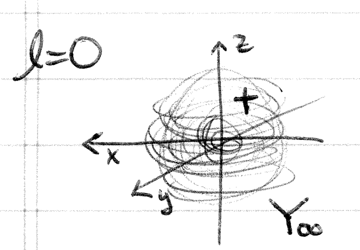
$l=0,1$:





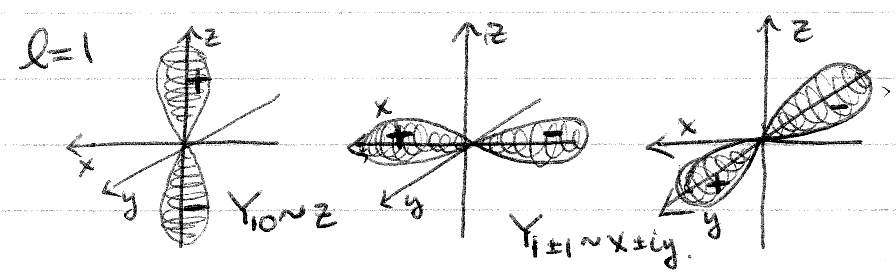
spect. notation	multipole order	l (L^2)	m (L_z)	$g_l = 2l+1$ degeneracy	$r^2 \cdot Y_{lm}(\theta,\phi)$ in cartesian co-ords.
s	monopole	0	0	1	$1^{(0)}$
p	dipole	1	$0, \pm1$	3	$z = \cos\theta$, $x \pm iy \sim \sin\theta\, e^{\pm i\phi}$
d	quadrupole	2	$0, \pm1, \pm2$	5	$3z^2 - r^2$, $z(x \pm iy)$, $(x \pm iy)^2 = (x^2 - y^2) + i(2xy)$
f	octupole	3	$0, \pm1, \pm2, \pm3$	7	$5z^3 - 3zr^2$, $(5z^2 - r^2)(x \pm iy)$, $z(x \pm iy)^2$, $(x \pm iy)^3 \sim (x \pm iy)(x^2 - y^2)$
g, h, …	..	4, …	$0, \ldots \pm l$	$2l+1$	

$l=0$



Y_{00}

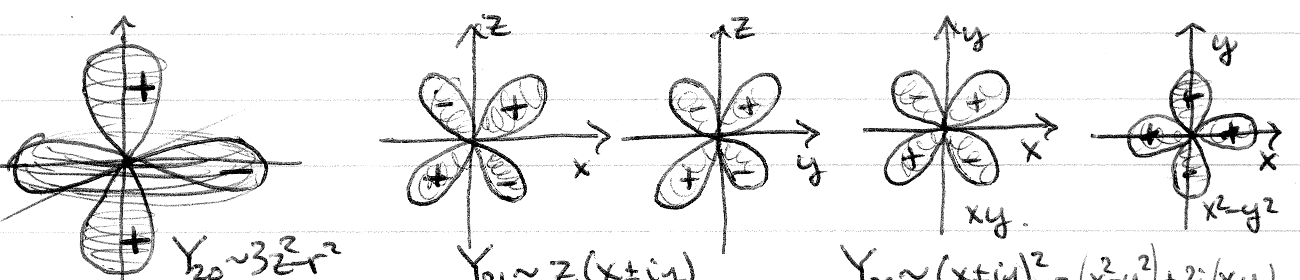
$l=1$



$Y_{10} \sim z$

$Y_{1\pm1} \sim x \pm iy$

$l=2$



$Y_{20} \sim 3z^2 - r^2$

$Y_{21} \sim z(x \pm iy)$

$Y_{22} \sim (x \pm iy)^2 = (x^2 - y^2) \pm 2i(xy)$