H-atom

Coulombic potential between electron and proton

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

Hamiltonian operator for H-atom (Born-Oppenheimer approximation)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

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

Schrodinger equation,

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - 2m_e r^2\left[\frac{e^2}{4\pi\varepsilon_0 r} + E\right]\psi(r,\theta,\phi) = 0$$

No r dependence

$$\therefore \psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$-\frac{\hbar^2}{R(r)}\left[\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) - 2m_e r^2\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R(r)\right]$$

Only function of r

$$-\frac{\hbar^2}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = 0$$

Only function of θ, ϕ

Both must be constant. Use β

Radial part

$$-\frac{1}{R(r)}\left[\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) - 2m_e r^2\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R(r)\right] = -\beta$$

Angular part

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

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} + (\beta\sin^2\theta)Y = 0$$

Which is exactly the same for the rigid-rotator wave functions.

Rigid-rotator wavefunctions

$$Y(\theta,\phi) = S(\theta)T(\phi)$$

$$\left\{\frac{\sin\theta}{S(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{dS}{d\theta}\right) + (\beta\sin^2\theta)\right\} + \frac{1}{T(\phi)}\frac{\partial^2 T}{\partial\phi^2} = 0$$

$$\left\{\frac{\sin\theta}{S(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{dS}{d\theta}\right) + (\beta\sin^2\theta)\right\} = m^2 \quad and \quad \frac{1}{T(\phi)}\frac{\partial^2 T}{\partial\phi^2} = -m^2$$

$$T(\phi) = A_m e^{im\phi} \quad or \quad A_{-m}e^{-im\phi}$$

$T(\phi)$ must be single valued → $T(\phi+2\pi) = T(\phi)$

Gives, $\cos(2\pi m) \pm i\sin(2\pi m) = 1 \;\Rightarrow m = 0, \pm1, \pm2\ldots \;\; \therefore \;\; T_m(\phi) = A_m e^{im\phi} \quad m = 0, \pm1, \pm2\ldots$

Normalized wavefunction → $A_m = 1/\sqrt{2\pi}$

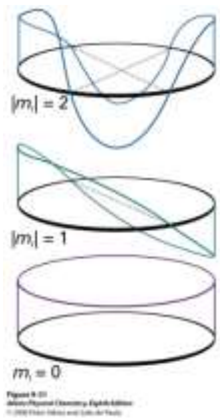


Figure 6.4: Real part of the wavefunctions - particle on a ring

The $S(\theta)$ part – Legendre equations and functions

Let $x = \cos\theta$, $\;S(\theta) = P(x) \quad 0 \le \theta \le \pi \; so -1 \le x \le 1$

The equation in θ above becomes, $(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[\beta - \frac{m^2}{1-x^2}\right]P(x) = 0$ Legendre's equation

Solution gives:

(1) $\beta = l(l+1) \quad where \;\; l = 0,1,2,\ldots$

(2) $|m| \leq l$

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P(x) = 0$$

Case a: $m = 0$ – solution are Legendre polynomials, $P_l(x)$ [even when l is even, odd when l is odd]

$$P_0(x) = 1, P_1(x) = x, P_2(x) = \frac{1}{2}(3x^2-1), P_3(x) = \frac{1}{2}(5x^3-3x), P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

Orthonormalized:

$$\int_{-1}^{1} P_l(x)P_n(x)dx = \int_0^{\pi} P_l(\cos\theta)P_n(\cos\theta)\sin\theta\, d\theta = \frac{2\delta_{ln}}{2l+1}$$

Case b: Associated Legendre functions (for all values of m)

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)$$

Because the leading term in $P_l(x)\ is\ x^l, P_l^{|m|}(x) = 0\ when\ m > l$

$P_0^0(x) = 1$

$P_1^0(x) = x = \cos\theta$

$P_1^1(x) = (1-x^2)^{1/2} = \sin\theta$

$P_2^0 = \frac{1}{2}(3x^2-1) = \frac{1}{2}(3\cos^2\theta - 1)$

$P_2^1(x) = 3x(1-x^2)^{1/2} = 3\cos\theta\sin\theta$

$P_2^2(x) = 3(1-x^2) = 3\sin^2\theta$

$$\int_{-1}^{1} P_l^{|m|}(x)P_n^{|m|}(x)dx = \int_0^{\pi} P_l^{|m|}(\cos\theta)P_n^{|m|}(\cos\theta)\sin\theta\, d\theta = \frac{2}{(2l+1)}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ln}$$

Rigid-rotator wavefunctions - complete

$$Y_l^m(\theta,\phi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\phi} \quad l = 0,1,2\ldots \quad m = 0, \pm1, \pm2\ldots$$

$$\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\ Y_l^m(\theta,\phi)^* Y_n^k(\theta,\phi) = \delta_{ln}\delta_{mk}$$

$Y_l^m(\theta, \phi)$ are orthonormal over the surface of a sphere → ***Spherical Harmonics***

