

14/11/2025

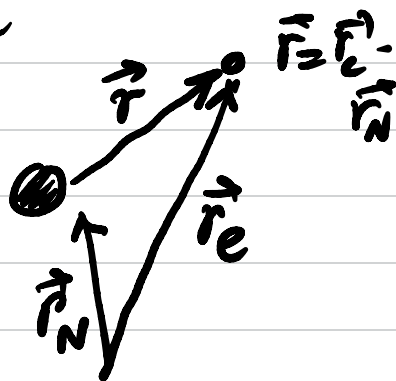
lec. 36.

The H atom problem

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_N} \nabla_N^2}_{\text{nucleus}} - \underbrace{\frac{\hbar^2}{2m} \nabla_e^2}_{\text{electron}} - \frac{KZe^2}{r} \quad \text{--- (1)}$$

We once again perform the CM. transform
defining:

$$\textcircled{2} \left\{ \begin{aligned} \vec{R} &= \frac{m_N \vec{r}_N + m \vec{r}_e}{M} \\ \vec{r} &= \vec{r}_e - \vec{r}_N \end{aligned} \right.$$



This gives for the relative motion:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{KZe^2}{r} \quad \text{--- (3)}$$

Here we have assumed a nuclear charge of Ze , (Hydrogenic atom)

Writing the Schrödinger equation in spherical polar coordinates we have:

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r} \frac{\partial^2}{\partial r^2} (r \psi(r, \theta, \varphi)) - \frac{1}{\hbar^2 r^2} \hat{L}^2 \psi(r, \theta, \varphi) \right] - \frac{KZe^2}{r} \psi(r, \theta, \varphi) = E \psi(r, \theta, \varphi) \quad - (4)$$

Since this is a central potential, we have that $[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = 0$ - (5)

$$\therefore \psi(r, \theta, \varphi) = R(r) Y_l^{m_l}(\theta, \varphi) \quad - (6)$$

substituting this in the eqn above and dividing both sides by $Y_l^{m_l}(\theta, \varphi)$

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r} \frac{d^2}{dr^2} (r R(r)) - \frac{l(l+1)}{r^2} R(r) \right] - \frac{KZe^2}{r} R(r) = E R(r) \quad - (7)$$

From (7) we expect that both $R(r)$ and, hence, E could depend on l , but not on m . This means that each energy level will have a $(2l+1)$ degeneracy coming from $\hat{L}_z$ eigenstates.

To simplify (7) let's consider

$$R(r) \equiv U(r)/r \quad - (8)$$

Substituting this in (7) yields

$$\left\{ \frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} \left[E + \underbrace{\frac{KZe^2}{r}}_{-V(r)} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] \right\} U(r) = 0 \quad - (9)$$

$l \rightarrow$ an effective potential.

$\rightarrow$ Unlike the usual 1-d eqn., $r = [0, \infty)$

$$\rightarrow V_l(r) = -\frac{KZe^2}{r} + \underbrace{\frac{l(l+1)\hbar^2}{2\mu r^2}}_{\text{repulsive centrifugal barrier for } l > 0} \quad - (10)$$

$\rightarrow$ Boundary conditions on $U(r)$ are different from a regular 1-d problem.

⑨ can be rewritten as an eigenvalue eqn.

$$\hat{D}_l U(r) = E U(r) \quad - (11)$$

$$\text{where } \hat{D}_l = \left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_l(r) \right\} \quad - (12)$$

Since $\hat{D}_l$ has to be Hermitian, we have, for 2 functions $U_1(r)$ & $U_2(r)$,

$$\langle U_1 | \hat{D}_l | U_2 \rangle = \langle U_2 | \hat{D}_l | U_1 \rangle^* \quad - (13)$$

That is,
$$\int_0^{\infty} U_1^* (\hat{D}_e U_2) dr = \left(\int_0^{\infty} U_2^* (\hat{D}_e U_1) dr \right)^*$$

$$= \int_0^{\infty} (\hat{D}_e U_1)^* U_2 dr \quad (14)$$

$$\Rightarrow \int_0^{\infty} dr \left[U_1^* \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \right) U_2 - U_2 \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} U_1^* \right) \right] = 0 \quad (15)$$

(Since $V_e(r)$ is a multiplicative or space-local operator).

