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Physics 2D Lecture Slides
Lecture 29: Mar 10th

Vivek Sharma
UCSD Physics
The hydrogen atom brought to you by the letters

\[ n = 1, 2, 3, 4, 5, \ldots, \infty \]
\[ l = 0, 1, 2, 3, 4, \ldots, (n-1) \]
\[ m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l \]

The Spatial Wave Function of the Hydrogen Atom

\[ \Psi(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{m_l}(\theta) \cdot \Phi_{m_l}(\phi) = R_{nl} Y_{lm}^m \] (Spherical Harmonics)

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

Cross Sectional View of Hydrogen Atom prob. densities in r,θ,φ

Birth of Chemistry (Can make Fancy Bonds \( \rightarrow \) Overlapping electron “clouds”)

What’s the electron “cloud”: It’s the Probability Density in r, θ,φ space!
Angular Momentum of the electron $\vec{L} = \vec{r} \times \vec{p}$ (Right Hand Rule)

Classically, direction & Magnitude of $\vec{L}$ always well defined

QM: Can/Does $\vec{L}$ have a definite direction? Proof by Negation:

Suppose $\vec{L}$ was precisely known/defined ...say $(\vec{L} \parallel \hat{z})$

Since $\vec{L} = \vec{r} \times \vec{p}$ ⇒ Electron MUST be PRECISELY in the x-y plane

$\Rightarrow \Delta z = 0 \ ; \ \Delta p_z \Delta z \sim h \Rightarrow \Delta p_z \sim \infty \ ; \ KE_z = \frac{p_z^2}{2m} \sim \infty \ \text{!!!}$

$\Rightarrow$ breaks the Hydrogen bound state.....

So, in the bound Hydrogen atom, $\vec{L}$ can not have precise measurable value

Uncertainty Principle & Angular Momentum $\Rightarrow \Delta L_z \Delta \phi \sim h$

---

In Hydrogen atom, $\vec{L}$ can not have precise measurable value

Arbitrarily picking Z axis as a reference direction:

$\vec{L}$ vector spins around Z axis (precesses).

The Z component of $\vec{L}$: $|L_z| = m_l \hbar; \quad m_l = \pm 1, \pm 2, \pm 3 \ldots \pm \ell$

Note: since $|L_z| < |L|$ (always)

since $m_l \hbar < \sqrt{l(l+1)} \hbar$ It can never be that $|L_z| = m_l \hbar = \sqrt{l(l+1)} \hbar$

(breaks Uncertainty Principle)

So......the Electron's dance has begun!
L=2, m_l=0,±1,±2 : Pictorially

\[ L = \hbar \sqrt{l(l+1)} = \hbar \sqrt{2(2+1)} = \hbar \sqrt{6} \]

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

\[ \Psi(r, \theta, \phi) = R_m(r) \cdot \Theta_{m_l}(\theta) \cdot \Phi_{m_l}(\phi) = R_m \cdot Y_{l_m}^{m_l} \]

Probability Density Function in 3D:

\[ P(r, \theta, \phi) = \Psi^* \Psi = |\Psi(r, \theta, \phi)|^2 = |R_m|^2 \cdot |Y_{l_m}^{m_l}|^2 \]

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

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

\[ P \cdot dV = |R_m|^2 \cdot |Y_{l_m}^{m_l}|^2 \cdot r^2 \sin \theta \cdot dr \cdot d\theta \cdot d\phi \]

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

\[ P(r)dr = |R_m|^2 \cdot r^2 dr \int_0^\pi |\Theta_{m_l}(\theta)|^2 d\theta \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2 d\phi \]

When \( \Theta_{m_l}(\theta) \) & \( \Phi_{m_l}(\phi) \) are auto-normalized then

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

Normalization Condition:

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

Expectation Values

\[ <f(r)> = \int_0^\infty f(r) \cdot P(r)dr \]
To solve, employ change of variable

\[ P(r)dr = |\psi(r)|^2 A\pi r^2 dr \]