ℓ	m_ℓ	$Y_{\ell m_l}(\theta,\phi) = \Theta_{\ell m_l}(\theta)\Phi_{m_l}(\phi)$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	± 1	$\mp(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta - 1)$
2	± 1	$\mp(15/8\pi)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	± 2	$(15/32\pi)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

$$\Phi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}} e^{i m_\ell \phi}$$

$$\Theta_{\ell m_\ell}(\theta) = \left[\frac{2\ell+1}{2}\frac{(\ell - m_\ell)!}{(\ell + m_\ell)!}\right]^{1/2} P_\ell^{m_\ell}(\theta)$$

some sphercial harmonics

$$P_\ell^{m_\ell}(\theta) = associated \;\; Legendre \;\; polynomial$$

Angular momentum

Remember, $-\frac{1}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = \beta$ and that $\beta = l(l+1)$

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

βY

Spherical harmonics are also eignefunctions of $\hat{L}^2$

Square of the angular momentum = $\hbar^2 l(l+1) \quad l = 0,1,2 \ldots$

Energy is therefore, $\hbar^2 l(l+1)/2I$

Components of angular momentum

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

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

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

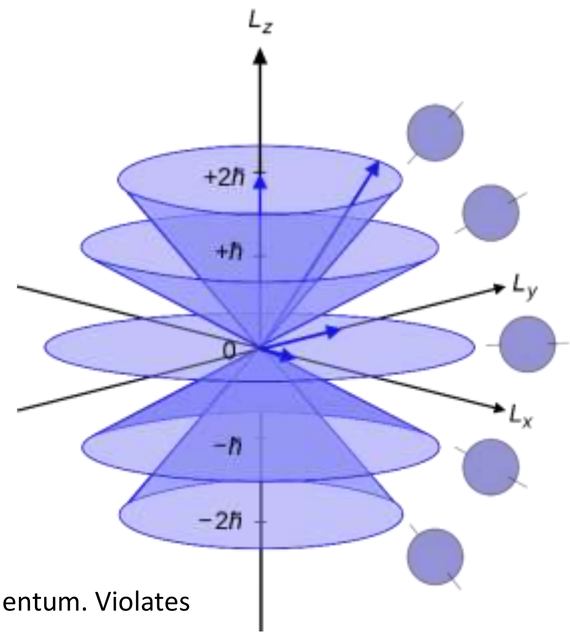
$$\hat{L}_z = = -\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\phi}$$

$$L_z e^{im\phi} = -i\hbar\frac{\partial}{\partial\phi}e^{im\phi} = m\hbar\, e^{im\phi}$$

So, spherical harmonics when operated by $\hat{L}_z$

$$\hat{L}_z Y_l^m(\theta,\phi) = N_{lm}P_l^{|m|}(\cos\theta)\,\hat{L}_z\ e^{im\phi} = m\hbar\, Y_l^m(\theta,\phi)$$

$\hbar$ is a fundamental measure of the angular momentum.



$Y_l^m(\theta,\phi)$ are not eigenfunctions of $\hat{L}_x$ *or* $\hat{L}_y$. What is $< \hat{L}_x >$

Commutation: $\hat{L}^2$ *and* $\hat{L}_z$ commute.

$|\boldsymbol{m}| \le \boldsymbol{l}$. Use $\hat{L}_z^2 Y_l^m(\theta,\phi)$ *and* $\hat{L}^2 Y_l^m(\theta,\phi)$ to prove.

Precession

$2l + 1$ values of m for each value of l

For $l = 2, m = 0, \pm1, \pm2$

Eigenvalue of $\hat{L}^2 \rightarrow l(l+1)\hbar^2 = 6\hbar^2 \therefore$ *of* $|L| \rightarrow \sqrt{6}\hbar$

Eigenvalue of $\hat{L}_z \rightarrow m\hbar = -2\hbar, -\hbar, 0, +\hbar, +2\hbar$

Never can the z-component be equal to the total angular momentum. Violates uncertainty! Except for one case!!!

