\[ \hat{L} = \hat{r} \times \hat{p} \text{ (Right Hand Rule)} \]
Classically, direction & Magnitude of \( \hat{L} \) always well defined

QM: Can/Does \( \hat{L} \) have a definite direction? Proof by Negation:
Suppose \( \hat{L} \) was precisely known/defined (\( \hat{L} \parallel \hat{z} \))
Since \( \hat{L} = \hat{r} \times \hat{p} \Rightarrow \) Electron MUST be in x-y orbit plane

\[ \Rightarrow \Delta z = 0 ; \Delta p_z \Delta z - h \Rightarrow \Delta p_z - \infty ; E = \frac{p_z^2}{2m} - \infty \] !!

So, in Hydrogen atom, \( \hat{L} \) can not have precise measurable value
Uncertainty Principle & Angular Momentum : \( \Delta L, \Delta \phi - h \)
Consider $\ell = 2$

$|L| = \sqrt{l(l+1)} = \sqrt{6}\hbar$

In Hydrogen atom, $\vec{L}$ cannot have precise measurable value
Arbitrarily picking $Z$ axis as a reference direction:
$\vec{L}$ vector spins around $Z$ axis (precesses).
The $Z$ component of $\vec{L}$: $L_z = m_l\hbar; \ m_l = \pm 1, \pm 2, \pm 3 \ldots \pm \ell$

Note: since $|L_z| < |L|$ (always)
since $m_l \hbar < \sqrt{(l+1)} \ h$ It can never be that $|L_z| = m_l\hbar = \sqrt{(l+1)} \ h$
(breaks Uncertainty Principle)

So.....the Electron's dance has begun!

$L=2, m_l=0, \pm 1, \pm 2$ ; Pictorially

Electron “sweeps”
Conical paths of different $\vartheta$

$\cos \vartheta = \frac{L_z}{L}$

On average, the angular momentum
Component in x and y cancel out

$<L_x> = 0$
$<L_y> = 0$
Where is it likely to be? \( \rightarrow \) Radial Probability Densities

\[
\Psi(r, \theta, \phi) = R_n(r) \cdot \Theta_m(\theta) \cdot \Phi_n(\phi) = R_n Y_l^m
\]

Probability Density Function in 3D:

\[
P(r, \theta, \phi) = \Psi^* \Psi = |R_n|^2 \cdot |Y_l^m|^2
\]

Note: 3D Volume element \( dV = r^2 \sin \theta \, dr \, d\theta \, d\phi \)

Prob. of finding particle in a tiny volume \( dV \) is

\[
P.dV = |R_n|^2 \cdot |Y_l^m|^2 \cdot r^2 \sin \theta \, dr \, d\theta \, d\phi
\]

The Radial part of Prob. distribution: \( P(r)dr \)

\[
P(r)dr = |R_n|^2 \cdot r^2 \, dr \int_0^\theta \Theta_m(\theta)^2 \, d\theta \int_0^{2\pi} \Phi_n(\phi)^2 \, d\phi
\]

When \( \Theta_m(\theta) \) & \( \Phi_n(\phi) \) are auto-normalized then

\[
P(r)dr = |R_n|^2 \cdot r^2 \, dr, \text{ in other words } P(r) = r^2 |R_n|^2
\]

Normalization Condition:

\[
1 = \int_0^\infty r^2 |R_n|^2 \, dr
\]

Expectation Values

\[
<f(r)> = \int_r^\infty f(r) \cdot P(r) \, dr
\]

Ground State: Radial Probability Density

\[
P(r)dr = |\Psi(r)|^2 \cdot 4\pi r^2 \, dr
\]

\[
\Rightarrow P(r)dr = \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}}
\]

Probability of finding Electron for \( r > a_0 \)

\[
P_{r > a_0} = \int_{a_0}^\infty \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}} \, dr
\]

To solve, employ change of variable

Define \( z = \frac{2r}{a_0} \); change limits of integration

\[
P_{r > a_0} = \frac{1}{2} \int_z^\infty z^2 e^{-z} \, dz \quad \text{ (such integrals called Error. Fn)}
\]

\[
= \frac{1}{2} [z^2 + 2z + 2] e^{-z} \bigg|_0^\infty = 5e^2 = 0.667 \Rightarrow 66.7\% \]

!!

