

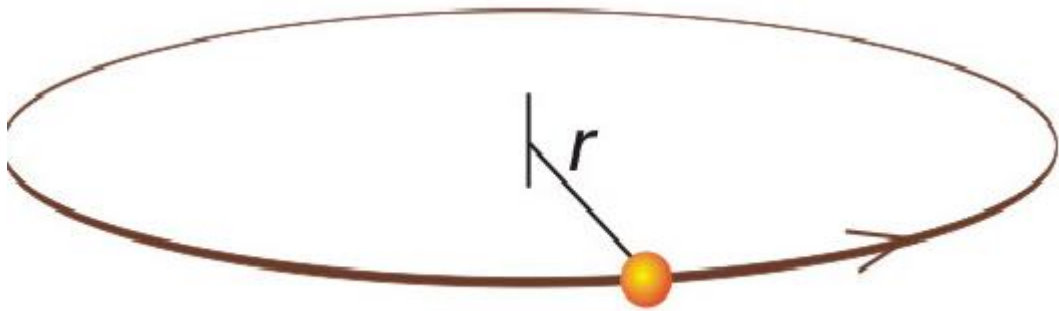


CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-08, 29-01-2018

Summary: Lecture - 05



$$E = \frac{m^2 \hbar^2}{2I}$$

r and θ are fixed

Cartesian to polar coordinates:

$$\Psi(x, y) \rightarrow \Psi(\phi)$$

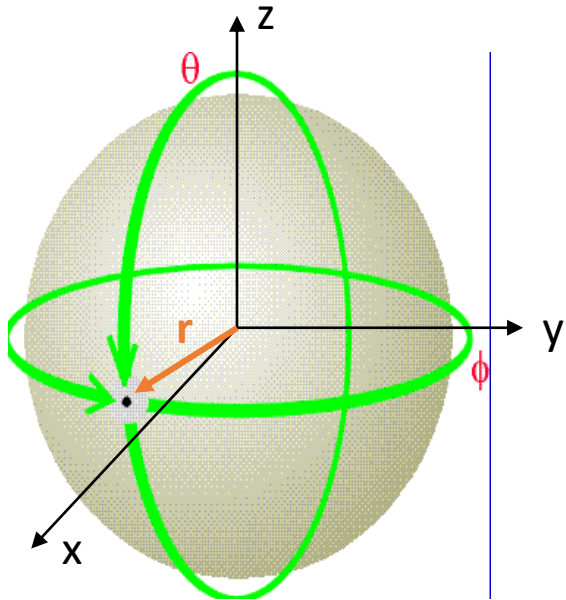
$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

Wave functions: $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$

Angular momentum: $L_z = m\hbar$

Next we have considered rotation on a sphere (rigid rotor): θ will also change

Summary: Lecture - 07



r is constant, Thus, $\Psi(\theta, \phi)$

Separation of variable: $\Psi(\theta, \phi) = \Theta(\theta) \Phi(\phi)$

Variables, θ & ϕ are separated; we have two equations:

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m_l^2$$

...Equn. 1

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$$

Summary: Lecture - 07



$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \epsilon \sin^2\theta = + m_l^2 \dots \text{Equn. 2}$$

Solution of above equation provides the condition:

$$\epsilon = l(l + 1) \Rightarrow E_l = \frac{\hbar^2}{2I} l(l + 1), \text{ with } l = 0, 1, 2, \dots \dots \dots$$

$$m_l = l, l - 1, \dots \dots \dots, -l$$

- Angular momentum is represented by a vector of length proportional to its magnitude, $\sqrt{l(l + 1)} \hbar$.
- m_l : projection of angular momentum on the Z-axis
- A rotating body may not take up an arbitrary orientation w.r.t. some **specified axis** (an axis defined by the direction of an externally applied electric or magnetic field)– called space quantization.

Summary: Lecture - 07



Spherical harmonics, $Y_{l,m_l}(\theta, \phi)$.

$$E_l = l(l+1) \frac{\hbar^2}{2I}$$

$$J^2 = l(l+1)\hbar^2$$

$$J = \sqrt{l(l+1)} \hbar, \\ l = 0, 1, 2, 3, \dots$$

$$L_z = m_l \hbar \quad m_l = l, l-1, \dots, -l$$

l	m_l	Y_{l,m_l}
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	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$

