Three Dimensional Example
Hydrogen Atom

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Previous Problems

Particle in a box

$$H = T + V = \frac{p_x^2}{2m} + V(x) \qquad V(x) = 0 \quad for \;\; 0 < x < L$$

$$V(x) = \infty \quad for \;\; x \le 0, x \ge L$$

$$\psi_n(x) = C \sin \frac{n\pi}{L} x$$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Harmonic Oscillator

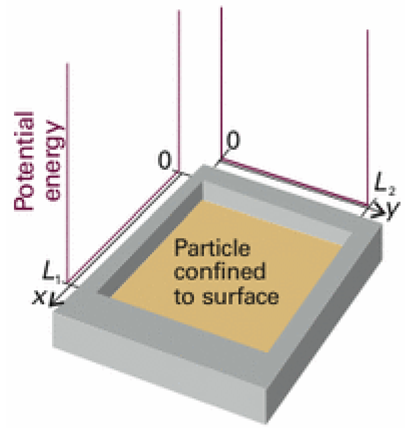
$$\left[-\frac{\eta^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right] \psi(x) = E\psi(x)$$

$$\psi_n(y) = C_n H_n(y) \exp\left(-\frac{y^2}{2} \right) \qquad y = \sqrt{\frac{m\omega}{\eta}} x$$

$$E_n = \left(n + \frac{1}{2} \right) \eta\omega$$

Separation of Variables 1

$$-\frac{\eta^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\psi(x,y)=E\psi(x,y)$$



define $\psi(x,y)=X(x)Y(y)$

$$-\frac{\eta^2}{2m}Y(y)\frac{\partial^2 X(x)}{\partial x^2}-\frac{\eta^2}{2m}X(x)\frac{\partial^2 Y(y)}{\partial y^2}=EX(x)Y(y)$$

divide both sides by $X(x)Y(y)$

$$-\frac{\eta^2}{2m}\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}-\frac{\eta^2}{2m}\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=E$$

Separation of Variables 2

$$-\frac{\eta^2}{2m}\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}-\frac{\eta^2}{2m}\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=E$$

First term on left is independent of y, so if y is varied only second term can change.
BUT from the right hand side which says sum of two left hand terms is constant the value of the second term can not change

$$-\frac{\eta^2}{2m}\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=E_y \rightarrow -\frac{\eta^2}{2m}\frac{\partial^2 Y(y)}{\partial y^2}=E_y Y(y)$$

Second term on left is independent of x, so if x is varied only first term can change.
BUT from the right hand side which says sum of two left hand terms is constant the value of the first term can not change

$$-\frac{\eta^2}{2m}\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}=E_x \rightarrow -\frac{\eta^2}{2m}\frac{\partial^2 X(x)}{\partial x^2}=E_x X(x)$$

Separation of Variables 3

$$-\frac{\eta^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\psi(x,y)=-\frac{\eta^2}{2m}\frac{\partial^2\psi(x,y)}{\partial x^2}-\frac{\eta^2}{2m}\frac{\partial^2\psi(x,y)}{\partial y^2}$$

$$=\left[h_x(x)+h_y(y)\right]\psi(x,y)=E\,\psi(x,y)$$

$$\text{define }\ \psi(x,y)=X(x)Y(y)$$

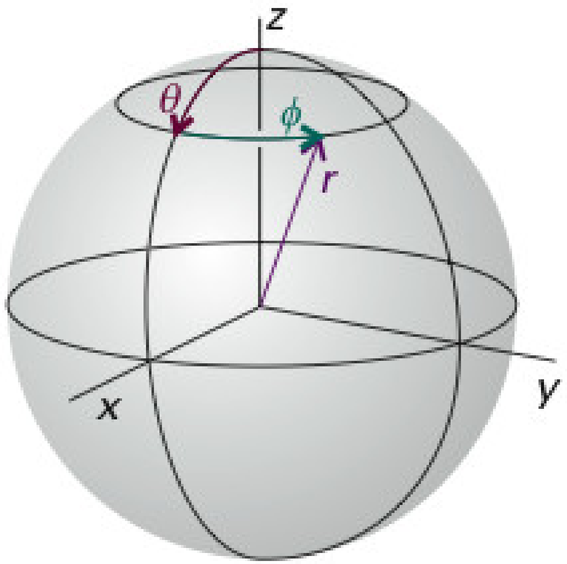
$$\hat{h}_x(x)X_{n_x}(x)=E_{n_x}X_{n_x}(x)$$

$$\hat{h}_y(y)Y_{n_y}(y)=E_{n_y}Y_{n_y}(y)$$

$$E_{n_x,n_y}=E_{n_x}+E_{n_y}$$

If Hamiltonian Operator can be separated into those variables, the wave function is given as the direct product of those variables. It is always simpler to solve N one dimensional problems than one N dimensional problem!