3
Most Probable & Average Distance of Electron from Nucleus

Most Probable Distance:

In the ground state \((n=1, l=0, m_l=0)\):

\[ P(r) = \frac{4}{a_0^3} r^2 e^{-r/a_0} \]

Most probable distance \(r\) from Nucleus \(\Rightarrow\) What value of \(r\) is \(P(r)\) max?

\[
\frac{dP}{dr} = 0 \Rightarrow \frac{4}{a_0^3} \left[ \frac{d}{dr} r^2 e^{-r/a_0} \right] = 0 \Rightarrow \left[ -2r^2/a_0 + 2r \right] e^{-r/a_0} = 0
\]

\[
2r/a_0 + 2r = 0 \Rightarrow r = 0 \text{ or } r = a_0
\]

Which solution is correct?

(see past quiz): Can the electron BE at the center of Nucleus \((r=0)\)?

\[ P(r=0) = \frac{4}{a_0^3} 0^2 e^{-0/a_0} = 0 ! \Rightarrow \text{Most Probable distance } r = a_0 \] (Bohr guessed right)

What about the AVERAGE location \(<r>\) of the electron in Ground state?

\[
<r> = \int_0^\infty r P(r)dr = \frac{4}{a_0^3} \int_0^\infty r^2 e^{-r/a_0} dr \ldots \text{change of variable } z = \frac{2r}{a_0}
\]

\[
<r> = \frac{a_0^4}{4} \int_0^{2a_0} z^2 e^{-z/2} dz \ldots \text{Use general form } \int_0^a z^n e^{-z} dz = n! \frac{\Gamma(n+1)}{a^{n+1}}
\]

\[
<r> = \frac{a_0^4}{4} \frac{3a_0^2}{2} = \frac{3a_0^2}{2} \Rightarrow \text{Average & most likely distance is not same. Why?}
\]

Answer is in the form of the radial Prob. Density: Not symmetric

---

Radial Probability Distribution \(P(r) = r^2 R(r)\)

<table>
<thead>
<tr>
<th>(n)</th>
<th>(l)</th>
<th>(R_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>(\frac{2}{a_0^3} e^{-r/a_0})</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>(\frac{4}{3a_0^3} e^{-r/a_0})</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>(\frac{4}{3a_0^3} e^{-r/a_0})</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>(\frac{8}{15a_0^3} e^{-r/a_0})</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>(\frac{8}{15a_0^3} e^{-r/a_0})</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>(\frac{8}{15a_0^3} e^{-r/a_0})</td>
</tr>
</tbody>
</table>

Because \(P(r) = r^2 R(r)\)

No matter what \(R(r)\) is for some \(n\)

The prob. of finding electron inside nucleus \(=0\)
Normalized Spherical Harmonics & Structure in H Atom

### Table 7-1 Spherical harmonics

<table>
<thead>
<tr>
<th>l = 0</th>
<th>m = 0</th>
<th>( Y_{00} = \frac{1}{\sqrt{4\pi}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>l = 1</td>
<td>m = 1</td>
<td>( Y_{11} = -\frac{\sqrt{3}}{8\pi} \sin \theta \cos \phi )</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>( Y_{10} = \frac{3}{4\pi} \cos \theta )</td>
</tr>
<tr>
<td></td>
<td>m = -1</td>
<td>( Y_{1-1} = \frac{3}{8\pi} \sin \theta \cos \phi )</td>
</tr>
<tr>
<td>l = 2</td>
<td>m = 2</td>
<td>( Y_{22} = \frac{15}{32\pi} \sin^3 \theta )</td>
</tr>
<tr>
<td></td>
<td>m = 1</td>
<td>( Y_{21} = -\frac{15}{8\pi} \sin \theta \cos \phi )</td>
</tr>
<tr>
<td></td>
<td>m = 0</td>
<td>( Y_{20} = \frac{5}{16\pi} (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td></td>
<td>m = -1</td>
<td>( Y_{2-1} = \frac{15}{8\pi} \sin \theta \cos \phi )</td>
</tr>
<tr>
<td></td>
<td>m = -2</td>
<td>( Y_{2-2} = \frac{15}{32\pi} \sin^3 \theta )</td>
</tr>
</tbody>
</table>

Features of Wavefunction in \( \theta \) & \( \phi \):

Consider \( n = 2, \ l = 0 \Rightarrow \psi_{20} = \) Spherically Symmetric (last slide)