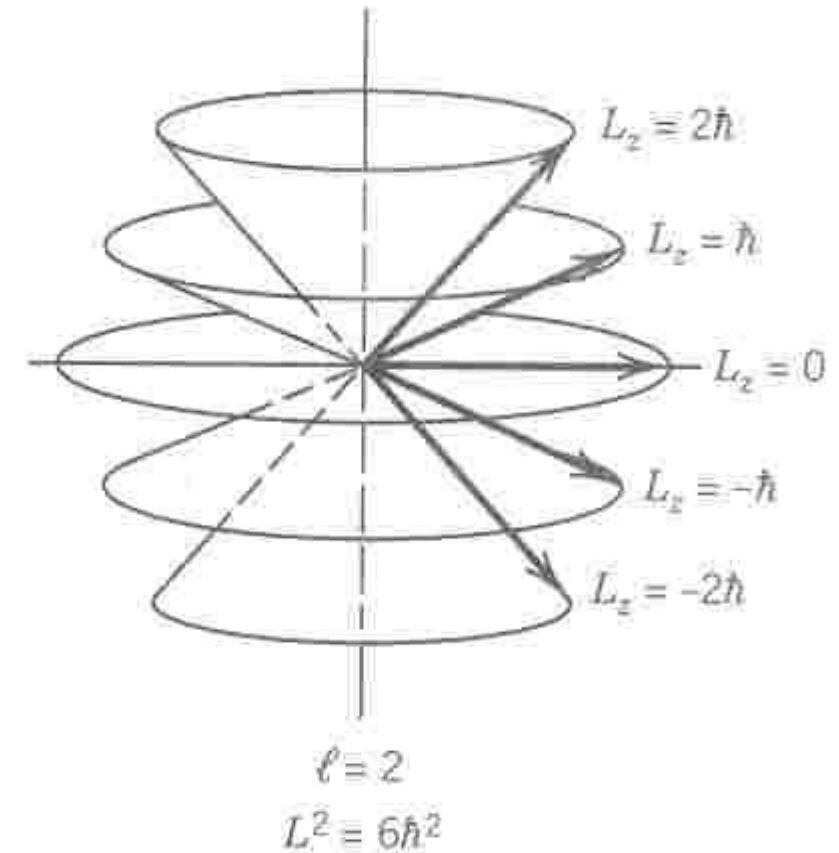
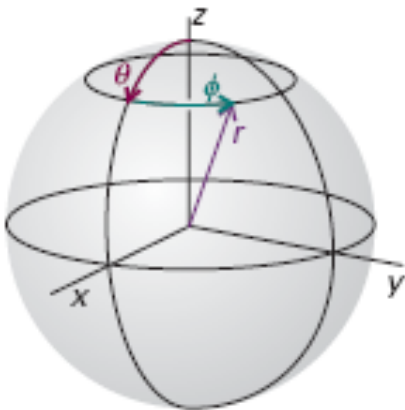
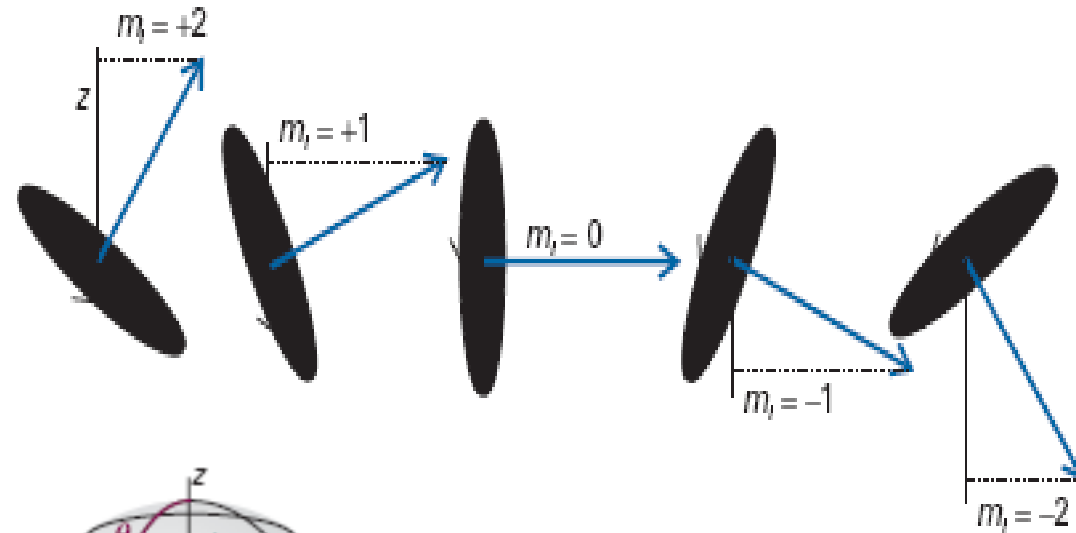
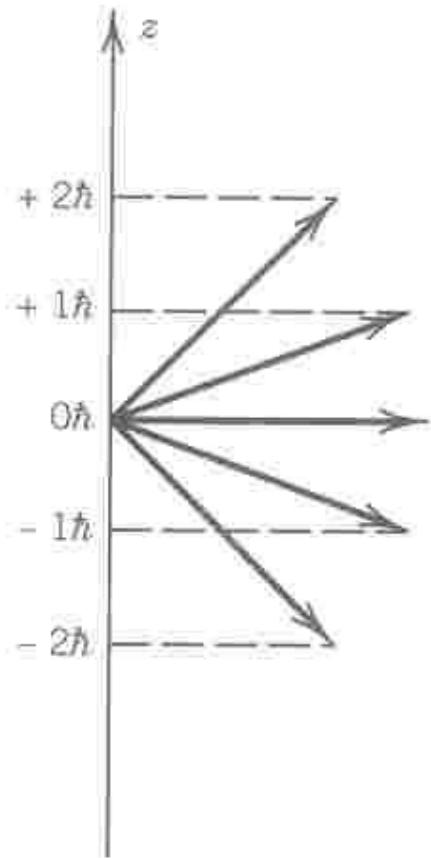
Summary: Lecture - 07

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Case-II: $l = 2, m_l = 2, 1, 0, -1, -2$



Hydrogen atom



- Atom with nuclear charge of Ze and mass m_N .
- A single electron (e^-) with mass m_e .
- Potential energy is Coulomb potential, $V(r)$:

$$V(r) = - \frac{Ze^2}{4\pi\epsilon_0 r}$$

where, r is the distance of e^- from nucleus and ϵ_0 is the vacuum permittivity.