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

Table 9-3
Atkins Physical Chemistry, Eighth Edition

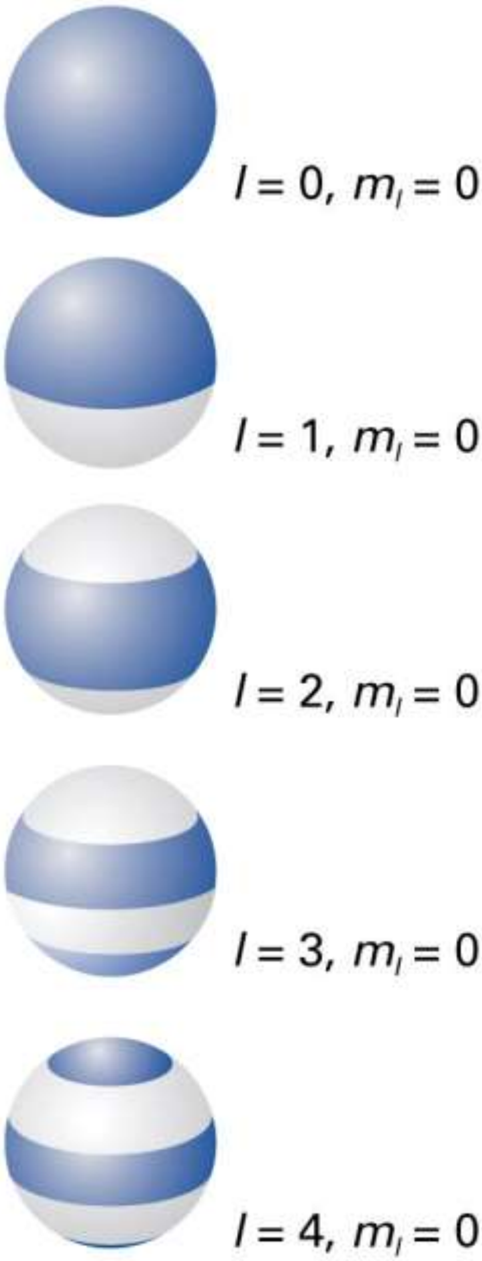


Figure 9-36
Atkins Physical Chemistry, Eighth Edition

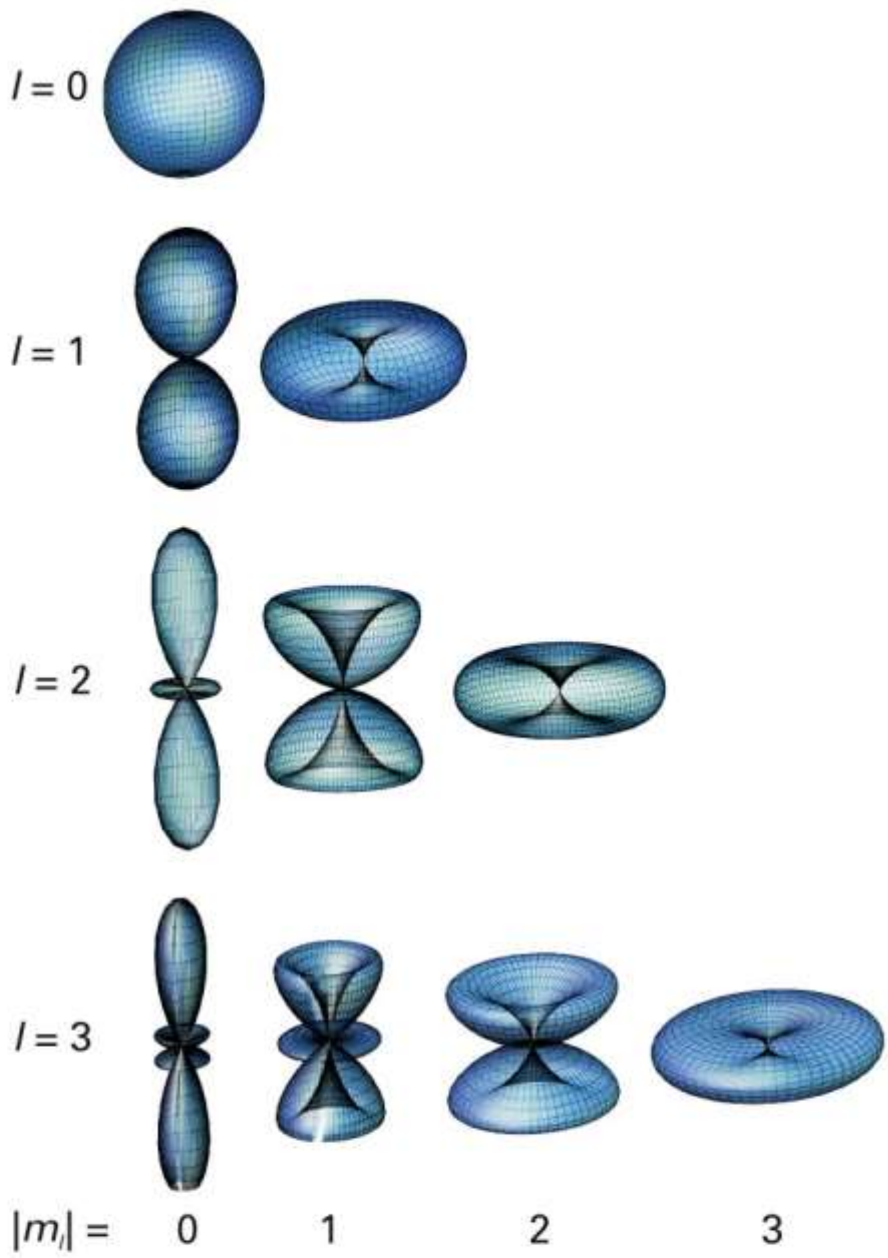


Figure 9-37
Atkins Physical Chemistry, Eighth Edition

Linear operators and degeneracy

$\hat{A}(\phi_1 + \phi_2) = \hat{A}\phi_1 + \hat{A}\phi_2 = a_1\phi_1 + a_2\phi_2 = a(\phi_1 + \phi_2)$ for degenerate eigenvalues. So, one could use any linear combination.

Add/Subtract p_1 and p_{-1} to get p_x and p_y