Hydrogen Atom Energy of Electron



The only interaction between electron and proton is coulombic

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$r =$ distance between electron and nucleus/proton

Reduced Mass:

When discussing the motion between two particles you must separate motion of the center of mass and inter particle vector

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}; \qquad \vec{r} = \vec{r}_1 - \vec{r}_2$$

Mass that is used for each motion is

$$M = m_1 + m_2; \qquad \mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

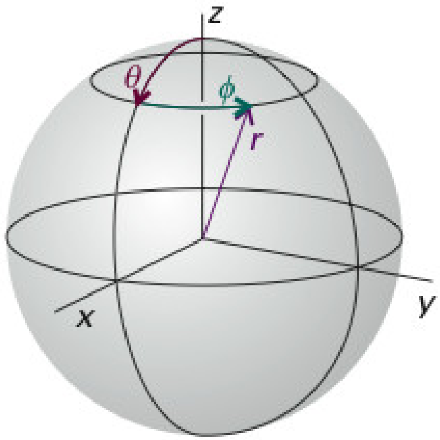
Reduced Mass of electron in hydrogen atom

$$\mu = \frac{m_{electron} \times m_{proton}}{m_{electron} + m_{proton}} \approx \frac{m_{electron} \times m_{proton}}{m_{proton}} = m_{electron}$$

$$\vec{r} = \vec{r}_{electron} - \vec{r}_{proton} \quad \text{set proton position to be zero} \quad \vec{r} = \vec{r}_{electron}$$

$$\vec{r} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$$

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2\mu}\left[p_x^2 + p_y^2 + p_z^2\right] - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$



$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

Spherical Coordinates

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

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\Downarrow$$

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

$$\theta = \tan^{-1}\frac{\sqrt{x^2 + y^2}}{z}$$

$$\phi = \tan^{-1}\frac{x}{y}$$

$$r = 0 \to \infty$$

$$\theta = 0 \to \pi$$

$$\phi = 0 \to 2\pi$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

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

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

$$= \sin\theta\cos\phi\frac{\partial}{\partial r}$$

$$dxdydz = r^2\sin\theta drd\theta d\phi$$

Kinetic Energy Term

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\hat{H}\psi(r,\theta,\phi)=\left[-\frac{\eta^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+V(r)\right.$$

$$\left.-\frac{\eta^2}{2\mu}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{\eta^2}{2\mu}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)$$

$$=E\psi(r,\theta,\phi)$$

multiply both sided by $2\mu r^2$

Hydrogen Atom Electron Wavefunction

$$\left[-\eta^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)+2\mu r^2\left(V(r)-E\right)\right.$$

$$\left.-\eta^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right]\psi(r,\theta,\phi)=0$$

$$\hat{h}_r(r)+\hat{h}_{\theta,\phi}(\theta,\phi)$$

$$\hat{H}(r,\theta,\phi)=\hat{h}_r(r)+\hat{h}_{\theta,\phi}(\theta,\phi)\rightarrow\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

$$-\eta^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi)=LY(\theta,\phi)$$

Solving the Angular Part

$$-\eta^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi)=LY(\theta,\phi)$$

$$\text{multiply}\frac{\sin^2\theta}{-\eta^2}$$

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{\partial^2}{\partial\phi^2}+\frac{\sin^2\theta}{\eta^2}L\right]Y(\theta,\phi)=0$$

$$\text{define}\quad Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

$$\Phi(\phi)\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\Theta(\theta)\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+\frac{\sin^2\theta}{\eta^2}L\Theta(\theta)\Phi(\phi)=0$$

Solving the Angular Part

$$\Phi(\phi)\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\Theta(\theta)\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+\frac{\sin^2\theta}{\eta^2}L\Theta(\theta)\Phi(\phi)=0$$

divide by $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+\frac{\sin^2\theta}{\eta^2}L=0$$

Second term only depends on ϕ so define that this term is given by a constant value

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{\sin^2\theta}{\eta^2}L=m^2$$