- Since $m_N \gg m_e$, the nucleus may be considered to be at rest.
- Thus, electron is moving around the nucleus.

$$V(r) = - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$V(r)$ is spherically symmetric and depends only on the distance r

Hydrogen atom – Schrödinger equation



The Hamiltonian operator for internal motion of the electron relative to the nucleus:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r)$$

Laplacian in polar coordinate:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$$

where Legendrian, $\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)$

Hydrogen atom – Schrödinger equation



The Hamiltonian operator for internal motion of the electron relative to the nucleus:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \quad l \text{ \& } m_l$$

Laplacian in polar coordinate:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \boxed{\frac{1}{r^2} \Lambda^2}$$

The wave function of hydrogen atom in spherical polar coordinate can be represented as:

$$\Psi(r, \theta, \phi) = R(r) Y_l^{m_l}(\theta, \phi)$$

$R(r)$: Radial part of the wave function: Requirement that the wave function must be well behaved – leads to the result that functions must be labelled by three quantum numbers, $n, l, \text{ \& } m_l$

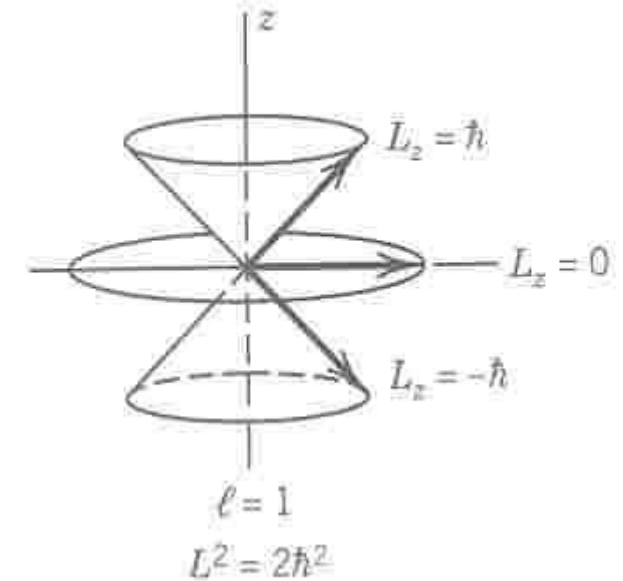
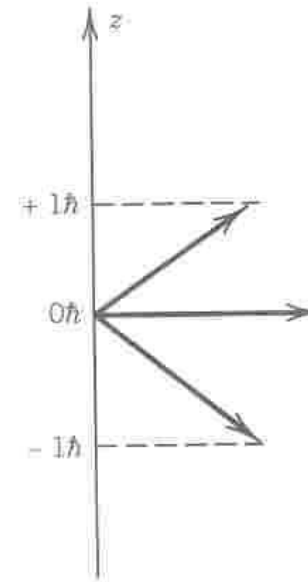
Hydrogen atom – Angular solution



- The solutions of angular part are Spherical harmonics, $Y_{l,m_l}(\theta,\phi)$ and are specified by the quantum numbers l and m_l .
- Magnitude of angular momentum = $[l(l+1)]^{1/2}\hbar$ with $l = 0,1,2,3..$
- Z-component of angular momentum = $m_l\hbar$; $m_l = l, l-1,, -l$

Spherical harmonics, $Y_l^{m_l}(\theta, \phi)$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
	± 1	$\mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$



Hydrogen atom – Energy and wave function



The acceptable solutions can be found only for integral values of a quantum number n , and that the allowed energies are

$$E_n = -\mu e^4 Z^2 / 32 \pi^2 \epsilon_0^2 \hbar^2 n^2$$

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

- The general form of the radial part of the hydrogen/hydrogenic atom wave functions are obtained by solving radial part of the Schrödinger equation.

$$\Psi_{n, l, m_l}(r, \theta, \phi) = R_{n, l}(r) Y_l^{m_l}(\theta, \phi)$$

Hydrogen atom – Radial solution



$$R_{n,l} \propto r^l (\text{polynomial of degree } \{n - l - 1\}) e^{-Zr/na_0}$$

- First factor determined the behavior at $r = 0$ (only $l = 0$ wave functions are non-zero at the origin).
- The second factor determines the number of radial nodes ($n - l - 1$).
- The third ensures that the function goes to zero as $r \rightarrow \infty$

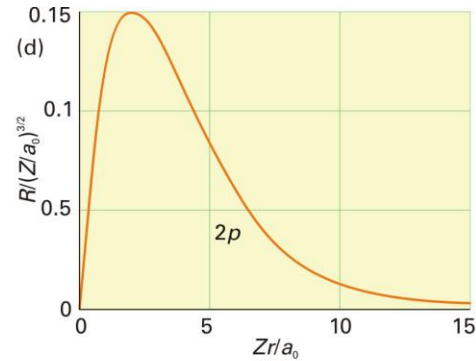
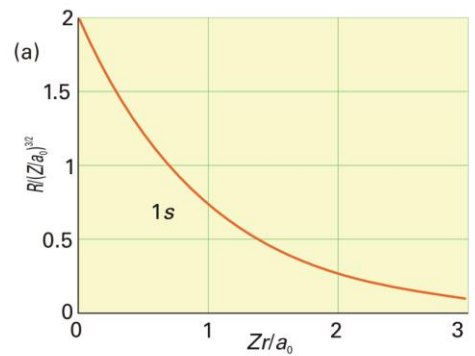
Hydrogen atom – Radial wave function