Excited States (3 & each with same \( E_n \)):

\( \psi_{21}, \psi_{01}, \psi_{01} \) are all 2p states

\[ \psi_{21} = R_2 Y_{21} = \frac{1}{\sqrt{8\pi}} \left( \frac{2}{a_0} \right)^{\frac{3}{2}} \left( \frac{r}{a_0} \right)^{-\frac{1}{2}} \sin \theta \cos \phi \]

\[ |\psi_{21}|^2 = |\psi_{01}|^2 = \sin^2 \theta \]

Max at \( \theta = \frac{\pi}{2} \), min at \( \theta = 0 \), Symm in \( \phi \)

What about (\( n=2, \ l=1, \ m=0 \)):

\[ \psi_{20} = R_2 \left( \frac{r}{a_0} \right)^{l} Y_l^m(\theta, \phi) \]

\[ Y_l^m(\theta, \phi) = \frac{1}{\sqrt{\pi}} \sum_{m_l} \sqrt{\frac{(2l+1)!}{(l-m)!}} \cos^m \theta \]

Function is max at \( \theta = 0 \), min at \( \theta = \frac{\pi}{2} \)

We call this 2p state because of its extent in \( z \)

---

Excited States (\( n>1 \)) of Hydrogen Atom: Birth of Chemistry!

Features of Wavefunction in \( \theta \) & \( \phi \):

Consider \( n = 2, \ l = 0 \Rightarrow \psi_{20} = \) Spherically Symmetric (last slide)

Excited States (3 & each with same \( E_n \)):

\( \psi_{21}, \psi_{01}, \psi_{01} \) are all 2p states

\( \psi_{21} = R_2 Y_{21} = \frac{1}{\sqrt{8\pi}} \left( \frac{2}{a_0} \right)^{\frac{3}{2}} \left( \frac{r}{a_0} \right)^{-\frac{1}{2}} \sin \theta \cos \phi \)

\( |\psi_{21}|^2 = |\psi_{01}|^2 = \sin^2 \theta \)

Max at \( \theta = \frac{\pi}{2} \), min at \( \theta = 0 \), Symm in \( \phi \)

What about (\( n=2, \ l=1, \ m=0 \)):

\( \psi_{20} = R_2 \left( \frac{r}{a_0} \right)^{l} Y_l^m(\theta, \phi) \)

\( Y_l^m(\theta, \phi) = \frac{1}{\sqrt{\pi}} \sum_{m_l} \sqrt{\frac{(2l+1)!}{(l-m)!}} \cos^m \theta \)

Function is max at \( \theta = 0 \), min at \( \theta = \frac{\pi}{2} \)

We call this 2p state because of its extent in \( z \)
Excited States (n>1) of Hydrogen Atom: Birth of Chemistry!

Remember Principle of Linear Superposition for the TISE which is basically a simple differential equation:

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + U \psi = E \psi \]

Principle of Linear Superposition \( \Rightarrow \) If \( \psi_1 \) and \( \psi_2 \) are sol. of TISE then a "designer" wave function made of linear sum

\[ \psi = a \psi_1 + b \psi_2 \]

is also a sol. of the diff. equation!

To check this, just substitute \( \psi \) in place of \( \psi \) & convince yourself that

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + U \psi = E \psi \]

The diversity in Chemistry and Biology DEPENDS on this superposition rule.

Designer Wave Functions: Solutions of S. Eq!

Linear Superposition Principle means allows me to "cook up" wave functions

\[ \psi_{2p_x} = \frac{1}{\sqrt{2}} [\psi_{211} + \psi_{211-1}] \]......has electron "cloud" oriented along x axis

\[ \psi_{2p_y} = \frac{1}{\sqrt{2}} [\psi_{211} - \psi_{211-1}] \]......has electron "cloud" oriented along y axis

So from 4 solutions \( \psi_{200}, \psi_{210}, \psi_{211}, \psi_{211-1} \) \( \rightarrow 2s, 2p_x, 2p_y, 2p_z \)

Similarly for n=3 states ...and so on ...can get very complicated structure in \( \theta \) & \( \phi \)......which I can then mix & match to make electrons "most likely" to be where I want them to be!
Designer Wave Functions: Solutions of S. Eq

\begin{align*}
\frac{d^2 \Phi}{d\phi^2} + \frac{m_e^2}{\hbar^2} \Phi &= 0, \quad (1) \\
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) \Phi + \left[ \frac{l(l+1) - \frac{m_e^2}{\sin^2 \theta}}{\sin^2 \theta} \right] \Phi(\theta) &= 0, \quad (2) \\
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \Phi + \left[ \frac{2m_e^2}{\hbar^2} \left( E + \frac{k^2}{2m_e} \right) - \frac{l(l+1)}{r^2} \right] \Phi(r) &= 0, \quad (3)
\end{align*}

These 3 "simple" diff. eqns describe the physics of the Hydrogen atom.