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2$$

Solving Angular Part

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2 \rightarrow \frac{\partial^2\Phi(\phi)}{\partial\phi^2} = -m^2\Phi(\phi)$$

$$\Phi_m(\phi) = \frac{1}{(2\pi)^{1/2}}\exp(im\phi); \qquad m = 0,\pm1,\pm2,\ldots$$

$$\frac{1}{\Theta(\theta)}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) + \frac{\sin^2\theta}{\eta^2}L = m^2$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) + \frac{\sin^2\theta}{\eta^2}L\Theta(\theta) = m^2\Theta(\theta)$$

$$\Theta_l^{m_l}(\theta) = \left[\frac{2l+1}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}\right]^{1/2} P_l^{|m_l|}(\cos\theta)$$

WaveFunction $\Theta\Phi$

$$\Theta_l^{m_l}(\theta) = \left[\frac{2l+1}{2} \frac{(l-|m_l|)!}{(l+|m_l|)!} \right]^{1/2} P_l^{|m_l|}(\cos\theta)$$

$P_l^{|m_l|}(\cos\theta)$: Associated Legendre Polynomial

$m_l \leq l$ (only integers allowed)

$$P_0^0(x) = 1$$

$$P_1^0(x) = x$$

$$P_1^1(x) = \left(1 - x^2\right)^{1/2}$$

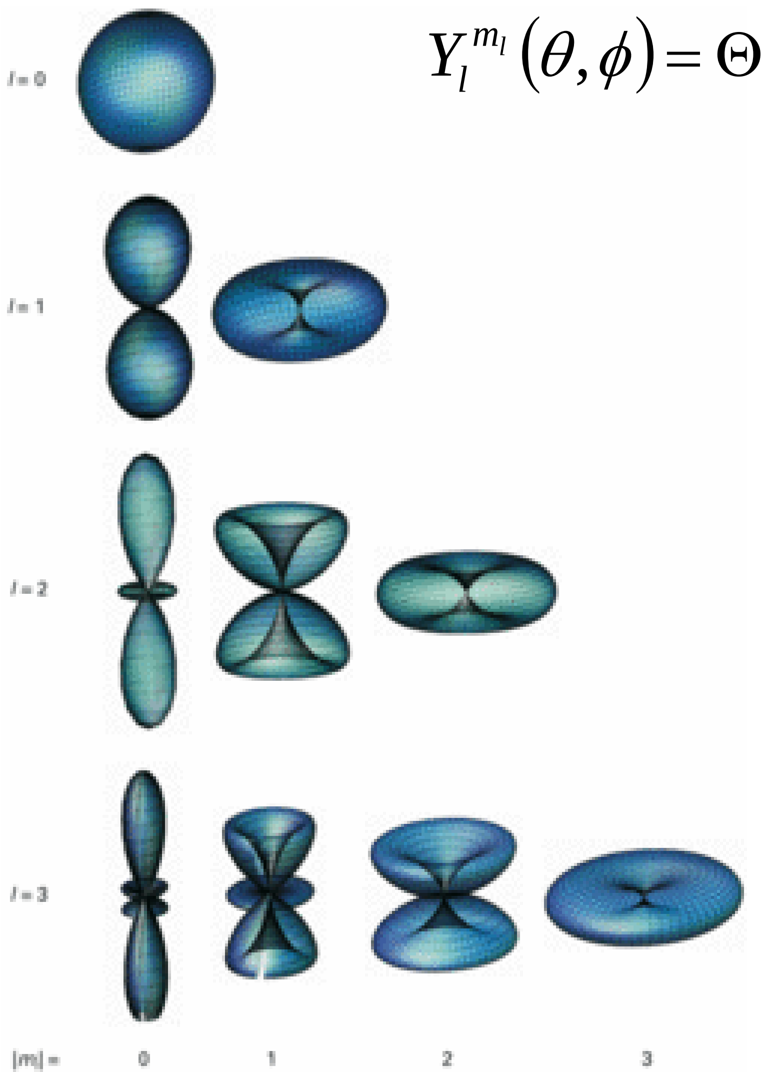
$$-\eta^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y_l^{m_l}(\theta,\phi) = l(l+1) Y_l^{m_l}(\theta,\phi)$$