Orbital	n	l	$R_{n,l}$
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{1}{2}\rho\right) e^{-\rho/4}$
2p	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/4}$
3s	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(6 - 2\rho + \frac{1}{9}\rho^2\right) e^{-\rho/6}$
3p	3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(4 - \frac{1}{3}\rho\right) \rho e^{-\rho/6}$
3d	3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/6}$

$$\rho = 2Zr/a_0$$

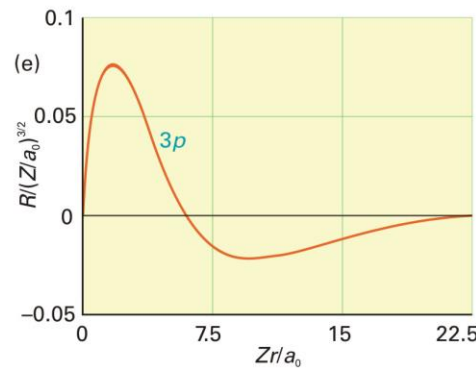
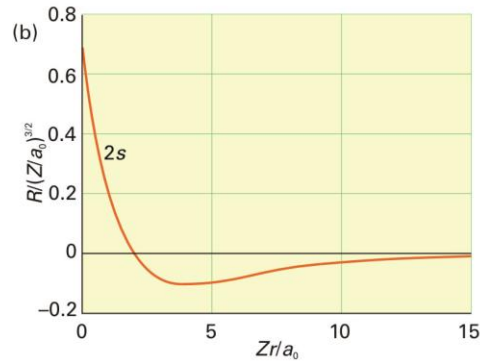
Hydrogen atom – Radial wave function



$$R_{3,0}(r) = \frac{1}{9(3)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(6 - 2\rho + \frac{1}{9}\rho^2 \right) e^{-\rho/6}$$

$$\begin{aligned} n &= 3 \\ l &= 0 \end{aligned}$$

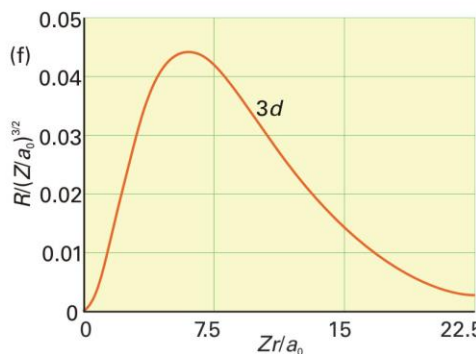
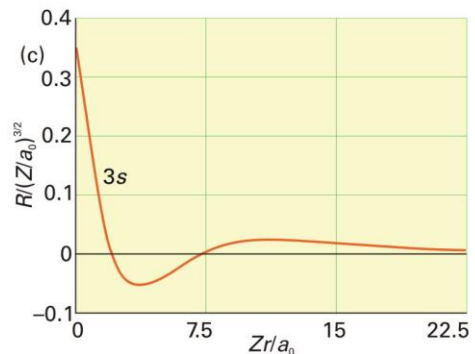
No. of radial nodes $(n-l-1) = 2$



$$R_{3,1}(r) = \frac{1}{27(6)^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(4 - \frac{1}{3}\rho \right) \rho e^{-\rho/6}$$

$$\begin{aligned} n &= 3 \\ l &= 1 \end{aligned}$$

No. of radial nodes $(n-l-1) = 1$



How do we define an orbital?

The wave function of an electron in hydrogen atom or hydrogenic atom is called an atomic orbital – An orbital is one-electron wave functions

$$\Psi_{n, l, m_l}(r, \theta, \phi) = R_{n, l}(r) Y_l^{m_l}(\theta, \phi)$$

Atomic orbitals are specified by three quantum numbers: n, l, m_l

We can precisely determine:

- Energy,
- Total angular momentum
- Z-component of angular momentum

Quantum numbers for H-atom



- Energy – Principal quantum number n

The energy levels are $E_n = -\mu e^4 Z^2 / 32 \pi^2 \epsilon_0^2 \hbar^2 n^2$; $n = 1, 2, 3, \dots$

The energy depends only on the quantum number n , and not on l or m_l . The energy expression also coincides with the Bohr model result. Here the reduced mass $\mu = mm_N / (m + m_N) \approx m$

- Orbital angular momentum or Azimuthal quantum number l . Orbital angular momentum = $[l(l+1)]^{1/2} \hbar$, $l = 0, 1, 2, \dots, n-1$ for given n
- Magnetic quantum number m_l
- Any one spatial component (say z), of the orbital angular momentum $m_l \hbar$