Integrating each term in (15) by parts we get

$$\left(U_1^* \frac{d}{dr} U_2 - U_2 \frac{d}{dr} U_1^* \right) \Big|_0^{\infty} = 0 \quad (16)$$

Therefore, solution to (9) must satisfy (16).

Normalization of ψ , for bound states,

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r, \theta, \varphi)|^2 r^2 dr \sin \theta d\theta d\varphi$$
$$= \int_0^\infty |R(r)|^2 r^2 dr \int d\Omega \underbrace{|Y_l^{m_l}(\Omega)|^2}_{=1}$$

$$= \int_0^\infty |R(r)|^2 r^2 dr = 1 \quad \text{--- (17)}$$

or

$$\int_0^\infty |U(r)|^2 dr = 1 \quad \text{--- (18)}$$

That is for bound states

$$\lim_{r \rightarrow \infty} U(r) \rightarrow 0 \quad \text{--- (19)}$$

For unbound states $U(r \rightarrow \infty) \rightarrow e^{ikr}$ --- (20)

For either case,

$$\left. U_1^* \frac{dU_2}{dr} - U_2 \frac{dU_1^*}{dr} \right|_a = 0 \quad \text{--- (21)}$$

(check)

So $\hat{D}_l$ is Hermitian if

$$\left[U_1^* \frac{dU_2}{dr} - U_2 \frac{dU_1^*}{dr} \right] \Big|_0 = 0 \quad \text{--- (22)}$$

in this case

This condition is satisfied if

$$U \xrightarrow[r \rightarrow 0]{} \text{constant} \quad \text{--- (23)}$$

For $C \neq 0$, this implies

$$R(r) = \frac{U}{r} \sim \frac{C}{r} \quad \text{--- (24)}$$

at $r \rightarrow 0$.

$\Rightarrow$ it diverges at the origin.

$$\Rightarrow \text{for } l=0, m=0 \quad \psi \sim \frac{c}{r} Y_0^0 \quad - (25)$$

$$\text{and} \quad \nabla^2\left(\frac{1}{r}\right) = -4\pi \delta(\vec{r}) \quad - (26)$$

i.e. it doesn't satisfy the Schrödinger eqn. at the origin.

$\therefore$ we must have that $c=0$

$$\text{or} \quad V \xrightarrow{r \rightarrow 0} 0 \quad - (27)$$

Now as $r \rightarrow 0$, the dominant term in the potential is the

$$\text{centrifugal term i.e. } \frac{l(l+1)}{r^2} \gg \frac{1}{r} \quad (r \rightarrow 0)$$

and $\gg E$.

$\therefore$ (9) becomes in this limit (28)

$$\frac{d^2 u}{dr^2} \approx \frac{l(l+1)}{r^2} u \quad - (29)$$

A trial solution of the form

$$U_l(r) \sim r^\alpha \quad \text{yields}$$

$$\alpha(\alpha-1) r^{\alpha-2} = \frac{l(l+1)}{r^2} \cdot r^\alpha \quad (29)$$

$$\text{or } \alpha = l+1 \text{ or } -l. \quad (30)$$

$$\Rightarrow U_l \sim \begin{cases} r^{l+1} & \text{regular} \\ r^{-l} & \text{irregular} \end{cases} \quad (31)$$

(doesn't depend on E)

r^{-l} blows up at $r \rightarrow 0$ against our condition (27). So we reject it.

$$\therefore U_l(r) \sim r^{l+1} \quad (r \rightarrow 0) \quad (32)$$

Consider now the behavior of U as $r \rightarrow \infty$.

$V(r) \rightarrow 0$ as $r \rightarrow \infty$ in our case.

At large r the eqn (9) becomes.