The hydrogen atom brought to you by the letters

\begin{align*}
&n = 1, 2, 3, 4, 5, \ldots, \infty \\
&l = 0, 1, 2, 3, 4, \ldots (n-1) \\
&m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l
\end{align*}

The Spatial Wave Function of the Hydrogen Atom

\[ \Psi(r, \theta, \phi) = R_n(r) \cdot \Theta_{m_l}(\theta) \cdot \Phi_{m_l}(\phi) = R_n Y_{m_l}^m \] (Spherical Harmonics)
Cross Sectional View of Hydrogen Atom prob. densities in r,θ,φ
Birth of Chemistry (Can make Fancy Bonds→ Overlapping electron “clouds”)

What’s the electron “cloud” : Its the Probability Density in r,θ,φ space!

What’s So “Magnetic” ?

Precessing electron→ Current in loop → Magnetic Dipole moment µ

The electron’s motion ⇒ hydrogen atom is a dipole magnet
The “Magnetism” of an Orbiting Electron

Precessing electron → Current in loop → Magnetic Dipole moment $\mu$

Electron in motion around nucleus ⇒ circulating charge ⇒ current $i$

$$i = \frac{-e}{T} = \frac{-e}{2\pi r} = \frac{-ep}{2\pi mr}; \quad \text{Area of current loop } A = \pi r^2$$

Magnetic Moment $|\mu| = iA = \left(\frac{-e}{2m}\right)ip; \quad \mu = \left(\frac{-e}{2m}\right)i \times \vec{p} = \left(\frac{-e}{2m}\right)\vec{L}$

Like the $\vec{L}$, magnetic moment $\mu$ also precesses about "$z"$ axis

$z$ component, $\mu_z = \left(\frac{-e}{2m}\right)L_z = \left(\frac{-eh}{2m}\right)m_i = -\mu_y m_i = \text{quantized!}$

Quantized Magnetic Moment

$$\mu_z = \left(\frac{-e}{2m}\right)L_z = \left(\frac{-eh}{2m}\right)m_i = -\mu_y m_i$$

$\mu_y = \text{Bohr Magnetron} = \left(\frac{eh}{2m}\right)$

Why all this? Need to find a way to break the Energy Degeneracy & get electron in each $(n,l,m_i)$ state to identify itself, so we can "talk" to it and make it do our bidding: "Walk this way, talk this way!"
“Lifting” Degeneracy: Magnetic Moment in External B Field

Apply an External B field on a Hydrogen atom (viewed as a dipole)
Consider $\mathbf{B} \parallel \mathbf{Z}$ axis (could be any other direction too)
The dipole moment of the Hydrogen atom (due to electron orbit) experiences a Torque $\tau = \mathbf{\mu} \times \mathbf{B}$ which does work to align $\mathbf{\mu} \parallel \mathbf{B}$
but this can not be (same Uncertainty principle argument)

$\Rightarrow$ So, Instead, $\mathbf{\mu}$ precesses (dances) around $\mathbf{B}$... like a spinning top
The Azimuthal angle $\phi$ changes with time: calculate frequency

Look at Geometry: projection along x-y plane: $|d\mathbf{L}| = L\sin \theta \ d\phi$

$\Rightarrow d\phi = \frac{|d\mathbf{L}|}{L \sin \theta}$: Change in Ang. Mom. $|d\mathbf{L}| = \tau \ |dt| = \frac{qLB \sin \theta}{2m}$

$\Rightarrow \omega = \frac{d\phi}{dt} = \frac{1}{L \sin \theta} \frac{|d\mathbf{L}|}{dt} = \frac{1}{L \sin \theta} \frac{q}{2m} LB \sin \theta = \frac{qB}{2m}$ Larmor Freq