Principle quantum number, n: Energy levels



- The energy levels are

$$E_n = -\mu e^4 Z^2 / 32 \pi^2 \epsilon_0^2 \hbar^2 n^2$$

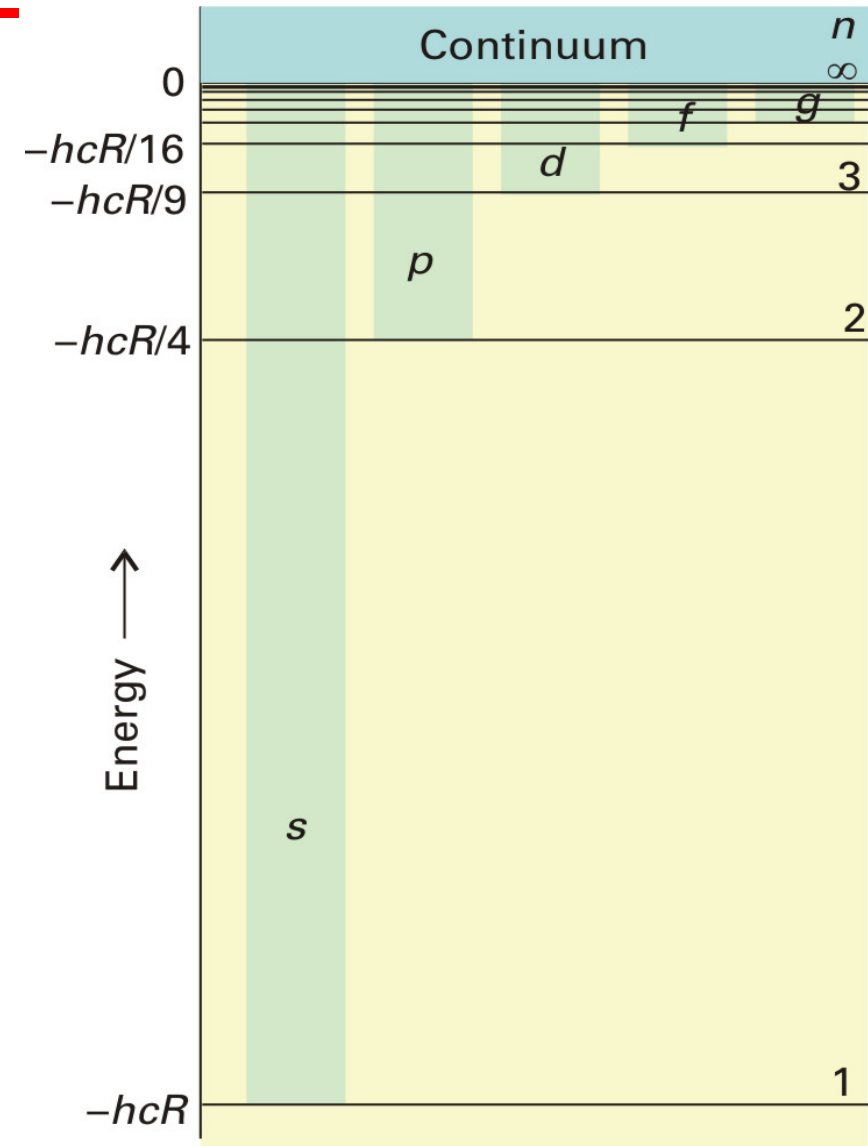
$$n = 1, 2, 3, \dots$$

$$E_n = -hcRZ^2/n^2$$

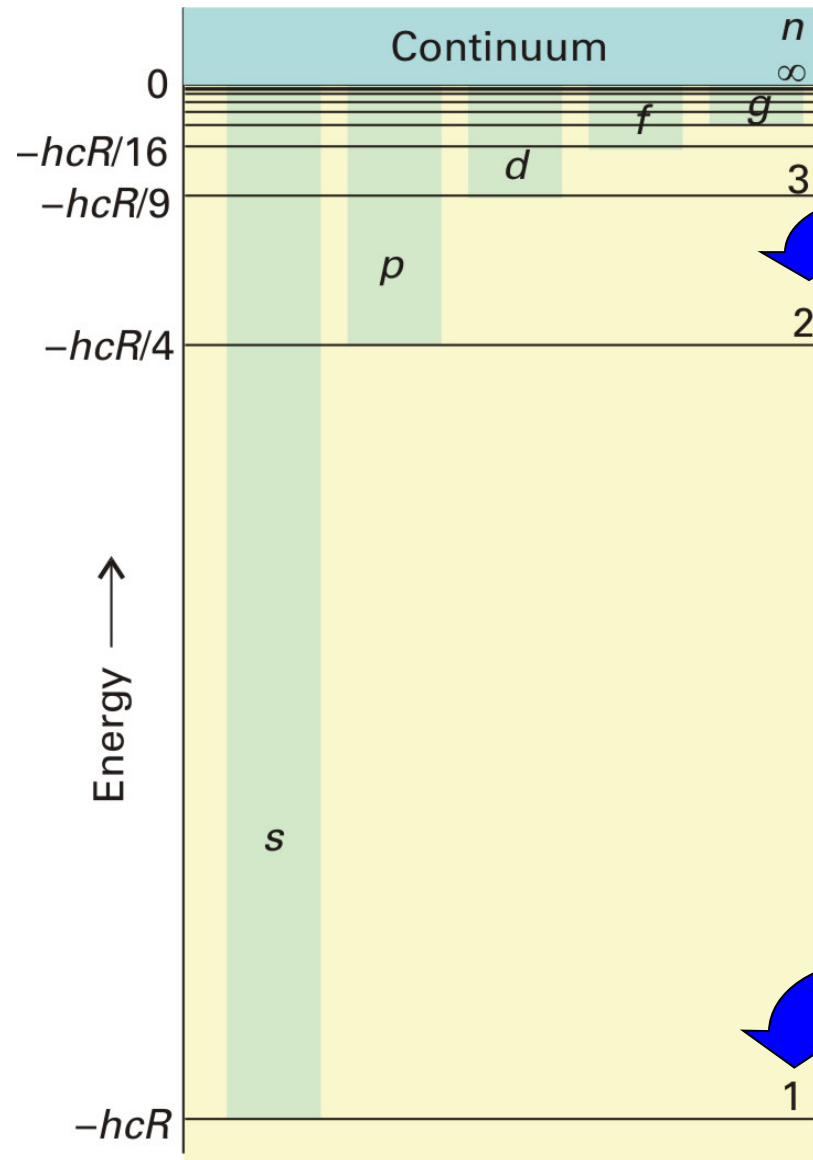
$$hcR = \mu e^4 / 32 \pi^2 \epsilon_0^2 \hbar^2$$