→ doesn't depend on l .

$$\frac{d^2 U_E}{dr^2} = -\frac{2\mu E}{\hbar^2} U_E \quad \text{--- (36)}$$

1) $E > 0$: U_E will oscillate as $r \rightarrow \infty$

2) $E < 0$: $U_E \rightarrow 0$ as $r \rightarrow \infty$ and should drop exponentially in the classically forbidden regions

Let us focus on bound states $E < 0$.

$$(36) \Rightarrow U_E(r \rightarrow \infty) \sim e^{-\kappa r} \quad \text{--- (37)}$$

$$\text{where } \kappa = \sqrt{\frac{2\mu|E|}{\hbar^2}} \quad \text{--- (38)}$$

There are some subtleties to this expectation coming from the $1/r$ decay of the potential. But motivated by this behaviour, we can define

$$U_{E,l}(r) = f_{E,l}(r) e^{-\kappa r} \quad \text{--- (39)}$$

$$\text{let } \rho = kr \quad - (40) \quad k = \sqrt{\frac{2m|E|}{\hbar^2}}$$

Then

$$U_{El}(\rho) = e^{-\rho} f_{El}(\rho) \quad - (41)$$

f then satisfies:

$$\frac{d^2 f}{d\rho^2} - 2 \frac{df}{d\rho} + \left[\frac{KZe^2 \lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] f$$

$$\text{where } \lambda = \sqrt{\frac{2m}{\hbar^2 |E|}} \quad - (43) \quad = 0 \quad - (42)$$

We try a polynomial expansion for f motivated by the $\rho \rightarrow 0$ limit behaviour ~~be~~ obtained earlier.

Since $U(\rho) \sim \rho^{l+1}$ ($\rho \rightarrow 0$) we can choose

$$f_{El}(\rho) = \rho^{l+1} \sum_{k=0}^{\infty} C_k \rho^k \quad - (43)$$

Substituting this in (42) and

collecting same power terms together we get

$$\frac{C_{k+1}}{C_k} = \frac{-(Zke^2)\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - l(l+1)}$$

→ (44)

Energy levels:

$$\text{Now, } \lim_{k \rightarrow \infty} \frac{C_{k+1}}{C_k} = \frac{2}{k} \quad - (45)$$

This is the same behaviour of coeff. we would get for the power series of $V/A: p^m e^{2p}$. — (46)

So we are tempted to equate

$$f = V \quad - (47)$$

But, this would imply

$$U = r^m e^{2r} \cdot e^{-r} = r^m e^r \quad (48)$$

$$\rightarrow \infty \quad \text{as } r \rightarrow \infty$$

So we must terminate the series at some finite k . This would happen if, for some k , we have $\frac{C_{k+1}}{C_k} = 0$ (49)

$$\Rightarrow k_{\max} : (kZe^2)\lambda = 2(k_{\max} + 1) \quad (49)$$

or, from definition of λ .

$$E = -|E| \quad (E < 0)$$

$$= \frac{2m}{\hbar^2} / \lambda^2$$

$$= \frac{-m (kZe^2)^2}{2\hbar^2 (k_{\max} + 1)^2} \quad (50)$$

Since $k_{\max}$ is not fixed here beyond

being a non-negative integer
we get energy quantization
for $k_{\max} = 0, 1, 2, \dots$

$$\& \quad l = 0, 1, 2, \dots \quad (\text{from } \ell^2)$$

$$\therefore \quad n \equiv (k_{\max} + l + 1) \\ = 1, 2, 3, \dots$$

so that

$$E_n = \frac{-m (KZe^2)^2}{2\hbar^2 n^2} \quad (51)$$

$$\text{Defining } a_0 \equiv \frac{\hbar^2}{\mu e^2} \quad (52) \quad (\text{Bohr radius})$$

we have

$$E_n = - \left(\frac{Ke^2}{2a_0} \right) \frac{Z^2}{n^2} \quad (53)$$

It is convenient to define a unit
of energy $1 \text{ Ry} \equiv Ke^2/2a_0 \text{ J} \quad (53)$

$$\Rightarrow E_n = -\frac{Z^2}{n^2} R_y \quad - (54)$$

$$1 R_y \approx \underline{\underline{13.6 \text{ eV.}}}$$

Wavefunctions: Given the recursion relations and the $k_{\max} = n - l - 1$ we can work back the wavefn. (55)

