

# Quantum Mechanics

Week 10

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## Pre-Reading Note

Dear Students,

Welcome to the course on Quantum Mechanics. As part of your learning resources, I will prepare a series of educational materials and sheets designed to complement the lectures.

Please note that these materials are **abridged versions** of the content from the textbook *"Introduction to Quantum Mechanics By David J. Griffiths"*. They have been tailored to align with the class schedule and topics, providing you with concise summaries and key points for each topic covered.

It's important to understand that these sheets are **not standalone resources**. They are intended to be used in conjunction with the class material. For a deeper understanding and a more comprehensive view of each topic, I strongly encourage you to refer to the mentioned textbook.

The book provides detailed explanations, examples, and insights that go beyond the scope of our summaries. It will be an invaluable resource for you to solidify your understanding of Quantum Mechanics.

I cannot guarantee neither correctness nor completeness of the script. Please report any mistake directly to me.

Have fun with Quantum Mechanics!

Best regards,

*Mark Benazet Castells*

# 1 Atoms

## 1.1 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.

## 1.2 Hamiltonian for Multi-Electron Atoms

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

$$\hat{H} = \sum_{i=1}^Z \left( \frac{-\hbar^2}{2m} \nabla_i^2 \right) - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^Z \frac{Ze^2}{r_i} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{i=1 \\ k \neq i}}^Z \frac{e^2}{|r_i - r_k|} \quad (1)$$

where the first term represents the kinetic energy, the second term is the electron-nucleus interaction, and the third term is the electron-electron repulsion. In our approach, the last term presents significant complexities; hence, as a first approximation, it is often ignored to simplify the model.

**Remark:** The factor of  $\frac{1}{2}$  in the interactions between electrons is introduced to avoid double counting of forces. Additionally, it is crucial to note that in our Hamiltonian, we are deliberately omitting more intricate interactions, such as *spin-spin* and *spin-orbit* interactions. These interactions, while significant in a more detailed analysis, fall beyond the scope of this introductory course.

## 1.3 Handling Electron-Electron Interactions

To simplify the analysis of atoms, electron-electron interactions are sometimes ignored, allowing each electron to be considered in a single-particle hydrogenic state. These states are described by the notation  $\psi_{n\ell m_\ell m_s}$ . This approach, while not entirely accurate, provides a simplified model to understand atomic structure.

## 2 Quantum Numbers and Orbital Shapes

### 2.1 Quantum Numbers: Defining Electron States in Atoms

Recalling from last week's lecture, the unique quantum state of each electron in an atom is defined by a distinct set of quantum numbers.

1. **Principal quantum number** ( $n$ ): Determines the main energy level or shell in which the electron resides, influencing the size and relative distance of the orbital from the nucleus. Higher values of  $n$  correspond to electrons being further from the nucleus.
2. **Azimuthal quantum number** ( $\ell$ ): Identifies the subshell or the shape of the orbital, ranging from 0 (spherically symmetric s-orbitals) to  $n - 1$  (including p, d, f orbitals for higher  $\ell$  values).
3. **Magnetic quantum number** ( $m_\ell$ ): Specifies the orientation of the orbital in three-dimensional space, taking values from  $-\ell$  to  $+\ell$ .
4. **Spin quantum number** ( $m_s$ ): Represents the electron's intrinsic spin, with two possible orientations: "spin-up" ( $+1/2$ ) or "spin-down" ( $-1/2$ ).

These quantum numbers not only define the energy level, shape, and orientation of the electron's orbital but also its spin state. Together, they ensure that each electron in an atom occupies a unique quantum state, as mandated by the Pauli Exclusion Principle. This principle stipulates that no two electrons in an atom can have an identical set of all four quantum numbers, thereby governing the arrangement and behavior of electrons within the atom.

### 2.2 Orbital Arrangement: Shell, Subshells, and Electron Count

The arrangement of electrons in an atom follows a specific order determined by the quantum numbers. Electrons fill orbitals in order of increasing energy level, which generally correlates with the sum of  $n$  and  $\ell$ . The arrangement is as follows:

- **Shell** ( $n$ ): Each shell can contain up to  $2n^2$  electrons. Shells are identified by their principal quantum number and are typically labeled K, L, M, N, etc., starting from the nucleus outward.
- **Subshell** ( $\ell$ ): Within each shell, electrons fill subshells (s, p, d, f, etc.) in order of increasing energy. The number of subshells in a shell equals its principal quantum number  $n$ .
- **Electron Count**: Each orbital within a subshell can hold up to two electrons with opposite spins. The total number of electrons in a subshell is thus  $2(2\ell + 1)$ .