$$\mu = mm_N / (m + m_N)$$

Constant R is numerically same as Rydberg constant, R_H when m_N is set equal to the mass of proton.



Principle quantum number, n: Energy levels



$$E_n = -hcRZ^2/n^2$$

$$n=2, Z=1:$$

$$E_{n=2} = -hcR/4$$

$$E_n = -hcRZ^2/n^2$$

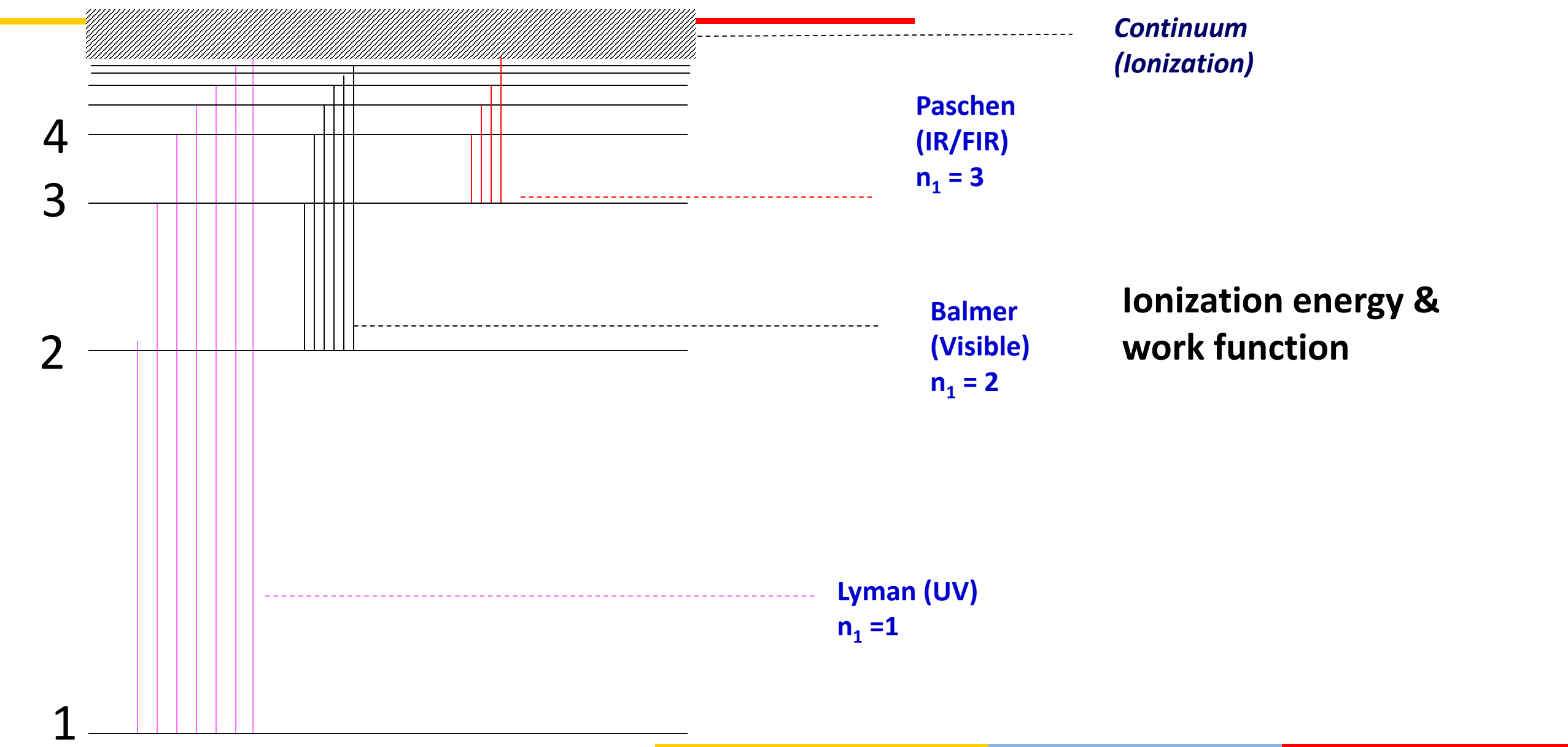
$$n=1, Z=1:$$

$$E_{n=1} = -hcR$$

$$\Delta E = -hcR/n_2^2 - (-hcR/n_1^2) \\ = h\nu$$

$$\nu = R[(1/n_1^2) - (1/n_2^2)]$$

Hydrogen atom spectra



Hydrogen atom wave function



$$\Psi_{n, l, m_l}(r, \theta, \varphi) = N R_{n, l}(r) \Theta_{l, m_l}(\theta) \Phi_{m_l}(\varphi)$$