The corresponding f_{El} are a set of polynomials called the Associate Laguerre polynomials denoted by

$$f_{El}(p) = p^{l+1} L_{n-l-1}^{2l+1}(2p) \quad - (56)$$

where
$$L_p^k(x) = (-1)^k \frac{d^k}{dx^k} L_{p+k}^0 \quad (57)$$

$$L_p^0(x) = e^x \left(\frac{d^p}{dx^p} \right) (e^{-x} x^p) \quad (58)$$

With this definition we get

$$R_{nl}(r) \sim e^{-r/na_0} \left(\frac{r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0} \right)$$

— (59)

Allowed values of l for a given n are restricted by the highest degree allowed for L .

$$\text{i.e. } l = n-1, n-2, \dots, 2, 1, 0 \quad \text{--- (60)}$$

for $p \leq$

The normalized eigenfunction of the H atom are given:

$$\psi_{100}(\vec{r}) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \quad (61)$$

1s

$$\psi_{200}(\vec{r}) = \left(\frac{1}{32\pi a_0^3} \right)^{1/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} \quad (62)$$

2s

$$\psi_{210}(\vec{r}) = \left(\frac{1}{32\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta \quad (63)$$

2p

$$\psi_{21\pm 1}(\vec{r}) = \mp \left(\frac{1}{64\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta e^{\pm i\phi} \quad (64)$$

complex orbitals

To get real orbitals we can form linear combinations:

$$\psi_{2p_x} = (\psi_{211} - \psi_{21-1}) / 2$$

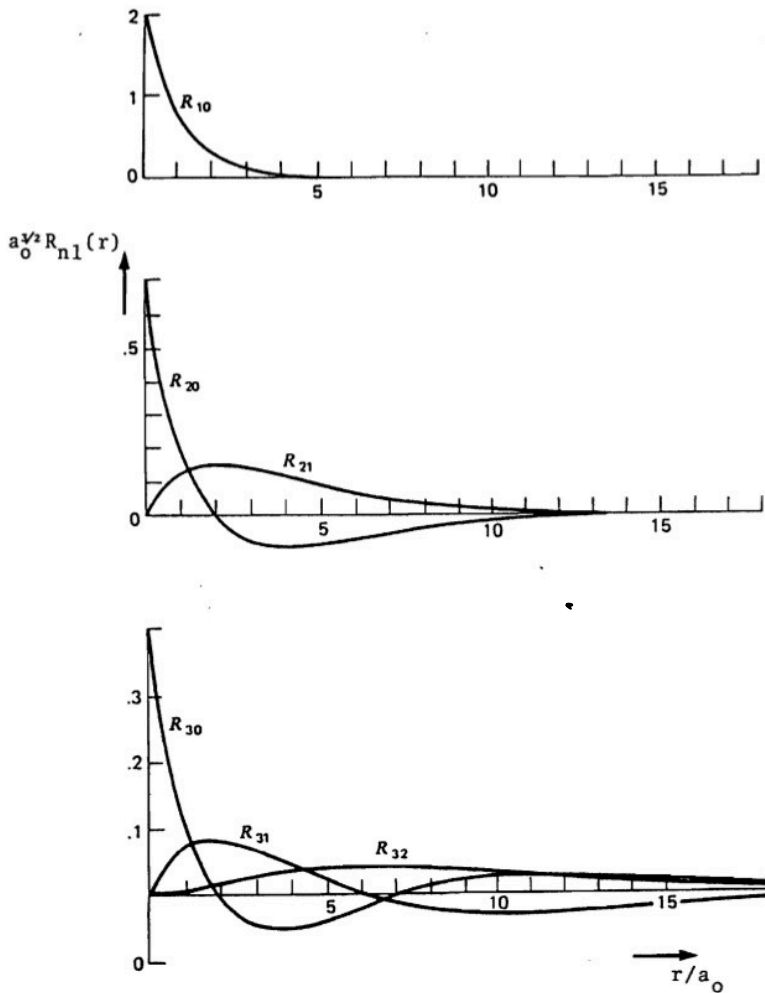
$$\textcircled{65} \quad = - \left(\frac{1}{64\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \underbrace{\sin\theta \cos\phi}_x$$