$\omega$ depends on B, the applied external magnetic field

“Lifting” Degeneracy: Magnetic Moment in External B Field

WORK done to reorient $\mathbf{\mu}$ against $\mathbf{B}$ field: $dW = \tau d\theta - \mu B \sin \theta d\theta$

$dW = d(\mu B \cos \theta)$: This work is stored as orientational Pot. Energy U

$dW = -dU$

Define Magnetic Potential Energy $U = -\mathbf{\mu} \cdot \mathbf{B} = -\mathbf{\mu} \cdot B \cos \theta = -\mathbf{\mu} \cdot B$

Change in Potential Energy $U = \frac{\epsilon h}{2m} \mu \cdot B = \hbar \omega_m m$

Zeeman Effect in Hydrogen Atom

In presence of External B Field, Total energy of H atom changes to

$$E = E_0 + \hbar \omega_m m$$

So the Ext. B field can break the E degeneracy "organically" inherent
in the H atom. The Energy now depends not just on $n$ but also $m$,
**Zeeman Effect Due to Presence of External B field**

Energy Degeneracy Is Broken

- **n = 2, \( \ell = 1 \)**
  - No magnetic field
  - Magnetic field present
  - Magnetic field present

- **n = 1, \( \ell = 0 \)**
  - \( m_\ell = 0 \)

**Electron has “Spin”: An additional degree of freedom**

- **Spin up**: \( s = +1/2 \)
- **Spin Down**: \( s = -1/2 \)

**Spin** is an additional degree of freedom just like \( r \), \( \theta \) and \( \phi \)

Quantum number corresponding to spin orientations: \( m_s = \pm \frac{1}{2} \)

Spinning object of charge Q can be thought of a collection of elemental charges \( \Delta q \) and mass \( \Delta m \) rotating in circular orbits.

So Spin \( \rightarrow \) Spin Magnetic Moment \( \rightarrow \) interacts with B field
Four (not 3) Numbers Describe Hydrogen Atom \(\rightarrow n, l, m_p, m_s\)

"Spinning" charge gives rise to a dipole moment \(\mu\):

Imagine (semi-classically, incorrectly) electron as sphere; charge \(q\), radius \(r\)
Total charge uniformly distributed: \(q = \sum \Delta q_i\);
as electron spins, each "chargelet" rotates \(\Rightarrow\) current \(\Rightarrow\) dipole moment \(\vec{\mu}_i\),

\[
\vec{\mu}_i = \frac{q}{2m} \sum \vec{\beta}_i = \frac{q}{2m} \vec{S}
\]

In a Magnetic Field \(\vec{B}\) \(\Rightarrow\) magnetic energy due to spin \(\vec{U}_s = \vec{\mu}_s \cdot B\)

Net Angular Momentum in H Atom \(\vec{J} = \vec{L} + \vec{S}\)

Net Magnetic Moment of H atom: \(\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = \frac{\mu_0}{2m} (\vec{L} + g \vec{S})\)

Notice that the net dipole moment vector \(\vec{\mu}\) is not \(\parallel\) to \(\vec{J}\)

(There are many such "ubiquitous" quantum numbers for elementary particle but we won't teach you about them in this course !)
Doubling of Energy Levels Due to Spin Quantum Number

Under intense B field, each \( n, m_\ell \) energy level splits into two depending on spin up or down.

**IN PRESENCE OF EXTERNAL B FIELD**

\[
\begin{align*}
\text{Without spin} & \quad \text{With spin} \\
n = 2, m_\ell = \{\pm 1, 0, \pm 1\} & \quad \{m_\ell = 1, m_s = 1/2, m_\ell = 0, m_s = 1/2, m_\ell = 0, m_s = -1/2, m_\ell = -1, m_s = -1/2\}
\end{align*}
\]

\[
\begin{align*}
n = 1, m_\ell = 0 & \quad l = 1 \\
\omega_L - \omega_L + \omega_L & \quad -3\omega_L + 3\omega_L
\end{align*}
\]

**Spectrum without spin** \( \omega_L, \omega_L \)**Spectrum with spin** \( -\omega_L, +\omega_L, -3\omega_L, +3\omega_L \)

Spin-Orbit Interaction: Angular Momenta are Linked Magnetically

Electron revolving around Nucleus finds itself in a "internal" B field because in its frame of reference, the nucleus is orbiting around it.