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

$$l = n - 1, n - 2, \dots, 0$$

$$m_l = l, l - 1, l - 2, \dots, -l$$

$$\Phi_{m_l} = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

$$\Psi(\theta, \phi) = N' \Theta_{l, m_l}(\theta) \Phi_{m_l}(\varphi) \equiv Y_l^{m_l}(\theta, \phi)$$

$$R_{n, l} \propto r^l (\text{polynomial of degree } \{n - l - 1\}) e^{-Zr/na_0}$$

Shells, subshells, and orbitals



What values can the quantum numbers take ?

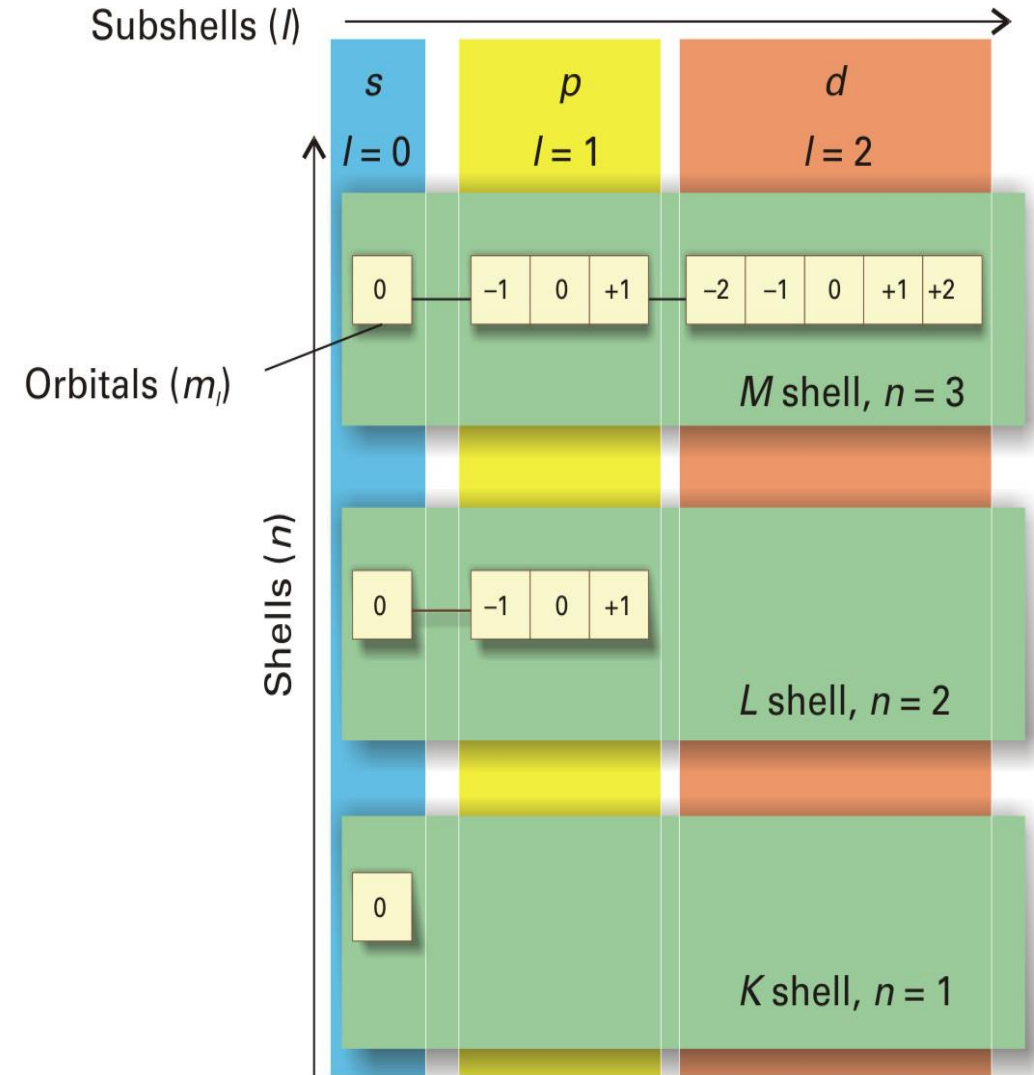
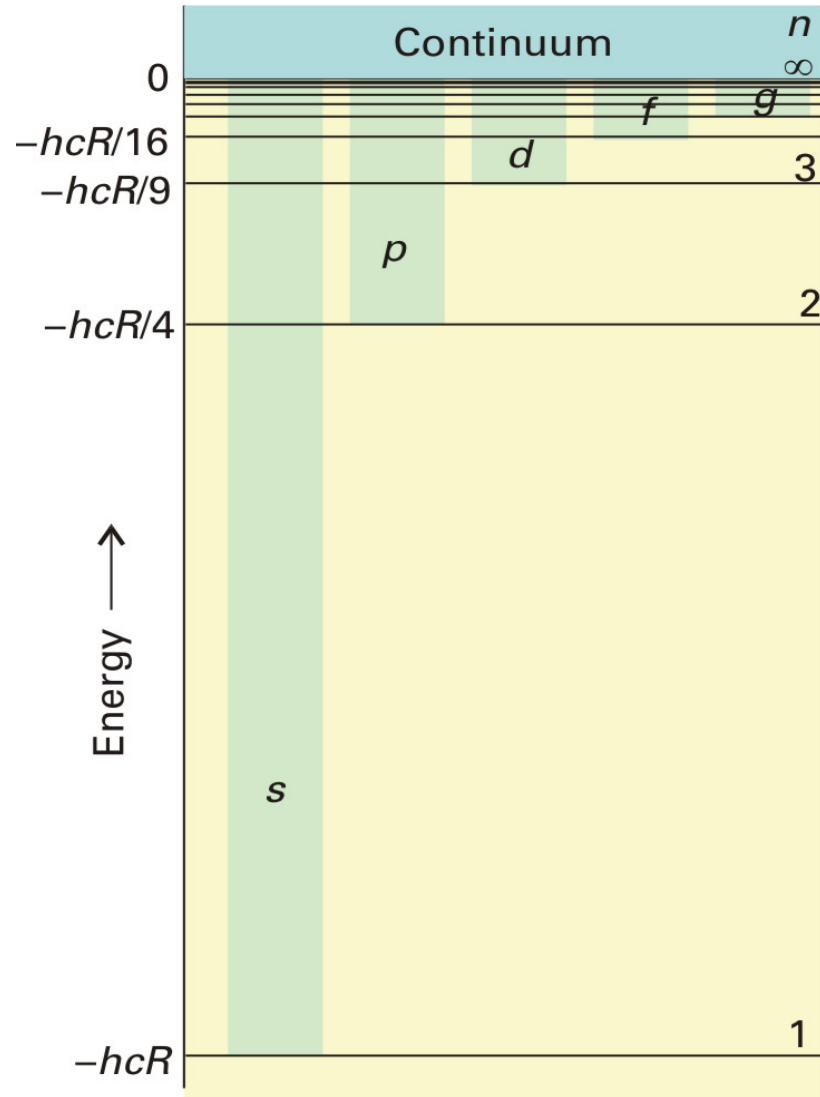
- $n = 1, 2, 3, \dots$ {Given n – shell}
- $l = 0, 1, 2, \dots, n-1$ (For given n , there are n possible values of l). {Given n and l – subshell}