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

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

\[ P_{r > a_0} = \frac{4}{a_0^3} \int_0^\infty r^2 e^{-\frac{2r}{a_0}} dr \]

To solve, employ change of variable

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

\[ P_{r = a_0} = \frac{1}{2} \int_0^\infty z^2 e^{-z} dz \quad \text{(such integrals called Error. Fn)} \]

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

Most Probable Distance

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

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

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

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

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

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

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

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

\[ <r> = \int_0^\infty r P(r)dr = \frac{4}{a_0^3} \int_0^\infty r r^2 e^{-\frac{2r}{a_0}} dr \]

...change of variable \( z = \frac{2r}{a_0} \)

\[ \Rightarrow <r> = \frac{a_0}{4} \int_0^\infty z^2 e^{-z} dz \]

Use general form \( \int_0^\infty z^2 e^{-z} dz = n! = n(n-1)(n-2) \ldots (1) \)

\[ \Rightarrow <r> = \frac{a_0}{4} 3! = \frac{3a_0}{2} \neq a_0 \]

Average & most likely distance is not same. Why?

Answer is in the form of the radial Prob. Density: Not symmetric
Radial Probability Distribution $P(r) = r^2 R(r)$

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

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

The probability of finding electron inside nucleus $= 0$

Normalized Spherical Harmonics & Structure in H Atom

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m$</th>
<th>$Y_l^m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$Y_0^0 = \sqrt{\frac{1}{4\pi}}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$Y_0^1 = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>$Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>$Y_0^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>$Y_0^2 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>$Y_{2,-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi}$</td>
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<td>2</td>
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</tr>
</tbody>
</table>
Excited States (n>1) of Hydrogen Atom: Birth of Chemistry!

Features of Wavefunction in $\theta$ & $\phi$:

Consider $n=2$, $l=0 \Rightarrow \psi_{200} =$ Spherically Symmetric (last slide)

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

$\psi_{211}, \psi_{210}, \psi_{21-}$ are all 2p states

$\psi_{211} = R_{21} Y_l^m = \frac{1}{\sqrt{8\pi}} \frac{Z}{a_0} \left( \frac{r}{a_0} \right) \frac{e^{-Z/r}}{\sin \theta \sin \phi}

\left| \psi_{211} \right|^2 = |\psi_{nl} \psi_{211}| = \sin^2 \theta \quad \text{Max at } \theta = \frac{\pi}{2}, \text{min at } \theta = 0; \text{ Symm in } \phi

What about $(n=2, \ell=1, m_z = 0)$

$\psi_{210} = R_{21}(r) Y_1^0(\theta, \phi)$:

$Y_1^0(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \cos \theta;

\text{Function is max at } \theta = 0, \text{ min at } \theta = \frac{\pi}{2}$

We call this 2p state because of its extent in $z$

---

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" wavefunction 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.
Linear Superposition Principle means allows me to "cook up" wavefunctions

\[
\psi_{2p_x} = \frac{1}{\sqrt{2}}[\psi_{211} + \psi_{21-1}] \quad \text{......has electron "cloud" oriented along x axis}
\]

\[
\psi_{2p_y} = \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}] \quad \text{......has electron "cloud" oriented along y axis}
\]

So from 4 solutions \(\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}\) \(\rightarrow 2s, 2p_x, 2p_y, 2p_z\)

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!
What's So “Magnetic”?

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

The electron’s motion $\Rightarrow$ hydrogen atom is a dipole magnet

The “Magnetism” of an Orbiting Electron

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

Electron in motion around nucleus $\Rightarrow$ circulating charge $\Rightarrow$ 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 $|\mu| = iA = \left(\frac{-e}{2m}\right)rp$; $\tilde{\mu} = \left(\frac{-e}{2m}\right)\tilde{r} \times \tilde{p} = \left(\frac{-e}{2m}\right)\tilde{L}$