2.2.1 Tabular Representation of Electron Distribution

n	Shell	Subshell	# Orbitals	# Electrons	
				Per Subshell	Per Shell
1	<i>K</i>	<i>s</i>	1	2	⇒ 2
2	<i>L</i>	<i>s</i>	1	2	⇒ 8
		<i>p</i>	3	6	
3	<i>M</i>	<i>s</i>	1	2	⇒ 18
		<i>p</i>	3	6	
		<i>d</i>	5	10	
4	<i>N</i>	<i>s</i>	1	2	⇒ 32
		<i>p</i>	3	6	
		<i>d</i>	5	10	
		<i>f</i>	7	14	

Table 1: Electron Distribution in Shells and Subshells

### 3 Electron Distribution in Atoms

#### 3.1 Hydrogenic Atoms

Hydrogenic atoms, characterized by a solitary electron orbiting a nucleus, offer a simplified model for understanding atomic structure. The energy of each level is solely a function of the principal quantum number  $n$ , as described by:

$$E_n = -\frac{1}{n^2} \left[ \frac{m}{2\hbar^2} \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right], \quad (2)$$

where  $Z$  represents the atomic number and  $m$  denotes the electron mass. In such atoms, orbitals of varying angular momentum quantum numbers ( $\ell$ ) share identical energy, a condition known as degeneracy.

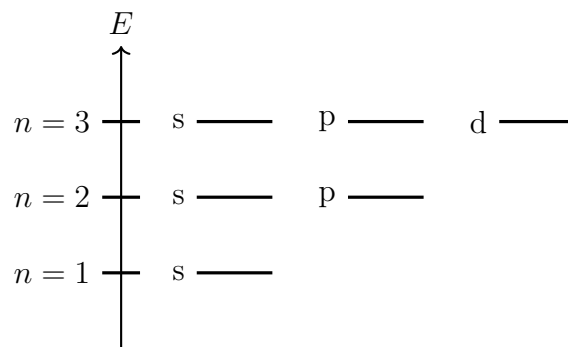


Figure 1: Filling order

For hydrogenic atoms (atoms with one single electron), this degeneracy persists across all energy levels within a principal quantum number. The diagram illustrates the  $1s$  orbital as the fundamental state, while  $2s$  and  $2p$  are equivalent excited states for  $n = 2$ , continuing similarly for higher levels. Electrons populate these levels following an ascending energy sequence.

#### 3.2 Multi-electron Atoms

The electron configuration in multi-electron atoms is more nuanced due to electron-electron interactions and other complexities. Unlike hydrogenic atoms, these interactions, along with spin-orbit coupling, lead to energy level splitting and subshells differentiated by the angular momentum quantum number  $\ell$ . Consequently, the energy levels in multi-electron atoms are not degenerate, as electron repulsion and other factors cause orbitals like  $2s$  and  $2p$  to diverge in energy.

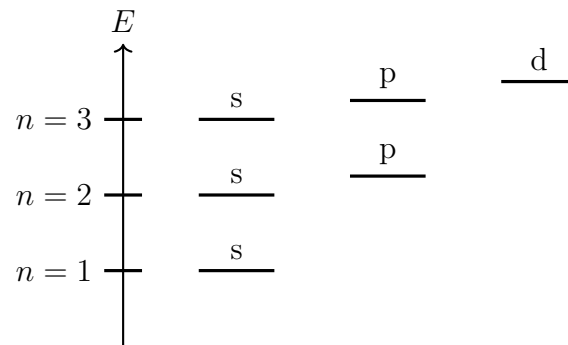


Figure 2: Energy levels of multi-electron atoms showing the lifting of degeneracy

The above figure delineates the energy levels in a typical multi-electron atom, highlighting the energy distinction between  $2s$  and  $2p$  orbitals. As we explore higher  $n$  and  $\ell$  values, energy variations become increasingly marked. The electron filling of these orbitals is governed by the Aufbau principle, Hund's rules, and the Pauli Exclusion Principle, commencing from the lowest energy levels.