This B field, due to orbital motion, interacts with electron's spin dipole moment \( \vec{\mu} \).

\[
U_m = -\mu \cdot \vec{B} \Rightarrow \text{Energy larger when } \vec{S} \parallel \vec{B}, \text{ smaller when anti-parallel}
\]

\( \Rightarrow \) States with same \( n, l, m_l \) but diff. spins \( \Rightarrow \) energy level splitting/doubling due to \( \vec{S} \)

\[
\Delta U = 2\mu B
\]

**UNDER NO EXTERNAL B FIELD THERE IS STILL A SPLITTING!**

Sodium Doublet & LS coupling
Neither Orbital nor Spin angular Momentum are conserved separately!

\[ J = L + S \] is conserved so long as there are no external torques present

Rules for Total Angular Momentum Quantization:

\[ \sqrt{j(j+1)} \hbar \quad \text{with} \quad j = |l + s|, \quad l + s - 1, \quad l + s - 2, \ldots, \quad |l - s| \]
\[ m_l = m \hbar \quad \text{with} \quad m = j, \quad j - 1, \quad j - 2, \ldots, \quad -j \]

Example: State with \((l = 1, s = \frac{1}{2})\)

\[ j = 3/2 \Rightarrow m_l = \pm 3/2, \pm 1/2, 1/2, 3/2 \]
\[ j = 1/2 \Rightarrow m_l = \pm 1/2 \]

In general, \(m_l\) takes \(2j + 1\) values

\( \Rightarrow \) Even \# of orientations

Spectrographic Notation: Final Label

---

Complete Description of Hydrogen Atom

Full description of the Hydrogen atom:
\[ \{n, l, m_l, m_s\} \]

\( \downarrow \)

LS Coupling

\( \downarrow \)

\[ \{n, l, j, m_j\} \]

corresponding to 4 D.O.F.

How to describe multi-electrons atoms like He, Li etc?

How to order the Periodic table?

- Four guiding principles:
  - Indistinguishable particle & Pauli Exclusion Principle
  - Independent particle model (ignore inter-electron repulsion)
  - Minimum Energy Principle for atom
  - Hund’s “rule” for order of filling vacant orbitals in an atom
Multi-Electron Atoms: >1 electron in orbit around Nucleus

In Hydrogen Atom \( \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) = \{ n, l, j, m \} \)

In n-electron atom, to simplify, ignore electron-electron interactions complete wavefunction, in "independent"particle approx":

\[ \psi(1,2,3,...n) = \psi(1) \psi(2) \psi(3) ... \psi(n) \quad ?? \]

Complication \( \rightarrow \) Electrons are identical particles, labeling meaningless!

Question: How many electrons can have same set of quantum #s?

Answer: No two electrons in an atom can have SAME set of quantum #s (if not, all electrons would occupy 1s state (least energy)... no structure!!

Example of Indistinguishability: electron-electron scattering

If we cant follow electron path, don't know between which of the two scattering Event actually happened

Helium Atom: Two electrons around a Nucleus

In Helium, each electron has: kinetic energy + electrostatic potential energy

If electron "1" is located at \( r_1 \) & electron "2" is located at \( r_2 \) then TISE has terms like:

\[ H = \frac{\hbar^2}{2m} \psi_1'' + \frac{\hbar^2}{2m} \psi_2'' + \frac{2Ze^2}{r_{12}} \quad \text{such that} \]

\[ \frac{\partial}{\partial r_{12}} \{ \psi_1 \psi_2 \} H_1 \text{ & } H_2 \text{ are zero except for "false"} \]

Independent Particle Approx \( \rightarrow \) ignore repulsive \( U = \frac{e^4}{r_{12}} \) term in \( H \)

Helium Wavefunction: \( \psi = \psi_1(\text{r}_1, \text{r}_2) \quad \text{Probability} \ P = \psi^* \psi_1(\text{r}_1, \text{r}_2) \)

That if we exchange location of (identical, indistinguishable) electrons \( \rightarrow \) \( \psi_1(\text{r}_1, \text{r}_2) = \psi_1(\text{r}_2, \text{r}_1) \)

In general, when \( \psi_1(\text{r}_1, \text{r}_2) = \psi_1(\text{r}_2, \text{r}_1) \quad \text{Bosonic system (made of photons, e.g.)} \)

when \( \psi_1(\text{r}_1, \text{r}_2) \neq \psi_1(\text{r}_2, \text{r}_1) \quad \text{Fermionic system (made of electron, proton e.g.)} \)

