Quantum Mechanics

Week 9

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Exercise Material

Webpage

Week 9

Review

Exercises

Review of Last Week

- Any questions on last week's topics?

- Feedback on the previous session?

Review

Atomic Number and Electron Interactions

In an atom, the atomic number Z defines the number of protons in the nucleus and, in a neutral atom, also the number of electrons orbiting the nucleus. Each electron in the atom contributes to its overall properties through:

- Kinetic energy due to its motion.

- Coulombic interaction with the nucleus.

- Interactions with other electrons.

Hamiltonian for Multi-Electron Atoms

The Hamiltonian for a multi-electron atom can be expressed as:

$$\hat{H} = \sum_{i=1}^{Z} \left(\frac{-\hbar^2}{2m} \nabla_i^2 \right) - \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{Z} \frac{Ze^2}{r_i} + \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{\substack{i=1 \\ k \neq i}}^{Z} \frac{e^2}{|r_i - r_k|} \quad (1)$$

where:

- The first term represents the kinetic energy.

- The second term is the electron-nucleus interaction.

- The third term is the electron-electron repulsion.

- The $\frac{1}{2}$ factor avoids double counting of electron-electron interactions.

- Simplifications often ignore spin-spin and spin-orbit interactions.

- This simplified model is useful for introductory understanding.

Handling Electron-Electron Interactions

- For simplification, electron-electron interactions are sometimes ignored.

- Electrons are considered in single-particle hydrogenic states $\psi_{n\ell m_\ell m_s}$.

- This provides a basic, though not entirely accurate, model for atomic structure.

Quantum Numbers: Defining Electron States in Atoms

Quantum Number	Symbol	Description
Principal	n	Main energy level or shell. Influences size and relative distance of orbital.
Azimuthal	ℓ	Subshell or shape of the orbital. Ranges from 0 (s) to $n-1$ (p, d, f).
Magnetic	m_ℓ	Orientation of the orbital in 3D space. Values range from $-\ell$ to $+\ell$.
Spin	m_s	Electron's intrinsic spin. Values are $+1/2$ (spin-up) or $-1/2$ (spin-down).

Orbital Arrangement: Shell, Subshells, and Electron Count

- **Shell (n):**

  - Each shell can contain up to $2n^2$ electrons.

  - Labeled K, L, M, N, etc.

- **Subshell (ℓ):**

  - Electrons fill subshells (s, p, d, f) in order of increasing energy.

  - Number of subshells equals principal quantum number n.

- **Electron Count:**

  - Each orbital holds up to 2 electrons with opposite spins.

  - Total electrons per subshell: $2(2\ell + 1)$.

n	Shell	Subshell	# Orbitals	# Electrons	
				Per Subshell	Per Shell
1	K	s	1	2	$\Rightarrow 2$
2	L	s	1	2	$\Rightarrow 8$
		p	3	6	
3	M	s	1	2	$\Rightarrow 18$
		p	3	6	
		d	5	10	
4	N	s	1	2	$\Rightarrow 32$
		p	3	6	
		d	5	10	
		f	7	14	

Hydrogenic Atoms

- Simplified model: one electron orbiting the nucleus.

- Energy of each level: function of principal quantum number n.

$$E_n = -\frac{1}{n^2} \left[\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \right] \tag{2}$$

- Z: atomic number

- m: electron mass

- Degeneracy: Orbitals of different ℓ but same n share identical energy.