### 3.3 Filling Order in Multi-electron Atoms

Electrons in multi-electron atoms occupy orbitals in an energy-optimized sequence, known as the Aufbau Principle. This sequence, reflecting a composite consideration of both the principal quantum number ( $n$ ) and the azimuthal quantum number ( $\ell$ ), is visually captured by a diagram portraying the relative energy levels of orbitals.

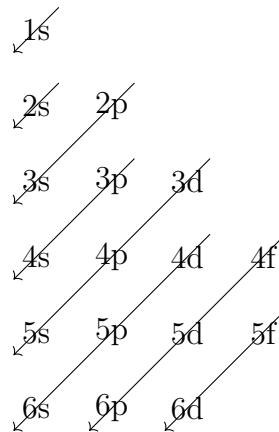


Figure 3: The filling order of orbitals in multi-electron atoms.

This diagram conveys the systematic filling of orbitals, initiating with the lowest energy  $1s$  orbital. As electrons continue to be added, they follow the dictated sequence, filling  $s$ ,  $p$ ,  $d$ , and  $f$  subshells corresponding to  $\ell$  values of 0, 1, 2, and 3, respectively.



## 4 Exceptions and Valence Electrons

### 4.1 Orbital Filling Exceptions

Despite the general guidelines provided by the Aufbau principle, there are notable exceptions, particularly in transition metals and lanthanides. These exceptions often occur when half-filled or fully filled  $d$  subshells offer enhanced stability due to minimal energy differences between orbitals. Key examples include:

- **Chromium** ( $Z = 24$ ): Exhibits the configuration  $[Ar]4s^13d^5$ , favoring a half-filled  $d$  subshell.
- **Copper** ( $Z = 29$ ): Has the configuration  $[Ar]4s^13d^{10}$ , opting for a completely filled  $d$  subshell.

### 4.2 Valence Electrons: Reactivity and Solid State Physics

Valence electrons, which occupy the outermost electron shells of an atom, serve as the primary agents in chemical reactions and the formation of compounds. These electrons are responsible for a wide range of phenomena:

1. The formation of chemical bonds, whether ionic, covalent, or metallic, is mediated by the exchange or sharing of valence electrons between atoms. This interaction is the foundation of molecule formation and the complex structures observed in chemistry.
2. The reactivity of an element is greatly influenced by the number of valence electrons. Atoms strive to reach a stable electronic configuration, often through reactions that achieve a full valence shell similar to that of noble gases.
3. In solid-state physics, the behavior of valence electrons is essential in understanding electrical conductivity. The presence of free or delocalized valence electrons in metals leads to high conductivity, while the absence of such electrons in insulators results in their non-conductive nature.
4. The band structure of materials, which is crucial in semiconductors, depends on the energy levels available to valence electrons. These energy bands determine how electrons can move through a material when an electric field is applied.

For example, the noble gas Argon ( $Z = 18$ ) exhibits chemical inertness due to its complete valence shell, with the electronic configuration  $[Ar] = 1s^22s^22p^63s^23p^6$ . This full valence shell aligns with the octet rule, making Argon stable and non-reactive under normal conditions. In contrast, transition metals like Iron ( $Z = 26$ ), with an electronic configuration of  $[Fe] = [Ar]4s^23d^6$ , display a variety of chemical behaviors due to their partially filled  $d$  orbitals.

### 4.3 Electron Configuration Ambiguities

The electron configuration of an atom does not fully specify the quantum state of the system. Particularly, the distribution of electrons within subshells can lead to multiple

possible configurations, each with a unique total energy for the system. This uncertainty is exemplified by the carbon atom, which has the electron configuration:

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

For the  $2p^2$  configuration, determining the exact placement of the two p orbital electrons becomes complex. There are several ways to distribute these electrons across the available states:

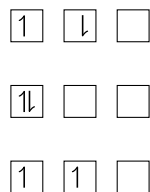


Figure 4: Possible electron distributions in the  $2p$  orbitals of carbon.

Each of these electron configurations significantly influences an atom's chemical properties and its interactions with other atoms or external fields. The decision on the correct electron placement within the orbitals is not arbitrary but is determined by quantum mechanical 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.

