# Multi-Electron Atoms: Beyond the Hydrogen Atom

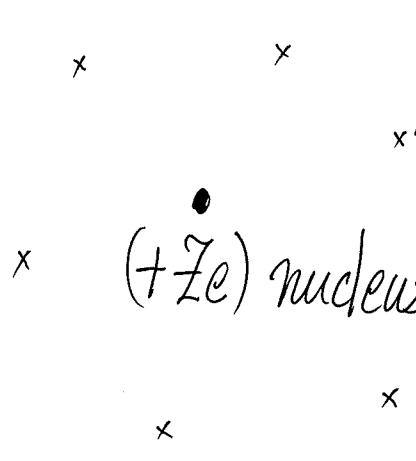
- Quantum Mechanics works for many-particle problems
- But TISE is hard to solve (can't be solved analytically)
- Need new ideas and concepts on:
  - Reducing many-particle problem to effective single-particle problems [approximations]
  - Proper form of many-particle wavefunction
    - in view of indistinguishable particles (e.g. electrons in an atom)
    - in terms of single-particle states
  - End result is: Fill particles (electrons) into single-particle states according to the Pauli Exclusion Principle

# A. Multi-electron atom is a Many-body Problem hard to solve

- Quantum Mechanics "solves" all atomic problems!

  [We know the physics, in principle!]

- Atom with atomic number $Z$




"The atom problem"

- Nucleus fixed at origin
- Include only Coulombic interactions, ignore other effects, e.g. spin-orbit interaction, relativistic correction, ...

Recall: Hydrogen Atom

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]}_{\text{give structure of order } \sim \text{eV}\ \left[\frac{-13.6}{n^2}\ \text{eV}\right]} + \overbrace{(\text{spin-orbit interaction}) + (\text{relativistic correction})}^{\text{order} \sim 10^{-4}\ \text{eV}} + \underbrace{(\text{hyperfine})}_{\text{even smaller}} + \underbrace{(\text{external } \vec{B}\text{-field, Zeeman})}_{\text{order} \sim 10^{-4}\ \text{eV}}$$

$\therefore$ More important to treat Coulomb term $\left(\frac{-e^2}{4\pi\varepsilon_0 r}\right)$ first.

- In atoms beyond hydrogen (and in molecules), there are many more Coulomb terms (electron-nucleus, electron-electron). It is more important to treat them first.

# Schrödinger Equation

$$\hat{H} = \frac{-\hbar^2}{2m}\left(\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2 + \cdots + \nabla_{\vec{r}_Z}^2\right) \leftarrow \text{k.e. of } Z \text{ electrons}$$

$\hat{H}$: Hamiltonian of many-electron atom

$$- \frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} + \cdots + \frac{Ze^2}{r_Z}\right) \leftarrow \text{p.e. due to nucleus } (+Ze) \text{ and electrons } (-e \text{ each}) \text{ Coulomb attraction}$$

Note sign

$$+ \sum_{(ij)\,\text{pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \leftarrow \text{p.e. due to electron-electron Coulomb repulsion} \quad (1)$$

- New term for atoms beyond hydrogen [NOT appear in hydrogen atom]
- Make the problem impossible to solve analytically

e.g. $Z = 2$ → Helium atom

[Different atoms ⇒ different $\hat{H}$]

Symbols:

$\vec{r}_i$ = position of the $i^{th}$ electron (origin (0,0,0) at the nucleus)

$\nabla^2_{\vec{r}_i} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ $\quad (\vec{r}_i = (x_i, y_i, z_i))$

$r_i = |\vec{r}_i|$ = distance of $i^{th}$ electron from origin

$|\vec{r}_i - \vec{r}_j|$ = distance between $i^{th}$ and $j^{th}$ electrons

$\sum_{(ij)\,pairs}$ each pair is counted once

$H(\vec{p}_1, \vec{r}_1; \vec{p}_2, \vec{r}_2; \cdots, \vec{p}_Z, \vec{r}_Z)$ formally

every variable appears in Eq. (1)

TISE: $\hat{H}\psi = E\psi$ (done, in principle!)

$$-\frac{\hbar^2}{2m}\left(\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2 + \cdots + \nabla_{\vec{r}_Z}^2\right)\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$$

$$-\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} + \cdots + \frac{Ze^2}{r_Z}\right)\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$$

$$+\left(\sum_{(ij)\,\text{pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}\right)\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z) = E\,\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z) \quad (2)$$

Eigenvalues give allowed energies of the atom

Note: Talking about the atom (formally not about electron)

Where is Spin?