\( \Rightarrow \) Helium wavefunction must be CARTER if electron "1" is in state a & electron "2" is in state b

Then the net wavefunction \( \psi_{n_1n_2}\text{r}_1(\text{r}_2) \psi_1(\text{r}_1, \text{r}_2) \) satisfies

\[ H \psi_{n_1n_2}\text{r}_1(\text{r}_2) \psi_1(\text{r}_1, \text{r}_2) = \text{E} \psi_{n_1n_2}\text{r}_1(\text{r}_2) \psi_1(\text{r}_1, \text{r}_2) \]

\[ H \psi_{n_1n_2}\text{r}_2(\text{r}_1) \psi_1(\text{r}_1, \text{r}_2) = \text{E} \psi_{n_1n_2}\text{r}_2(\text{r}_1) \psi_1(\text{r}_1, \text{r}_2) \]

and the sum

\[ \{ H + \text{E} \} \psi_{n_1n_2}\text{r}_1(\text{r}_2) \psi_1(\text{r}_1, \text{r}_2) = \text{E} \psi_{n_1n_2}\text{r}_1(\text{r}_2) \psi_1(\text{r}_1, \text{r}_2) \]

Total Helium Energy \( E \geq E_n + E_\text{c} \quad \text{sum of Hydrogen atom like E} \)
Energy capacity limited due to Pauli Exclusion principle

Shell is made of sub-shells:
1. Shell & subshell
2. Subshell ( ... inner shell electrons very small binding energy of "valence" electron large orbital radius of valence electron"

General Principles for Atomic Structure for n-electron system:

5. n-electron system is stable when its total energy is minimum

Only one electron can exist in a particular quantum state in an atom... not 2 or more!

1. Shells & SubShells in Atomic Structure
(a) ignore inter-electron repulsion (crude approx.)
(b) think of each electron in a common "effective" mean Electric field
(c) Effective field: "Sears" Nuclear charge (+Ze) reduced by partial screening due to other electrons
   "buzzing" closer (in r) to Nucleus

Electrons in a SHELL: have same n, are at similar <r> from nucleus, have similar energies
Electrons in a SubShell: have same principal quantum number n
- Energy depends on: those with lower l closer to nucleus, more tightly bound
- all electrons in sub-shell have same energy, with minor dependence on m_l

shell & subshell energies & capacity

1. Shell & subshell capacity limited due to Pauli Exclusion principle
2. Shell is made of sub-shells for same principal quantum number n
3. Subshell \( = (n,l) \), given \( n \Rightarrow l = 0,1,2,3, \ldots (n-1) \),
   
   for any \( l \Rightarrow m_l = 0, \pm 1, \pm 2, \ldots \pm l \), \( l+1 \), \( \frac{l}{2} \)
   
   \( \Rightarrow \) Max. # of electrons in a shell = \( \sum \) subshell capacity

4. The "K" Shell \( (n=1) \) holds 2 electrons, "L" Shell \( (n=2) \) holds 8 electrons,
   "M" shell \( (n=3) \) holds 18 electrons... 

5. Shell is closed when fully occupied
6. Sub-Shell closed when
   (a) \( \sum l \cdot m_l = 0 \Rightarrow \) 6, hence charge distribution symmetric
   (b) Electrons are tightly bound since they "see" large nuclear charge
7. Because \( \sum l \cdot m_l = 0 \Rightarrow \) No dense quantum = No ability to attract electrons

8. Hydrogen gas
9. Alkali/Alkaline earth: have a single "p" electron in outer orbit
   (a) Large electron, narrow orbit, strongly held by ion core
   (b) Large orbital radius of valence electron
   (c) Very small binding energy of "valence" electron
Electronic Configurations of n successive elements from Lithium to Neon

Hund’s Rule: Whenever possible
- electron in a sub-shell remain unpaired
- States with spins parallel occupied first
- Because electrons repel when close together
- \( \Rightarrow \) electrons in same sub-shell \((l)\) and same spin
  - Must have diff. \( m_l \)
  - (very diff. angular distribution)
- Electrons with parallel spin are further apart
  - Than when anti-parallel \( \Rightarrow \) lesser E state
  - Get filled first

That’s all I can teach you this quarter; Rest is all Chemistry!