WaveFunction ΘΦ

Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\varphi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\varphi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\varphi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\varphi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\varphi}$

$$Y_l^{m_l}(\theta,\phi)=\Theta_l^{m_l}(\theta)\Phi_{m_l}(\phi)$$



Hydrogen Atom Radial Part

$$\left[-\eta^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)+2\mu r^2\left(V(r)-E\right)\right.$$

$$\left.-\eta^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right]\psi(r,\theta,\phi)=0$$

$$\left[-\eta^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+2\mu r^2\left(-\frac{e^2}{4\pi\varepsilon_0 r}-E\right)+\eta^2 l(l+1)\right]R(r)Y_l^{m_l}(\theta,\phi)$$

$$\left[-\frac{\eta^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\left(-\frac{e^2}{4\pi\varepsilon_0 r}+\frac{\eta^2 l(l+1)}{2\mu r^2}\right)\right]R(r)=ER(r)$$

Hydrogen Atom Radial Part

$$\left[-\frac{\eta^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\left(-\frac{e^2}{4\pi\varepsilon_0 r}+\frac{\eta^2 l(l+1)}{2\mu r^2}\right)\right]=ER(r)$$

$$E_n=-\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2}=-\frac{\mu e^4}{32\pi^2\varepsilon_0^2\eta^2 n^2}=-\frac{e^2}{8\pi^2\varepsilon_0 a_0 n^2}$$

$a_0 = 4\pi\varepsilon_o\eta^2/\mu e^2$ Bohr Radius

$$R_{nl}(r)=\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{3/2}\left(\frac{2r}{na_0}\right)^{l}\exp\left(-\frac{r}{na_0}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

Associated Laguerre polynomial

$$L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right): \text{ Associated Laguerre polynomial}$$

$$n \geq l+1$$

$$L_0^{\alpha}(x) = 1$$

$$L_1^{\alpha}(x) = -x + \alpha + 1$$

$$L_2^{\alpha}(x) = \frac{x^2}{2} - (\alpha+2)x + \frac{(\alpha+2)(\alpha+1)}{2}$$

$$L_3^{\alpha}(x) = \frac{-x^3}{3!} + \frac{(\alpha+3)x^2}{2} - \frac{(\alpha+2)(\alpha+3)x}{2} + \frac{(\alpha+1)(\alpha+2)(\alpha+3)}{6}$$

TABLE 7.2

The Hydrogen-like Radial Wave Functions, $R_{nl}(r)$, for $n = 1, 2,$ and 3 [a]