- No spin-dependent term in $\hat{H}$
- Spin has to be introduced separately in Schrödinger QM
- But spin will play a significant role (see later)

# New ideas

- **Many-particle states** (vs single-particle states)

  Atoms are, in principle, MANY-ELECTRON QM Problems[+]

  $\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$ is a Many-particle (many-electron) wavefunction

  [OR many-particle state]

  TISE (Eq.(2)) is an equation to solve for allowed energies $E$ of the many-electron atom and the corresponding many-electron energy eigenstates $\Psi_E(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$

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[+] H-atom: $\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$ ; $\psi_{n\ell m_\ell}(\vec{r})$ is a single-electron wavefunction.

- $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z)$ is a <u>many-particle</u> (or many-electron) <u>wavefunction</u>

Consider 2-particle case[+] (coordinates $\vec{r}_1$ & $\vec{r}_2$)

($\vec{r}_1$: coordinates of particle 1; $\vec{r}_2$: coordinates of particle 2)

$$\psi^*(\vec{r}_1, \vec{r}_2)\,\psi(\vec{r}_1, \vec{r}_2)\,\underbrace{dx_1 dy_1 dz_1}_{\text{Volume element } d\tau_1}\,\underbrace{dx_2 dy_2 dz_2}_{\text{Volume element } d\tau_2} \qquad (3)$$

Physical meaning:

Probability that particle 1 lies in volume element $d\tau_1$ at $\vec{r}_1$ AND particle 2 lies in volume element $d\tau_2$ at $\vec{r}_2$

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[+] What if particle 1 and particle 2 are indistinguishable (e.g. electrons in helium)?

- Answering this leads to the ideas of <u>Fermions</u> and <u>Pauli Exclusion Principle</u>, as well as <u>Bosons</u> (see later). It is <u>a big question.</u>

- $\underbrace{\sum_{(ij)\text{ pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\text{interaction term}}$ is the term that "kills" the problem (see Eq.(2))
  - real many-particle problem that can't be solved!
- If it is not there, Eq.(2) can be solved!

$$\sum_{i=1}^{Z} \underbrace{\left( \frac{-\hbar^2}{2m} \nabla_{r_i}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right)}_{\text{depends on each } r_i \text{ only}} \psi(\vec{r}_1, \cdots, \vec{r}_Z) = E\,\psi(\vec{r}_1, \cdots, \vec{r}_Z) \quad (4)$$

- Separation of Variables $\Rightarrow$ ($\phi_1, \phi_2, \phi_Z$: single-particle states)

$$\psi(\vec{r}_1, \cdots, \vec{r}_Z) = \phi_1(\vec{r}_1) \cdot \phi_2(\vec{r}_2) \cdots \phi_Z(\vec{r}_Z)$$

$$E = E_1 + E_2 + \cdots + E_Z \quad (5)$$

($E_1$: particle 1, $E_Z$: particle Z)

Aside:

Recall 2D Harmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}m\omega^2(x^2+y^2)$$

$$= \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right]}_{\text{depends on } x \text{ only}} + \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}m\omega^2 y^2\right]}_{\text{depends on } y \text{ only}}$$

← Condition on why separation of variables works

$\psi(x,y) = X(x)\cdot Y(y)$ works

harmonic oscillator states

End result: $\psi_{n_x n_y}(x,y) = \phi_{n_x}(x)\cdot\phi_{n_y}(y)$ [product]

$$E_{n_x, n_y} = \left(n_x+\frac{1}{2}\right)\hbar\omega + \left(n_y+\frac{1}{2}\right)\hbar\omega \quad \text{[sum]}$$

Compare Eq.(4), Eq.(5) with this case.

- But don't be carried away! $\sum_{(ij)\text{ pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$ is <u>really there</u>!

Atoms are actually <u>Many-electron Problem</u>

$$\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z) \neq \phi_a(\vec{r}_1)\cdot\phi_b(\vec{r}_2)\cdots\phi_k(\vec{r}_Z)$$

↑ Not True strictly speaking!

← Product of some "single-electron states"

- <u>What to do?</u>

But really <u>WANT</u> to express $\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$ in terms of some "single-electron states" (e.g. an $e^-$ in "1s↑", an $e^-$ in "1s↓", an $e^-$ in "2s↑", etc.)

This cannot be correct formally! It is <u>at best an approximation</u>.

The question becomes how good the approximation can be made.

# What is the way out?

We know how to solve single-electron problems

$$\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + \underbrace{V(r)}_{\text{spherically symmetric}}\right]\phi(\vec{r}) = \mathcal{E}\,\phi(\vec{r}) \qquad (6)$$

This is basically all we know!

single-electron states → $\phi(\vec{r}) = \phi(r,\theta,\phi) = R_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\phi)$ (7)

and the eigenvalues are generally $\mathcal{E}_{n\ell}$

The point is: Single-electron problems are easier to do!

↳ This suggests a strategy

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- (Want do) focus on single-electron state, other $(Z-1)$ electrons' effects go into $V(r)$?
- Rule on filling electrons into single-electron states [Pauli Exclusion Principle]