## 5 Angular Momentum in Multi-electron Atoms

Understanding angular momentum is crucial in quantum mechanics as it significantly influences the quantum states and behaviors of multi-electron atoms.

### 5.1 Components of Angular Momentum

In quantum mechanics, angular momentum for electrons in an atom arises from two sources: their orbital motion around the nucleus, and their inherent spin. The angular momentum of an atom is characterized by three quantum numbers:  $L$ ,  $S$ , and  $J$ .

- **Total Orbital Angular Momentum ( $L$ ):** This is the sum of the orbital angular momenta ( $\ell$ ) of the electrons in unfilled subshells. The result will be a set of values for  $L$  depending on the alignment of each particle (addition rule).
- **Total Spin Angular Momentum ( $S$ ):** This is the sum of the intrinsic spin angular momenta ( $s$ ) of the electrons. The result will be a set of values for  $S$  depending on the alignment of each particle (addition rule).

The total angular momentum ( $J$ ) is a combination of  $L$  and  $S$ , and its projection is denoted as  $M_J = M_L + M_S$ , where  $M_L$  and  $M_S$  are the projections of  $L$  and  $S$ , respectively.

**Remark:** It's important to note that the actual values of angular momenta are obtained by multiplying the quantum numbers with  $\hbar$ .

#### 5.1.1 Addition Rule for Angular Momentum

Angular momentum addition in quantum mechanics follows specific rules that diverge from classical vector addition, which is vital for determining permissible quantum states for an atom:

$$\begin{aligned} J &= j_1 \oplus j_2 \\ &= (j_1 + j_2), \dots, |j_1 - j_2| \end{aligned}$$

### 5.2 Term Symbols and the Role of Filled Subshells

Term symbols provide a concise notation for the quantum states of atoms, crucial for understanding spectroscopy and chemical bonding. They are derived from the aggregate combinations of  $L$ ,  $S$ , and  $J$ :

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

In this notation,  ${}^{2S+1}L_J$  includes the total spin ( $S$ ), total orbital ( $L$ ), and total angular momentum ( $J$ ) quantum numbers, with letters S, P, D, F, G corresponding to  $L = 0, 1, 2, 3, 4$  respectively. It is essential to recognize that filled subshells do not contribute to these quantum numbers as their angular momenta are pairwise neutralized.

## 6 Hund's Rules and Electron Configurations

Hund's Rules are empirical guidelines that help predict the ground state electron configurations of atoms and molecules, particularly in the building of the periodic table and interpretation of atomic spectra. They describe how electrons fill subshells and are based on the principles of quantum mechanics, including the Pauli exclusion principle and electron-electron repulsion.

### 6.1 Hund's First Rule: Maximum Spin Multiplicity

Hund's first rule, derived from the Pauli exclusion principle, states that electrons occupy orbitals in a way that maximizes the total spin quantum number ( $S$ ), resulting in the lowest energy state with the greatest spin multiplicity ( $2S + 1$ ).

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

where  $S$  represents the total spin for electrons in an open subshell. The most stable state is thus the one with the highest  $S$ :

Rule 1:

The state with the largest  $S$  is most stable.

### 6.2 Hund's Second Rule: Orbit - Orbit interaction

Hund's second rule addresses electron repulsion in degenerate orbitals. It states that configurations with the highest total orbital angular momentum ( $L$ ) for a given spin multiplicity ( $S$ ) are favored energetically. This can be visualized classically: electrons with parallel spins (and thus parallel orbital motion) avoid each other more than those with anti-parallel spins, reducing repulsive interactions.

Rule 2:

For equal  $S$ , largest  $L$  is most stable.

This rule implies that electrons spread out over different orbitals with parallel orbital motion, minimizing repulsion and lowering the energy of the atom.

### 6.3 Hund's Third Rule: Minimum Energy J-State

Hund's third rule addresses the spin-orbit coupling in atoms, postulating that for a given term, if the shell is less than half-filled, the level with the lowest total angular momentum ( $J$ ) value lies lowest in energy, and if the shell is more than half-filled, the level with the highest  $J$  is favored.