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \rho e^{-\rho/2}$$

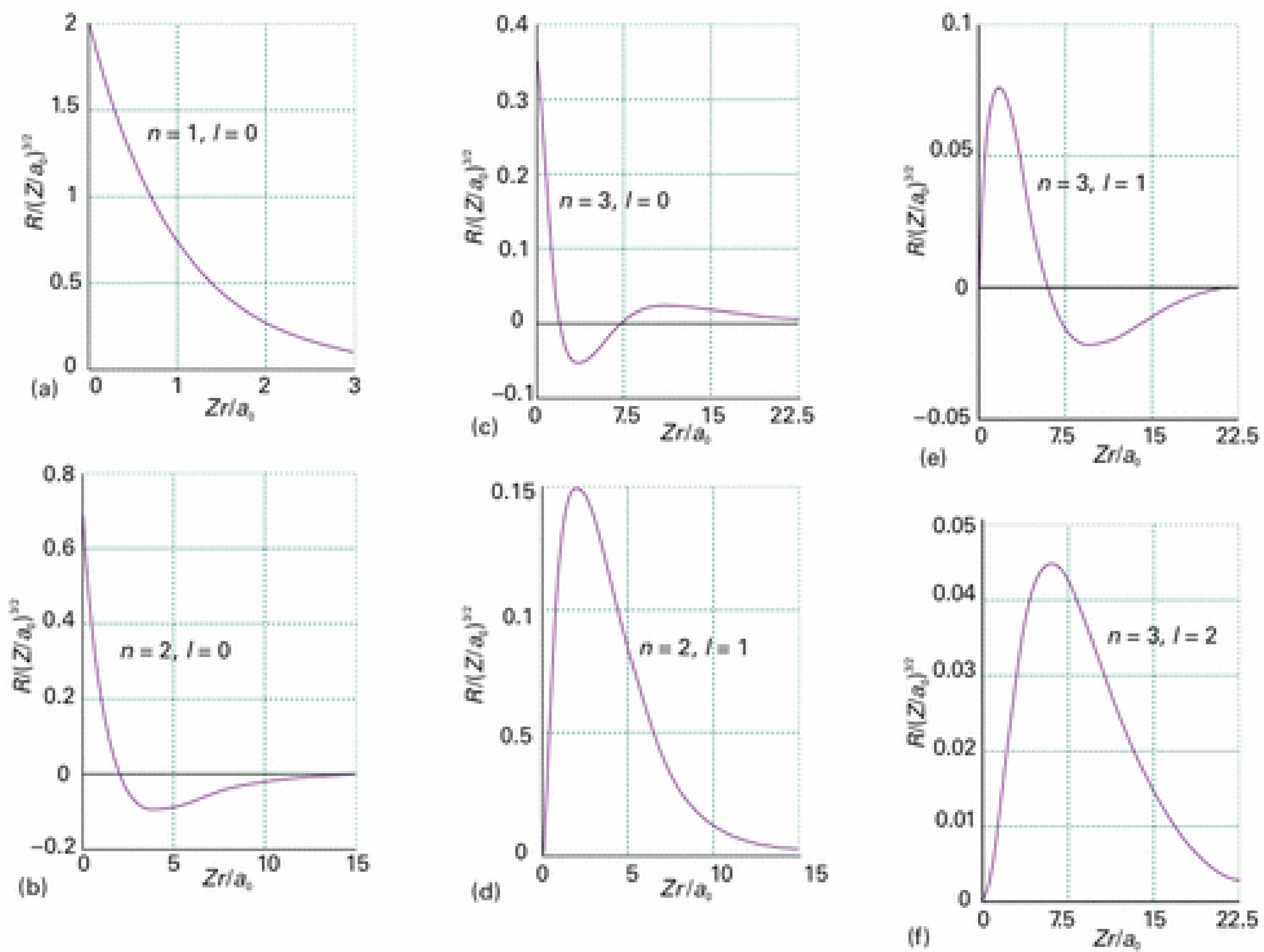
$$R_{30}(r) = \frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$$

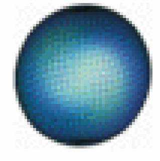
$$R_{31}(r) = \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/3}$$

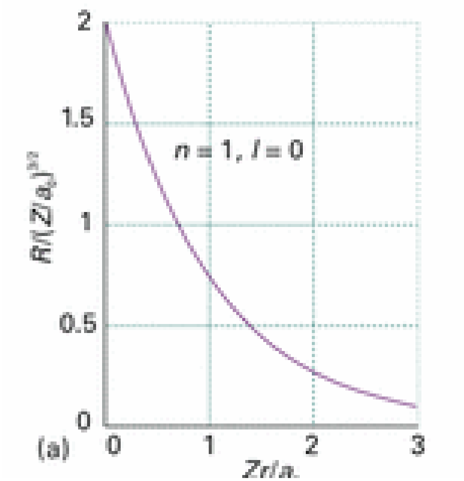
a. The quantity Z is the nuclear charge, and $\rho = Zr/a_0$, where a_0 is the Bohr radius.