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

$z$ component, $\mu_z = \left(\frac{-e}{2m}\right)L_z = \left(\frac{-eh}{2m}\right)m_j = -\mu \mu_j = \text{quantized}$!
Quantized Magnetic Moment

\[ \mu_z = \left( \frac{-e}{2m} \right) L_z = \left( \frac{-e\hbar}{2m} \right) m_l \]

\[ = -\mu_B m_l \]

\[ \mu_B = \text{Bohr Magnetron} \]

\[ = \left( \frac{e\hbar}{2m_e} \right) \]

Why all this? Need to find a way to break the Energy Degeneracy & get electron in each \((n,l,m_l)\) 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 \(\vec{B}\) field on a Hydrogen atom (viewed as a dipole)
Consider \(\vec{B} \parallel \vec{Z}\) axis (could be any other direction too)
The dipole moment of the Hydrogen atom (due to electron orbit) experiences a Torque \(\vec{\tau} = \vec{\mu} \times \vec{B}\) which does work to align \(\vec{\mu} \parallel \vec{B}\) but this can not be (same Uncertainty principle argument)
⇒ So, Instead, \(\vec{\mu}\) precesses (dances) around \(\vec{B}\)...like a spinning top
The Azimuthal angle \(\phi\) changes with time: calculate frequency
Look at Geometry: projection along x-y plane: \(|dL| = L \sin \theta \, d\phi\)

\[ d\phi = \frac{|dL|}{L \sin \theta} \]

⇒ Change in Ang Mom. \(|dL| = L \sin \theta \frac{d\phi}{dt} = L \sin \theta \frac{q LB \sin \theta}{2m} dt\)

\[ \omega_L = \frac{d\phi}{dt} = \frac{1}{L \sin \theta} \frac{|dL|}{L \sin \theta \frac{q LB \sin \theta}{2m}} \]

Larmor Freq \(\omega_L\) depends on \(B\), the applied external magnetic field
“Lifting” Degeneracy: Magnetic Moment in External B Field

WORK done to reorient \( \vec{\mu} \) against \( \vec{B} \) 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 \( U = -\mu B = -\mu \cos \theta \cdot B = -\mu_z B \)

Change in Potential Energy \( U = \frac{eh}{2m_e} m_t B = \hbar \omega \cdot m_i \)

Zeeman Effect in Hydrogen Atom

In presence of External B Field, Total energy of H atom changes to
\[
E = E_0 + \hbar \omega \cdot m_i
\]
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 \( m_i \)

Zeeman Effect Due to Presence of External B field

Energy Degeneracy Is Broken

\( n = 2, \ell = 1 \)

<table>
<thead>
<tr>
<th>No magnetic field</th>
<th>Magnetic field present</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_\ell = 1 )</td>
<td>( m_\ell = 0 )</td>
</tr>
<tr>
<td>( m_\ell = -1 )</td>
<td></td>
</tr>
</tbody>
</table>

\( \hbar \omega_0 \quad (\hbar \omega_0 - \hbar \omega_L) \quad (\hbar \omega_0 + \hbar \omega_L) \)

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

\( \omega_0 \quad (\omega_0 - \omega_L) \quad \omega_0 \quad (\omega_0 + \omega_L) \)

Spectrum without magnetic field

Spectrum with magnetic field present
Electron has “Spin”: An additional degree of freedom

Spin up
Even as the electron rotates around nucleus, it also “spins”
There are only two possible spin orientations:

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

“Spin” is an additional degree of freedom just
Like \( r, \theta \) and \( \varphi \)

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

Stern-Gerlach Expt: An additional degree of freedom: “Spin” for lack of a better name

In an inhomogeneous B field, experiment forces \( F \)
\( F = -\nabla U = -\nabla (-\mu B) \)
When gradient only along \( z \):
\[ \frac{\partial B}{\partial x} \neq 0, \frac{\partial B}{\partial x} = 0 \]
\( \mu = m \hat{\mu} \frac{\partial B}{\partial z} \) moves particle up or down
In addition to torque causing \( M_B \), moment to precess about B field direction