Rule 3:

For states with same  $S$  and  $L$  :

$$\begin{cases} \text{smallest } J \text{ is most stable for subshells } \leq \text{ half full} \\ \text{largest } J \text{ is most stable for subshells } > \text{ half full} \end{cases}$$

## 7 Recipe and Example

### 7.1 Recipe

#### 1. Determine Electron Configuration

Start by determining the electron configuration with the Aufbau principle.

#### 2. Identify Quantum Numbers

Proceed to identify the quantum numbers for each electron in partially filled subshells. These quantum numbers include spin ( $s_i$ ) and orbital ( $\ell_i$ ) quantum numbers.

#### 3. Calculate $L$ , $S$ , $J$

Utilize the obtained quantum numbers to calculate the total orbital angular momentum ( $L$ ) and the total spin angular momentum ( $S$ ). The formulas for these calculations are as follows:

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

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

Subsequently, determine  $J$  using vector addition rules:

$$J = L \oplus S$$

The  $J$  values correspond to the possible total angular momenta of the system.

#### 4. Derive Term Symbols

With the values of  $S$ ,  $L$ , and  $J$  determined, construct term symbols in the format  $^{2S+1}L_J$ . These term symbols represent the quantum state of the atom.

#### 5. Apply Hund's Rules

To pinpoint the ground state of the atom, apply Hund's rules, which help determine the most stable electron configuration:

Rule 1: Maximize  $S$  to achieve the highest possible total spin angular momentum. This rule reflects the tendency of electrons to align their spins in the same direction when possible.

Rule 2: For cases with the same  $S$ , maximize  $L$  to achieve the highest possible total orbital angular momentum. This rule accounts for the stability associated with maximizing orbital angular momentum within a given electron configuration.

Rule 3: For situations where  $S$  and  $L$  are equal, choose the lowest (or highest)  $J$  value depending on the occupancy of the subshell. This final rule accounts for the subtle variations in angular momentum that can occur within the same  $S$  and  $L$  values, based on the electron distribution in the subshells.

## 7.2 Example: Carbon

### Determine Electron Configuration

For carbon, the electron configuration is  $1s^2 2s^2 2p^2$ .

**Remark:** We only focus on the partially filled subshell, as the filled subshells do not contribute to these quantum numbers as their angular momenta are pairwise neutralized.

### Identify Quantum Numbers

The  $2p^2$  configuration implies two electrons with  $\ell_1 = \ell_2 = 1$ , and  $s_1 = s_2 = \frac{1}{2}$ .

### Compute $L$ , $S$ , $J$

The total orbital angular momentum  $L$  can be 0, 1, or 2, while the total spin angular momentum  $S$  can be 0 or 1, leading to different  $J$  values:

$$\begin{aligned}L &= 0, 1, 2, \\S &= 0, 1, \\J &= |L - S|, \dots, L + S.\end{aligned}$$

### Derive Term Symbols

The possible term symbols derived from the  $L$  and  $S$  values taking into account antisymmetry are:

$$^1S_0, ^3P_0, ^3P_1, ^3P_2, ^1D_2.$$

### Apply Hund's Rules

Hund's rules will determine the ground state term symbol:

1. The state with the largest  $S$  is most stable. Since  $S$  can be 0 (singlet) or 1 (triplet), the triplet state has a higher multiplicity and is therefore lower in energy.
2. For equal  $S$ , largest  $L$  is most stable. For carbon,  $L = 1$  ( $L = 2$  is symmetric) for  $S = 1$  is the highest possible  $L$  value.
3. For terms with the same  $S$  and  $L$ , the term with the smallest  $J$  value is most stable if the subshell is less than half full. Since the  $2p$  subshell of carbon is less than half full, the term with the smallest  $J$  (0) is favored.

Considering these rules, the ground state term symbol for carbon is  $^3P_0$ , with  $L = 1$ ,  $S = 1$ , and  $J = 0$ .

**Remark:** In this course, we focus on determining the ground state term symbol based on Hund's rules, without considering the antisymmetry of the wavefunction due to electron exchange. However, it is important to note that a comprehensive ground state estimation in quantum mechanics also demands antisymmetry in accordance with the Pauli exclusion principle. While this antisymmetry is a fundamental aspect for accurate predictions of quantum states, its detailed analysis falls outside the purview of the syllabus. For a deeper understanding and further reading on this topic, please refer to the additional notes provided on Moodle.