- Ground state is when the electron is in the $1s$ orbital, any other state is excited state.
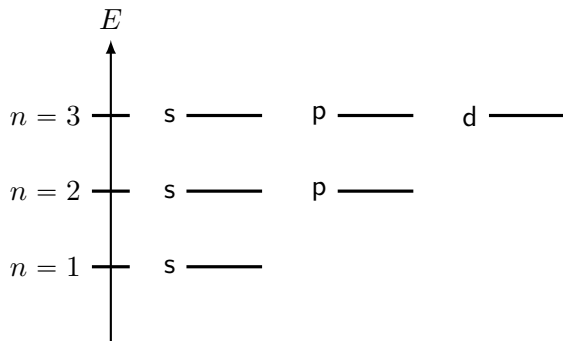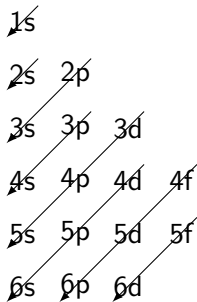
Multi-electron Atoms

- Electron configuration is more complex due to electron-electron interactions.

- Spin-orbit coupling leads to energy level splitting.

- Orbitals like $2s$ and $2p$ diverge in energy.

- Higher n and ℓ values show increasing energy variation.
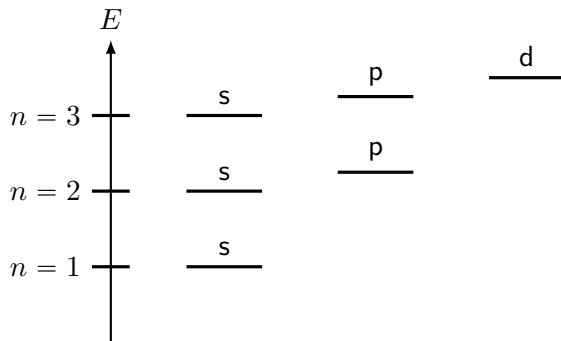
Filling Order in Multi-electron Atoms

$1s$

$2s$ $2p$

$3s$ $3p$ $3d$

$4s$ $4p$ $4d$ $4f$

$5s$ $5p$ $5d$ $5f$

$6s$ $6p$ $6d$

- Diagram shows systematic filling from the lowest energy level.

- Electrons fill s, p, d, and f subshells in the given order.

Orbital Filling Exceptions

- **Chromium** ($Z = 24$):

    - Configuration: $[Ar]4s^1 3d^5$

    - Half-filled d subshell provides stability instead of full s subshell.

- **Copper** ($Z = 29$):

    - Configuration: $[Ar]4s^1 3d^{10}$

    - Completely filled d subshell.

- Exceptions due to minimal energy differences between orbitals.

- Highlights the complex interplay of electronic repulsions and orbital energies.

**Valence Electrons: Reactivity and Solid State Physics**

- Valence electrons: Outer electron shells.

- **Roles:**

    1. Chemical bonds: Ionic, covalent, metallic.

    2. Reactivity: Strive for stable electronic configuration.

    3. Electrical conductivity: Free valence electrons in metals.

    4. Band structure: Energy levels for valence electrons.

Electron Configuration Ambiguities

- Electron configuration does not fully specify quantum state.

- Example: Carbon ($Z = 6$), configuration: $[C] = 1s^2 2s^2 2p^2$

$$[C] = 1s^2 2s^2 2p^2$$

The $2p$ orbtial can look like:
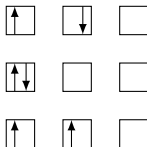
- Each configuration affects chemical properties.

- Energetically favorable configuration determined by angular momentum principles.

Remark: Beyond the three configurations depicted, there are additional possible arrangements for electrons. To determine which configuration is energetically most favorable, we must consider the principles of angular momentum in multi-electron atoms.

Define New Quantum Numbers

- Analogous to l, m_ℓ, s, m_s

- $L \Rightarrow$ total orbital angular momentum with projection $M_L = \sum_i m_{\ell,i}$

- $S \Rightarrow$ total spin angular momentum with projection $M_S = \sum_i m_{s,i}$

- $J \Rightarrow$ total angular momentum, combines L and S with projection $M_J = M_L + M_S$

Think of this as the multi-electron system quantum numbers.