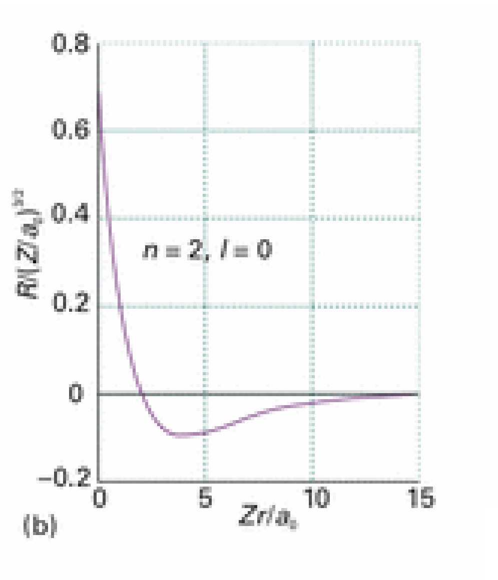
Wavefunction R

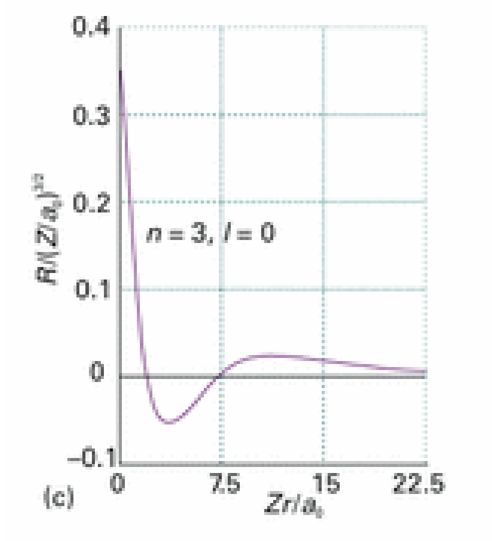




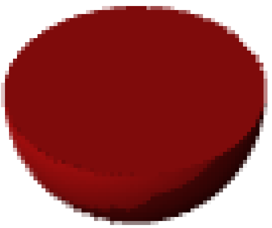
s Wavefunction







1s



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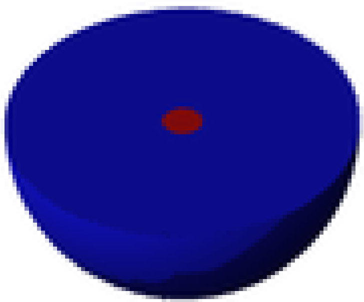
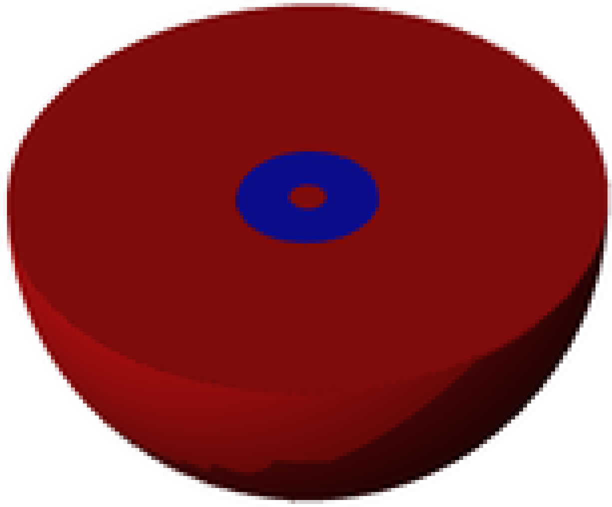
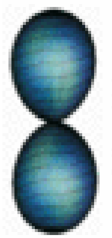
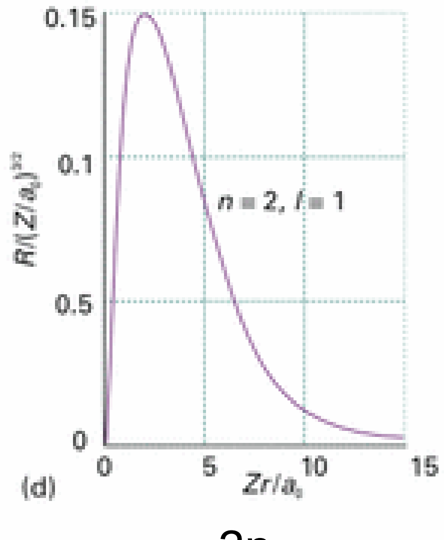
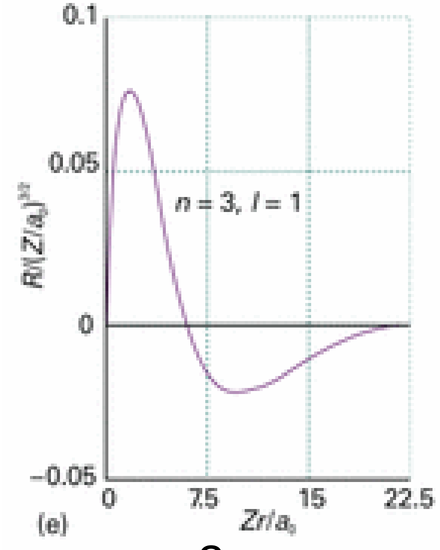




