Multi-Electron Atoms: Beyond the Hydrogen Atom

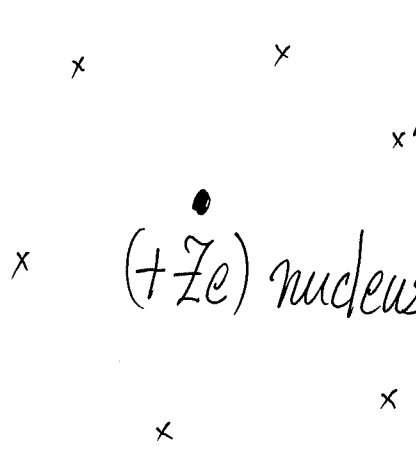
- Quantum Mechanics works for many-particle problems
- But TISE is hard to solve (can't be solved analytically)
- Need new ideas and concepts on:
  - Reducing many-particle problem to effective single-particle problems [approximations]
  - Proper form of many-particle wavefunction
    - in view of indistinguishable 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

$$\hat{H} = \frac{-\hbar^2}{2m}\left(\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2 + \cdots + \nabla_{\vec{r}_Z}^2\right) - \frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} + \cdots + \frac{Ze^2}{r_Z}\right) + \sum_{(ij)\text{ pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (1)$$

- $\hat{H}$: Hamiltonian of many-electron atom
- $\frac{-\hbar^2}{2m}\left(\nabla_{\vec{r}_1}^2 + \nabla_{\vec{r}_2}^2 + \cdots + \nabla_{\vec{r}_Z}^2\right)$: k.e. of Z electrons
- $-\frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} + \cdots + \frac{Ze^2}{r_Z}\right)$: p.e. due to nucleus ($+Ze$) and electrons ($-e$ each) Coulomb attraction
- Note sign
- $+\sum_{(ij)\text{ pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$: p.e. due to electron-electron Coulomb repulsion

- 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 <u>once</u>

$H(\vec{p}_1, \vec{r}_1; \vec{p}_2, \vec{r}_2; \cdots, \vec{p}_Z, \vec{r}_Z)$ 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 <u>allowed energies of the atom</u>

<u>Note:</u> Talking about the atom (formally not about electron)

<u>Where is Spin?</u>

- 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

- $\psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_z)$ 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 $\vec{r}_2$

[+] 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>

- $\sum_{(ij)\text{ pairs}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$ is the term that "kills" the problem,
  - 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 $\Rightarrow$ (ϕ_1, ϕ_2, ϕ_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

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

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

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

harmonic oscillator states

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

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

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>

- <u>Way Out</u>?

We <u>know</u> how to solve <u>single-electron problems</u>

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

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 $\mathcal{E}_{n\ell}$

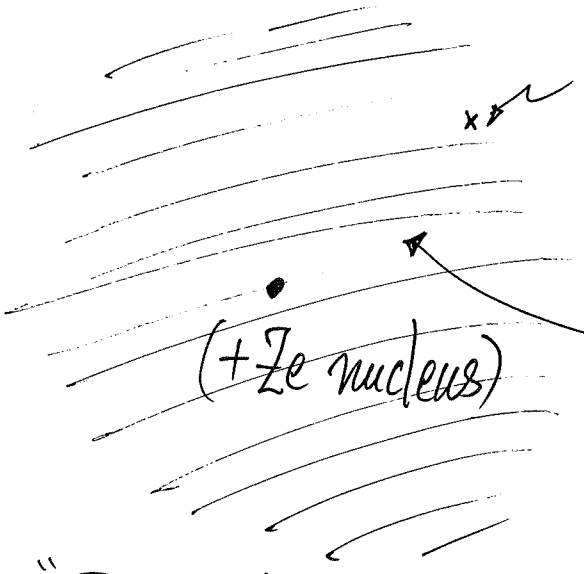
<u>The point is</u>: <u>Single-electron problems</u> are easier to do!