Addition Rule for Angular Momentum

$$J = j_1 \oplus j_2$$
$$J = (j_1 + j_2), (j_1 + j_2 - 1), \ldots, |j_1 - j_2|$$

Example:

- $j_1 = 3, j_2 = 1$

- Possible values of J: 4, 3, 2

Term Symbols and the Role of Filled Subshells

Term Symbols: Represent quantum states of atoms.

$$^{2S+1}L_J \quad \text{where} \quad L = \ell_1 \oplus \ell_2 \oplus \ldots \oplus \ell_n,$$
$$S = s_1 \oplus s_2 \oplus \ldots \oplus s_n,$$
$$J = L \oplus S.$$

- Example: $^2P_{3/2}$ for a state with $S = 1/2$, $L = 1$ (P), and $J = 3/2$.

- Letters S, P, D, F, G correspond to $L = 0, 1, 2, 3, 4$ respectively.

- **Note**: Filled subshells do not contribute as their angular momenta are pairwise neutralized.

Hund's Rules

- Hund's Rules are empirical guidelines.

- Help predict ground state electron configurations.

- Important for the periodic table and atomic spectra.

Hund's First Rule: Maximum Spin Multiplicity

- Derived from the Pauli exclusion principle.

- Electrons occupy orbitals to maximize total spin quantum number (S).

- Results in the lowest energy state with the greatest spin multiplicity ($2S + 1$).

$$\text{Maximized Multiplicity:} \quad 2S + 1$$

The state with the largest S is most stable.

Hund's Second Rule: Orbit-Orbit Interaction

- Addresses electron repulsion in degenerate orbitals.

- Configurations with the highest total orbital angular momentum (L) are favored energetically.

- Electrons with parallel spins (parallel orbital motion) avoid each other more, reducing repulsion.

  For equal S, largest L is most stable.

Hund's Third Rule: Minimum Energy J-State

- Addresses spin-orbit coupling in atoms.

- For a given term:

  - If the shell is less than half-filled, the level with the lowest total angular momentum (J) lies lowest in energy.

  - If the shell is more than half-filled, the level with the highest J is favored.

Same S and L : $\begin{cases} \text{smallest } J \text{ is most stable for subshells } \leqslant \text{ half full} \\ \text{largest } J \text{ is most stable for subshells } > \text{ half full} \end{cases}$

- **Hund's First Rule**: Maximize total spin (S) for the most stable state.

- **Hund's Second Rule**: For equal S, maximize total orbital angular momentum (L).

- **Hund's Third Rule**: For equal S and L, stability depends on the filling of the subshell:

  - Smallest J for subshells $\leqslant$ half full.

  - Largest J for subshells $>$ half full.

Recipe

1. **Determine Electron Configuration**
   Start by determining the electron configuration using the Aufbau principle.

2. **Identify Quantum Numbers**
   Identify the quantum numbers for each electron in partially filled
   subshells:

   - Spin (s_i)

   - Orbital (ℓ_i)

3. **Calculate L, S, J**
   Calculate total orbital angular momentum (L) and total spin angular momentum (S):

   $$L = \ell_1 \oplus \ell_2 \oplus \ldots \oplus \ell_n$$

   $$S = s_1 \oplus s_2 \oplus \ldots \oplus s_n$$

   Determine J using vector addition rules:

   $$J = L \oplus S$$

4. **Derive Term Symbols**
   Construct term symbols in the format:

   $$^{2S+1}L_J$$

5. **Apply Hund's Rules**

Rule 1: Maximize S for the highest total spin angular momentum.

Rule 2: For equal S, maximize L for the highest total orbital angular momentum.

Rule 3: For equal S and L:

- Smallest J is most stable for subshells $\leqslant$ half full.

- Largest J is most stable for subshells $>$ half full.

Example Carbon $Z = 6$

Exercises

Exercise 1

Important to understand today's topics, must-do!

Exercise 2

Also important, but $2b$ does not fall within the scopes of this course (see Moodle Announcements).