p Wavefunction



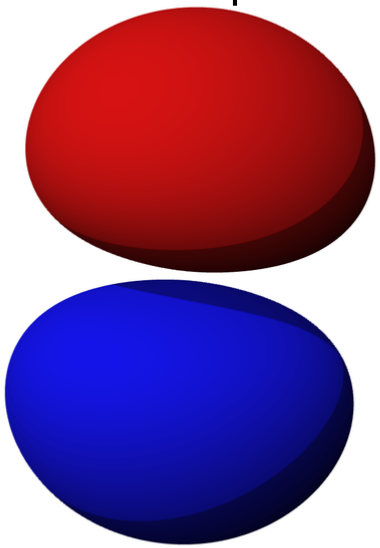


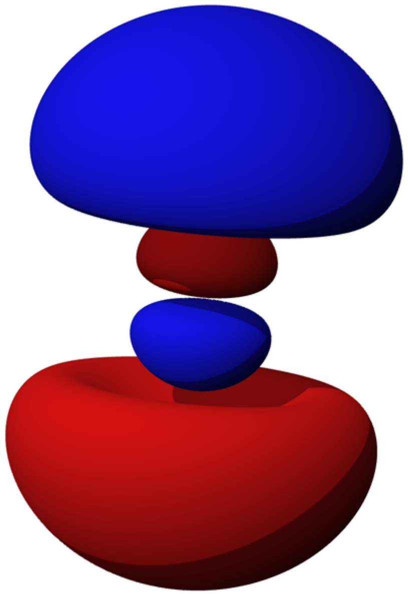


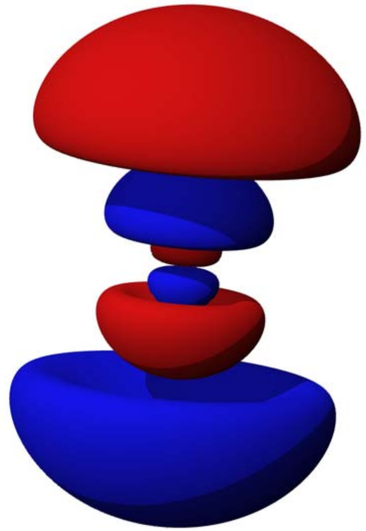
4p

2p

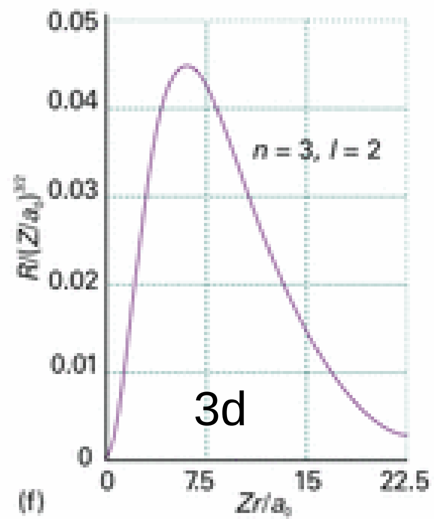
3p



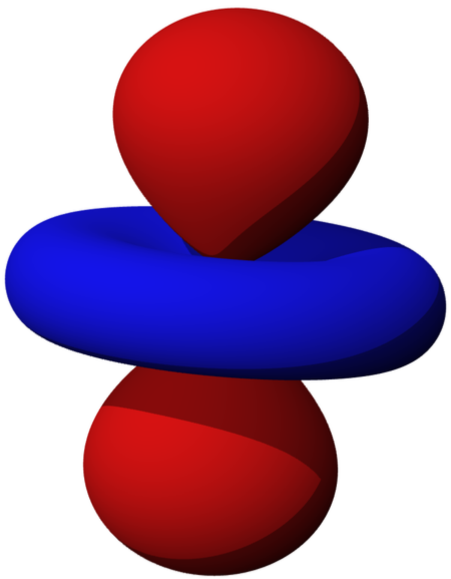




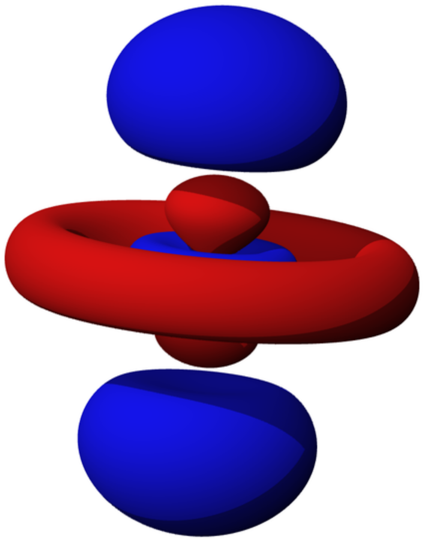
d Wavefunction



3d



4d



5d