Hydrogen atom (electron in an atom)

The Schrödinger equation in 3 dimensions

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+\underbrace{V}_{\substack{V(x,y,z)\\ \text{3-dimensional}}}\right]\psi(x,y,z)=E\,\psi(x,y,z) \quad (1)$$

or, $$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\,\psi(x,y,t)$$

Or in short $$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi}$$

Where ∇ is called '<u>Laplacian</u>'.

⇒ Now consider the hydrogen atom where the nucleus being ~2000 time ~~higher~~ heavier than the electron orbiting it remains stationary. So, we have two energy terms

– 1. Kinetic energy of the electron, whose operator is

$$-\frac{\hbar^2}{2m_e}\nabla^2$$

& 2. Potential energy

$$V(x,y,z)=-\frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{\sqrt{x^2+y^2+z^2}}$$

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

where $r=\sqrt{x^2+y^2+z^2}$ the radial distance of the electron from the nucleus.

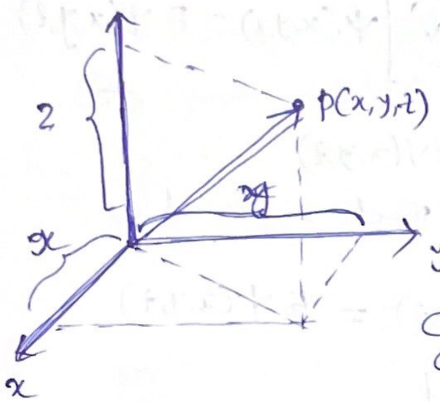
Z is the atomic number

Nuclear charge $=Ze$

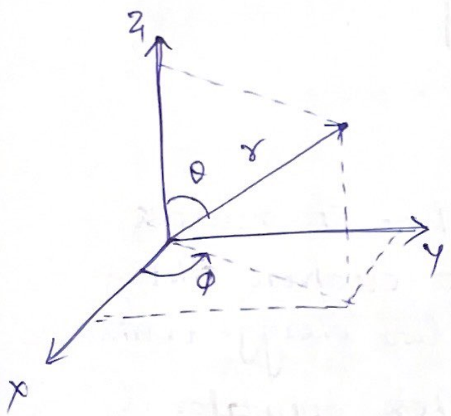
This potential is centro-symmetric which ~~only~~ depends only on 'r' and is independent of angle.

— 'Central potential'

In this system, we describe the position of the electron in terms of its distance (r), from the nucleus and two angles, θ and ϕ. Thus it is a natural choice for us to switch to <u>spherical coordinates</u> (r, θ, ϕ).



Cartesian coordinates



Spherical coordinates

The Schrödinger equation in spherical polar coordinates can be written as

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right]$$

$$+V\psi = E\psi \quad \text{—(1)}$$

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

Now, we write the total wave function as a product of a function which depends on r and another which is a function of the two angles θ and ϕ.

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \quad \text{—(2)}$$

Putting this in eqⁿ ② we get

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]$$
$$+VRY=ERY \quad -③$$

Dividing by RY and multiplying by $(-2mr^2/\hbar^2)$.

$$\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V-E]\right\}}_{\text{depends on only 'r'}}+\underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}}_{\text{depends on }(\theta,\text{ and }\phi)}=0 \quad -④$$

Each of these will be equal to a constant. Let's assume that this constant is $l(l+1)$.

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V-E)=l(l+1) \quad -⑤$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right\}=-l(l+1) \quad -⑥$$

$$\boxed{\psi_{nl,m_l}(r,\theta,\phi)=R_{nl}(r)\,Y_{lm}(\theta,\phi)}$$

Radial part

ψ_{1s} $\quad R_{10}(r)=2\left(\frac{Z}{a}\right)^{3/2}e^{-\rho/2}$

ψ_{2s} $\quad R_{20}(r)=\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)\,e^{-\rho/2}$

ψ_{2p} $\quad R_{21}(r)=\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho\,e^{-\rho/2}$

$$\rho=\left(\frac{2Z}{na}\right)r$$

$$a=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Angular part

	–
	–
$2p_x$	$\sin\theta\cos\phi$
$2p_y$	$\sin\theta\sin\phi$
$2p_z$	$\cos\theta$

$$\psi_{100}(r,\theta,\phi)=R_{10}(r)\,Y_{0,0}(\theta,\phi)$$
$$=2\left(\frac{Z}{a_0}\right)^{3/2}e^{-\rho/2}$$

$\Rightarrow$ The complete wave function is

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

These wave functions for hydrogen like atoms are called atomic orbitals.

Here n is the principal quantum number. It specifies the energy of the orbitals. $n = 1, 2, 3 \cdots$

The orbital angular momentum quantum number 'l' specifies the magnitude of the angular momentum of the electron as $\sqrt{l(l+1)}\,\hbar$ where $l = 0, 1, 2 \cdots (n-1)$

The magnetic quantum number m_l specifies the z-component of the angular momentum as $m_l\hbar$ where $m_l = 0, \pm 1, \pm 2 \cdots \pm l$.