In an inhomogeneous field, magnetic moment \( \mu \) experiences a force \( F_z \) whose direction depends on
component of the net magnetic moment & inhomogeneity \( dB/dz \). Quantization means expect \((2n+1)\) deflections. For \( l=0 \), expect all electrons to arrive on the screen at the center (no deflection)
"Spinning" charge gives rise to a dipole moment \( \vec{\mu} \):

Imagine (semi-classically, incorrectly!) electron as sphere: charge \( q \), radius \( r \)

Total charge uniformly distributed: \( q = \sum_i \Delta q_i \);

as electron spins, each "chargelet" rotates \( \Rightarrow \) current \( \Rightarrow \) dipole moment \( \vec{\mu}_i \)

\[
\vec{\mu} = \frac{q}{2m_e} \sum_i \vec{\mu}_i = g \left( \frac{q}{2m_e} \right) \vec{S}
\]

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

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

Net Magnetic Moment of H atom:

\[
\vec{\mu} = \vec{\mu}_0 + \vec{\mu}_s = \left( \frac{-e}{2m_e} \right) \vec{S} \left( \mathbf{L} + g \vec{S} \right)
\]

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**

**Without spin**

\( n = 2, m_\ell = \{ +1, 0, -1 \} \)

\( l = 1 \)

\( m_\ell = 1, m_s = 1/2 \)
\( m_\ell = 0, m_s = 1/2 \)
\( m_\ell = \pm 1, m_s = \mp 1/2 \)

\( m_\ell = 0, m_s = -1/2 \)
\( m_\ell = 0, m_s = -1/2 \)

**With spin**

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

\( l = 0 \)

\( m_\ell = 0, m_s = 1/2 \)
\( m_\ell = 0, m_s = -1/2 \)

**Spectrum without spin**

\( \omega_{2,1} \)

\( \omega_{1,1} \)

**Spectrum with spin**

\( -3\omega \pm 3\omega \)

\( \omega_{2,1} \)
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 \( \vec{\mu} \),

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

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

UNDER NO EXTERNAL B FIELD THERE IS STILL A SPLITTING!

Vector Model For Total Angular Momentum \( \mathbf{J} \)

Neither Orbital nor Spin angular Momentum are conserved separately!

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

Rules for Total Angular Momentum Quantization:

\[ |J| = \sqrt{j(j+1)} \hbar \text{ with } j = |l+s|, l+s-1, l+s-2..., |l-s| \]

\[ J_z = m_j \hbar \text{ with } m_j = j, j-1, j-2,..., -j \]

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

\[ j = 3/2 \Rightarrow m_j = -3/2, -1/2, 1/2, 3/2 \]

\[ j = 1/2 \Rightarrow m_j = \pm 1/2 \]

In general \( m_j \) takes \((2j+1)\) values

\( \Rightarrow \) Even \# of orientations

Spectrographic Notation: Final Label

Complete Description of Hydrogen Atom
Complete Description of Hydrogen Atom

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

\[ \Downarrow \]
LS Coupling
\[ \Downarrow \]
\[ \{n,l,j,m_s\} \]

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 \( \psi(r,\theta,\phi) = R(r) \Theta(\theta) \Phi(\phi) = \{n,l,j,m_s\} \)

In n-electron atom, to simplify, ignore electron-electron interactions.

complete wavefunction, in "independent"particle approx:
\[
\psi(1,2,3,\ldots,n) = \psi(1) \psi(2) \psi(3) \ldots \psi(n)
\]

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

Small angle scatter  large angle scatter

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

\[
H_1 = \frac{\hbar^2}{2m} \nabla^2_1 + \frac{k_1 (2e) (\sim e)}{r_1} \quad \text{and} \quad H_2 = \frac{\hbar^2}{2m} \nabla^2_2 + \frac{k_2 (2e) (\sim e)}{r_2}
\]

such that \( H_1, H_2 \) are same except for "label"

\[
[H_1, H_2] = 0 \quad \text{H, & H, are same except for "label"}
\]

Independent Particle Approx \( \Rightarrow \) ignore repulsive \( U = -\frac{e^2}{|r_1 - r_2|} \) term