This suggests a strategy

Strategy: Not to solve the many-electron problem in Eq. (2)

- Save the nice features of single-electron problems

"Make approximations to turn problem into effective single-electron problem"



Other $(Z-1)$ electrons treated as providing an averaged $V(\vec{r})_{\text{other electrons}}$ on the electron in focus

"atomic orbitals"

$$\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0 r} + V(r)_{\text{other electrons}}}\right]\phi(\vec{r}) = \mathcal{E}\phi(\vec{r}) \quad (8)$$

$$\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + V_{\text{eff}}(r)\right]\phi(\vec{r}) = \mathcal{E}\phi(\vec{r}) \quad (9)$$

$\Rightarrow$ hopefully (wanted it to be!) spherically symmetric

If this approximation works...

then $\hat{H} \approx \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 + V_{\text{eff}}(r_i) \right]$ life becomes easier! (c.f. Eq. (4))

- recuse the idea of single-electron states (atomic orbitals)
- But $V_{\text{eff}}(r_i)$, what is it?
  - <u>can't be</u> pure Coulomb form (∵ include other electrons' effects)
  - Screening effect

Roughly,

$$V_{\text{eff}}(r_i) \approx \begin{cases} -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_i} & (r_i \text{ far away from nucleus, other electrons } \underline{\text{screen}} \text{ out nuclear charge}) \\ -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i} & (r_i \text{ close to nucleus}) \end{cases}$$

but $V(r_i)$ only ↑ distance

End result: $\mathcal{E}_{n\ell} \Rightarrow \mathcal{E}_{1s}, \mathcal{E}_{2s}, \mathcal{E}_{2p}, \mathcal{E}_{3s}, \mathcal{E}_{3p}, \mathcal{E}_{3d}, \cdots$

[different series of $\mathcal{E}_{n\ell}$ for different atoms]

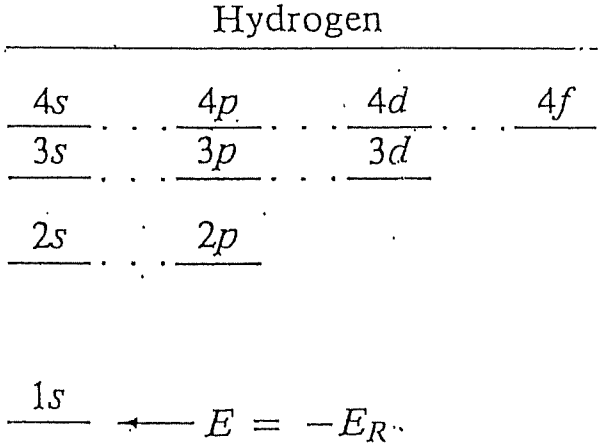
- Need a rule to fill Z electrons into atomic orbitals (states $\phi(\vec{r})$)
  - Pauli Exclusion Principle[+] [indistinguishability of electrons in atoms]

→ Explains the periodic table and more!

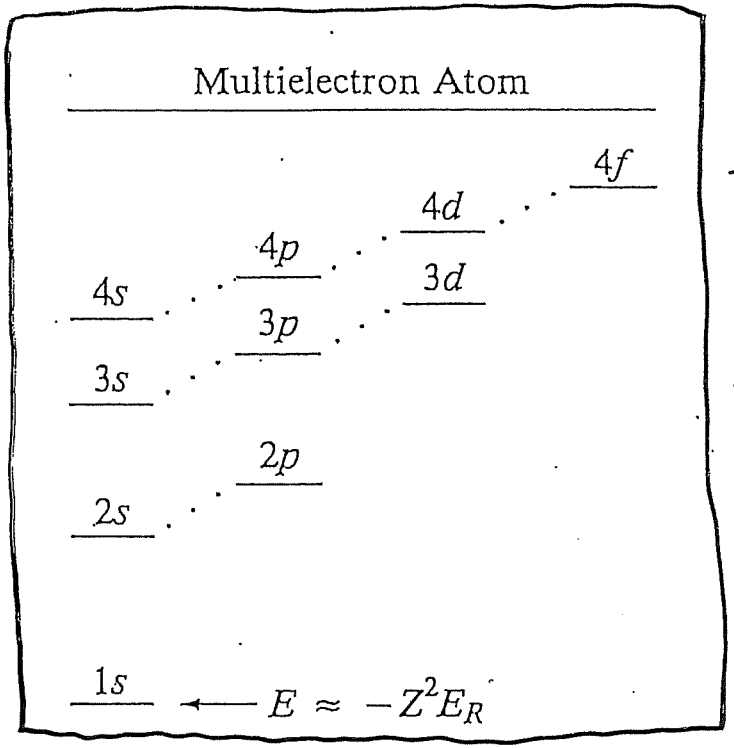
- This is the big picture.
- The rest is to fill in some details.

[+] Spin plays an important role

End Result (expected)



Schematic†



†Each atom is a separate QM problem (∵ different Z)

- fill in electrons (Pauli Exclusion Principle)
- then we have electronic configuration for ground state
  e.g. Na $1s^2\ 2s^2\ 2p^6\ 3s^1$
- Do it for different atoms ⇒ Periodic Table!