The wave functions obtained after solving the Schrödinger equation are atomic orbitals. A few of them are written as,

$n=1$, $l=0$, $m_l=0$:
$$\psi_{100} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$n=2$, $l=0, m=0$:
$$\psi_{200} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$l=1$ $m=0$:
$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0} \cos\theta$$

$l=1$ $m=+1$:
$$\psi_{211} = \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/a_0} \sin\theta \cos\phi$$

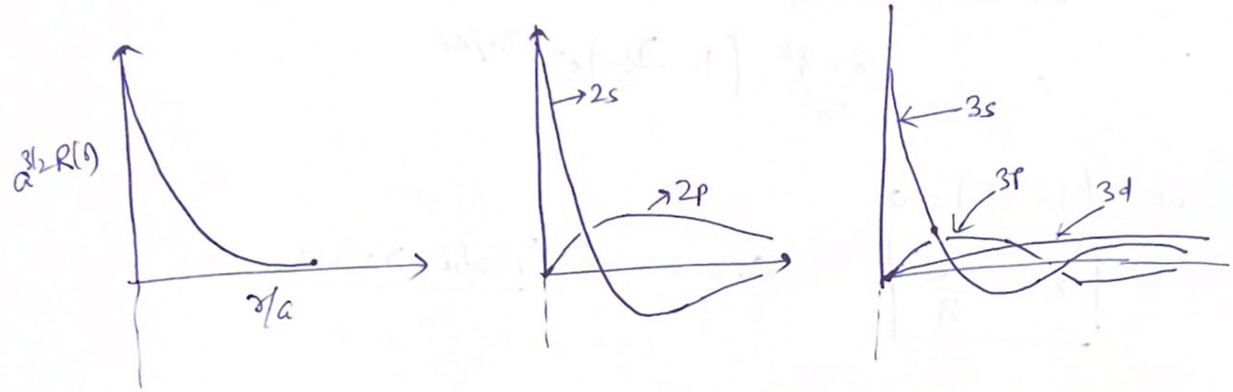
$l=1$ $m=-1$:
$$\psi_{211} = \psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/a_0} \sin\theta \sin\phi$$

The radial wave function

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

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

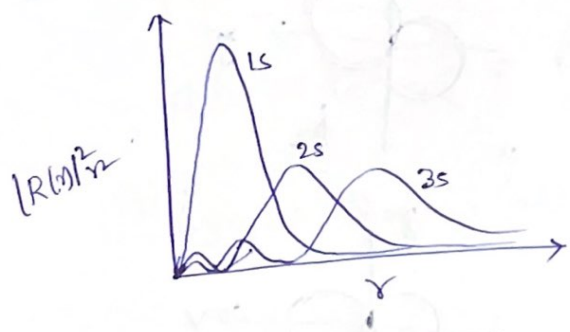
$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{5/2} r e^{-Zr/2a_0}$$

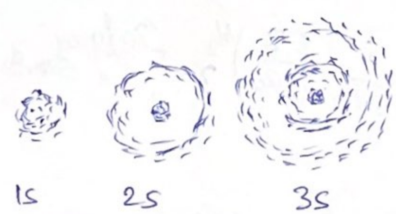


Radial distribution function or probability density ($|\psi(r)|^2 r^2$)

$[R(r)]^2 r^2$ the probability of finding the electron at a distance r from the nucleus.

(r to $r+dr$)





Probability density

$$P(r) = |R(r)|^2 r^2$$

$$= 4\left(\frac{Z}{a_0}\right)^3 e^{-2Zr/a_0}\, r^2$$

$$\frac{dP(r)}{dr} = 4\left(\frac{Z}{a_0}\right)^3\left(2r - \frac{2Zr^2}{a_0}\right)e^{-2Zr/a_0}$$

$$0 = \frac{8rZ^3}{a_0^3}\left(1 - \frac{Zr}{a_0}\right)e^{-2Zr/a_0}$$

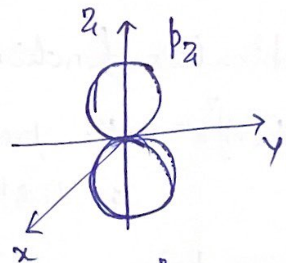
or $\left(1 - \frac{Zr}{a_0}\right) = 0$

or $\boxed{r = \frac{a_0}{Z}}$ $\quad a_0 = 0.529\,\text{Å}$ 'Bohr radius'.

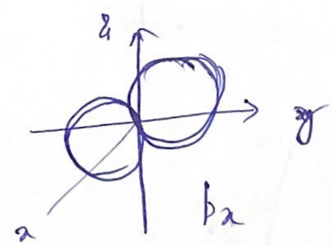
P-orbitals:

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{-Zr/2a_0}\cos\theta$$

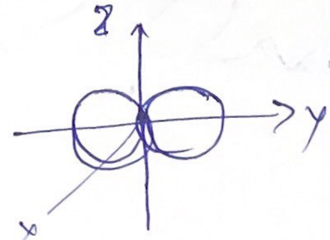
$n=2,\ l=1,\ m=0$



$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{-Zr/2a_0}\sin\theta\cos\phi$$



$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{-Zr/2a_0}\sin\theta\sin\phi$$



* $\boxed{\text{Read d-orbitals}}$

Energy levels

$$E = -\frac{Z^2}{n^2}\frac{e^2}{8\pi\varepsilon_0 a_0}$$

$$= -\frac{hc Z^3 \bar{R}_H}{n^2}$$

where R_N atomic Rydberg constant

$$R_N = \frac{\mu e^4}{8\pi\varepsilon_0 c h^3}$$

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_2 - E_1}{hc}$$

$$= \frac{e^2}{8\pi\varepsilon_0 a_0 hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$R_H = 109677.6\ \text{cm}^{-1}$$

Atomic spectra

$$\Delta E = E_1 - E_2 = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

(i) Lyman, Balmer and Paschen series - Read.