$$\begin{aligned}\psi_{2p_y} &= \frac{\psi_{211} + \psi_{21-1}}{2i} \\ &= - \left(\frac{1}{64\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \underbrace{\sin\theta \sin\varphi}_{-y} \quad \text{--- (66) } y\end{aligned}$$

Similar combinations are possible for d orbitals.

Note that the real orbitals are NOT eigenfunctions of $\hat{L}_z$ but continue to be eigenfunctions of $\hat{L}^2$.

Plots of the radial function



Source: MIT Open Courseware

Probability of finding the electron in a spherical shell of radius r and thickness dr :

$$\begin{aligned} &= \int_r^{r+dr} \int_{\Omega} |\psi(r)|^2 r'^2 dr' d\Omega \\ &= \int_{\Omega} P(r) r^2 dr \end{aligned}$$

In the ground (1s) state this

$$\propto e^{-2r/a_0} r^2 dr.$$

reaches a maximum when

$$\frac{d}{dr} (e^{-2r/a_0} r^2) = 0$$

$$\Rightarrow r_{\max} = \underline{\underline{a_0}}$$

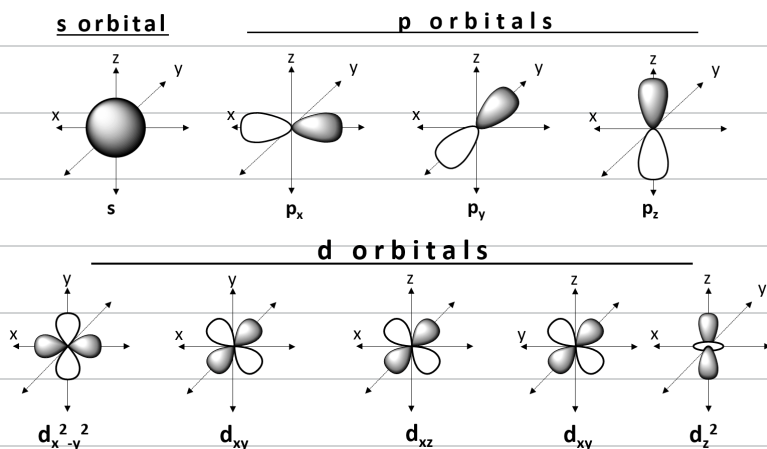
Hence, the Bohr radius has a physical meaning.

Plots of orbitals.

These are 3-d functions so hard to plot usually plotted as isosurfaces of density. That is an image shows the surface made by points $(\vec{r}, \psi)$ having the same density $|\psi|^2$.

A nice visualization of the orbitals can be found at [.. This Site](#)

A rough sketch of the spatial orientations of the orbitals are given below.



The shaded/unshaded regions denote that the wavefn. is positive/negative.

At the boundary of the shaded & unshaded regions (pts, lines, planes, etc) the wavefunction goes to zero yielding a node.

$$\Psi_{nlm}(r, \theta, \varphi) \sim R_{nl}(r) P_l^m(\cos\theta) e^{im\varphi}$$

$$r^l L_{n-l-1}^{2l+1}(2\kappa r)$$

↓
degree $n-l-1$



$n-l-1$ radial nodes

$$\sim (1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l$$

↑
degree m

$\frac{d^{l+m}}{dx^{l+m}}$

degree $l-m$

degree l



l angular nodes