Helium WaveFunction: \( \psi = \psi (r_1, r_2) \);

Probability \( P = \psi^* (r_1, r_2) \psi (r_1, r_2) \)

But if we exchange location of (identical, indistinguishable) electrons \( \Rightarrow |\psi (r_1, r_2)| = |\psi (r_2, r_1)| \)

In general, when electrons are identical, indistinguishable \( \Rightarrow \) Bosonic System (made of photons, e.g)

when \( \psi (r_1, r_2) = - \psi (r_2, r_1) \) \( \Rightarrow \) Fermionic System (made of electron, proton e.g)

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

Then the net wavefunction \( \psi_{ab} (r_1, r_2) = \psi_a (r_1) \psi_b (r_2) \) satisfies

\[
[H_1 \psi_a (r_1) \psi_b (r_2)] = E_1 \psi_a (r_1) \psi_b (r_2)
\]

\[
[H_2 \psi_a (r_1) \psi_b (r_2)] = E_2 \psi_a (r_1) \psi_b (r_2)
\]

\[
[H_1 + H_2] \psi_a (r_1) \psi_b (r_2) = (E_1 + E_2) \psi_a (r_1) \psi_b (r_2)
\]

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

If both are in the same quantum state \( \Rightarrow a = b \) & \( \psi_{ab} (r_1, r_2) = \psi_a (r_1) \psi_b (r_2) = 0 \)

Pauli Exclusion Principle

General Principles for Atomic Structure for n-electron system:

1. n-electron system is stable when its total energy is minimum
2. Only one electron can exist in a particular quantum state in an atom; not 2 or more!
3. Shells & Subshells In Atomic Structure:
   a) ignore inter-electron repulsion (crude approx.)
   b) think of each electron in a constant "effective" mean Electric field
   "Buzzing" closer in \( r \) to Nucleus
   Electric field: "seen" Nuclear charge (+Ze) reduced by partial screening due to other electrons
   "effective" mean Electric field
   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 \( l \), those with lower \( l \) closer to nucleus, more tightly bound
   - all electrons in sub-shell have same energy, with minor dependence on \( m_l, m_s \)
Shell & Sub-Shell Energies & Capacity

1. Shell & subshell capacity limited due to Pauli Exclusion principle.
2. Shell is made up of sub-shells (of same principal quantum # n).
3. Subshell \((n,l)\), given \(n \Rightarrow l = 0,1,2,3,\ldots(n-1)\),

   \[ m_l = 0, \pm 1, \pm 2, \ldots \Rightarrow (2l+1) m_l = \pm \frac{l}{2} \]

   \[ \Rightarrow \text{Max. # of electrons in a shell} = \sum \text{subshell capacity} \]

   \[ N_{\text{max}} = \sum_{l=0}^{2l} (2l+1) = 2[l + 3 + 5 + \ldots + 2(n-1) + 1] = 2n \left( \frac{1}{2} (l + (2n-1)) \right) = 2n^2 \]

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) \[ \sum i \cdot \hat{L}_i = 0, \sum i \cdot \hat{S}_i = 0, \Rightarrow \text{Effective charge distribution is symmetric} \]
   (b) Electrons are tightly bound since they "see" large nuclear charge.
   (c) Because \[ \sum i \cdot \hat{L}_i = 0 \Rightarrow \text{No dipole moment} \Rightarrow \text{No ability to attract electrons} \]
   \[ \Rightarrow \text{Inert! Noble gas!} \]
6. Alkali Atoms: have a single "s" electron in outer orbit;
   nuclear charge heavily shielded by inner shell electrons
   \[ \Rightarrow \text{very small binding energy of "valence" electron} \]
   \[ \Rightarrow \text{large orbital radius of valence electron} \]

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.
- Electrons in same sub-shell \((l)\) and same spin.
- Must have different \(m_l\).
- (Very different angular distribution).
- Electrons with parallel spin are further apart.
- Than when anti-parallel \(\Rightarrow \) lesser E state.
- Get filled first.

\[ \Rightarrow \text{Periodic table is formed!} \]

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