l	=	0	1	2	3
		s	p	d	f

- $m_l = -l, -l+1, \dots, l-1, l$ (For given l , there are $2l + 1$ possible values of m_l).

How many orbitals for a given n ? n^2

Electronic structure of hydrogenic atom



Hydrogen like atomic wave function



Try to construct the $\psi_{2,1,0}$ wave function for hydrogen atom like system:

$$\Psi_{n,l,m_l}(r, \theta, \varphi) = N R_{n,l}(r) \Theta_{l,m_l}(\theta) \Phi_{m_l}(\varphi)$$

$$\Theta_{1,0}(\theta) \Phi_0(\varphi) = Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

Energy??
Angular momentum??
Z-component of angular momentum??

$$R_{2,1}(r) = \frac{1}{\sqrt{24}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

No. of radial nodes??
($n - l - 1$)

$$\Psi_{2,1,0}(r, \theta, \varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos \theta$$

Ground state of hydrogenic atom



Ground State: $n = 1, l = 0, m_l = 0 \rightarrow 1s$ orbital

- $\Psi_{100} = (4\pi)^{-1/2} (4/a_0^3)^{1/2} e^{-r/a_0} = (1/\pi a_0^3)^{1/2} e^{-r/a_0}$

(independent of θ and ϕ , true for all s states since $Y_0^0 = (4\pi)^{-1/2}$).

- All s orbitals are spherically symmetrical - zero angular momentum
- Probability density depends only on r
- Maximum at $r = 0$, the nucleus.
- Decays exponentially with distance r
- No nodes
- Above function is normalized

Hydrogen atom – Supporting information

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Schrödinger Equation in terms of angular part of wave function

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\theta, \phi) = E \Psi(\theta, \phi)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{1}{r^2} [\Lambda^2 \Psi(\theta, \phi)] = E \Psi(\theta, \phi),$$

We can rearrange the above equation:

$$\Rightarrow \Lambda^2 \Psi(\theta, \phi) = -\frac{2mr^2 E}{\hbar^2} \Psi(\theta, \phi) = -\frac{2IE}{\hbar^2} \Psi(\theta, \phi)$$

$$\Lambda^2 \Psi(\theta, \phi) = -l(l+1) \Psi(\theta, \phi), \quad \Psi(\theta, \phi) \equiv Y_l^{m_l}(\theta, \phi)$$

Angular part of the wave function is spherical harmonics