Lecture Notes: Basics of Structure and Properties of Matter

1 Introduction

The structure and properties of matter are foundational concepts in physics and material science. At the microscopic scale, everything is made up of atoms and molecules, held together by various types of bonds. In this lecture, we'll delve deep into understanding these basic units and their arrangements, especially focusing on crystalline structures.

2 Atoms and Molecules

2.1 Atoms

An atom is the smallest unit of a chemical element, comprising a nucleus of protons and neutrons with electrons orbiting this nucleus. The atomic number (denoted Z) defines the number of protons and thus the chemical element.

2.1.1 Atomic Orbitals and Energy Levels

Electrons in an atom are located in specific regions around the nucleus known as atomic orbitals. These orbitals represent the probability distribution for finding an electron at any given point in space. They are organized into energy levels or shells. The primary types of orbitals are denoted as s, p, d, and f, each with a characteristic shape and orientation in space. The number of electrons that can fit into each type of orbital is fixed: s can hold 2, p can hold 6, d can hold 10, and f can hold 14.

The energy levels represent different distances from the nucleus, with electrons in higher energy levels being further away. Each energy level can

contain a certain number of electrons, with the first level (closest to the nucleus) being filled first, followed by the second, and so on.

2.1.2   Interaction of Atomic Orbitals

When atoms bond, their atomic orbitals interact and combine to form molecular orbitals. The manner in which these orbitals interact determines the type of bond formed: for example, sigma (σ) and pi (π) bonds in covalent bonding. The overlapping of atomic orbitals can result in constructive interference (bonding orbitals) or destructive interference (antibonding orbitals).

Sigma (σ) and pi (π) bonds are two fundamental types of covalent bonds formed between atoms. A sigma bond is formed by the head-on overlapping of atomic orbitals, resulting in electron density concentrated between the two bonding atoms, providing a direct pathway of electron sharing. It is the strongest type of covalent bond and is found in all single bonds. On the other hand, a pi bond arises from the lateral or side-to-side overlapping of adjacent atomic orbitals, typically p orbitals. This leads to electron density being distributed above and below the plane of the nuclei of the bonding atoms. Pi bonds are generally weaker than sigma bonds and are typically found in double and triple bonds; for instance, a double bond consists of one sigma and one pi bond, while a triple bond comprises one sigma and two pi bonds.
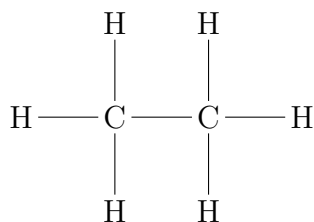
2.1.3   Sigma (σ) Bonds

2.1.4   Hydrogen Molecule (H_2)

The simplest example of a sigma bond is found in the hydrogen molecule. Two hydrogen atoms come together, and their 1s orbitals overlap head-on to form a σ bond.

$$H \text{——} H$$

2.1.5   Ethane (C_2H_6)

In ethane, each carbon atom forms sigma bonds with three hydrogen atoms and one with another carbon atom.

$$\begin{array}{ccc} & \text{H} & \text{H} \\ & | & | \\ \text{H} - \text{C} & - & \text{C} - \text{H} \\ & | & | \\ & \text{H} & \text{H} \end{array}$$

3 Pi (π) Bonds

3.0.1 Ethene (C_2H_4)

In ethene, apart from the sigma bonds formed by overlapping sp2 hybridized orbitals, a π bond is formed by the side-to-side overlapping of the unhybridized p orbitals of the two carbon atoms.

$$\text{H} - \text{C} = \text{C} - \text{H}$$

3.0.2 Acetylene (C_2H_2)

Acetylene has a triple bond between the two carbon atoms, consisting of one σ bond (from head-on overlapping of sp hybridized orbitals) and two π bonds (from side-to-side overlapping of two pairs of unhybridized p orbitals).

$$\text{H} - \text{C} \equiv \text{C} - \text{H}$$
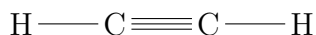
3.0.3 Importance in Material Science

Atomic orbitals play a crucial role in determining the electronic, optical, and magnetic properties of materials. The arrangement and interactions of these orbitals influence how electrons move through a material, which in turn affects its conductivity, reflectivity, and other key properties. Understanding these interactions at the atomic and molecular levels allows scientists and engineers to design and synthesize new materials with desired properties.
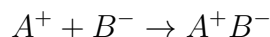
3.1 Molecules

Molecules are groups of two or more atoms held together by chemical bonds. A molecule can be homogeneous (same type of atoms) or heterogeneous (different types of atoms).

4 Chemical Bonds

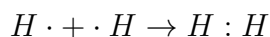There are mainly three types of chemical bonds:

4.1   Ionic Bonds

Formed when one atom donates an electron to another atom. Represented by the equation:
$$A^+ + B^- \rightarrow A^+B^-$$
where A^+ is a cation and B^- is an anion.

4.2   Covalent Bonds

Formed when atoms share electrons. For instance, in a hydrogen molecule:

$$H \cdot + \cdot H \rightarrow H : H$$

where the dots represent valence electrons.

4.3   Metallic Bonds

In metals, atoms release their outer electrons to form a 'sea' of delocalized electrons around a lattice of positively charged ions.

5   Chemical Bonds: A Detailed Comparison

Sigma (σ), pi (π), ionic, and metallic bonds are fundamental types of chemical bonds with distinct characteristics and roles in chemical structures.

5.1   Formation and Nature

- **Sigma (σ) Bond**: Formed by the direct (head-on) overlap of atomic orbitals with electron density concentrated between the bonding atoms.

- **Pi (π) Bond**: Arises from the lateral (side-to-side) overlap of adjacent atomic orbitals.

- **Ionic Bond**: Forms when atoms transfer electrons, resulting in oppositely charged ions that are held together by electrostatic forces.

- **Metallic Bond**: Characterized by a lattice of positive ions (cations) surrounded by a sea of delocalized electrons. These electrons are free to move throughout the lattice, leading to the characteristic properties of metals.

5.2   Occurrence

- **Sigma and Pi Bonds**: Predominantly between nonmetals where atoms share electrons.

- **Ionic Bond**: Typically between metals and nonmetals.

- **Metallic Bond**: Observed in metals and their alloys.

5.3   Strength and Properties

- **Sigma (σ) Bond**: Strongest due to direct overlap.

- **Pi (π) Bond**: Weaker than sigma bonds due to more diffuse overlap.

- **Ionic Bond**: Varies in strength depending on the ions involved.

- **Metallic Bond**: Generally strong, leading to properties like malleability, ductility, electrical conductivity, and luster in metals.

5.4   Electron Distribution

- **Sigma (σ) Bond**: Between the atomic nuclei.

- **Pi (π) Bond**: Above and below (or to the sides of) the atomic nuclei.

- **Ionic Bond**: Electrons are localized around one of the atoms.

- **Metallic Bond**: Delocalized electrons freely moving throughout the metal lattice.

## 5.5   Rotational Freedom and Other Characteristics

- **Sigma (σ) Bond**: Allows free rotation around the bond axis.

- **Pi (π) Bond**: Restricts rotation due to the lateral overlap.

- **Ionic Bond**: High melting and boiling points due to strong electrostatic forces.

- **Metallic Bond**: Results in electrical conductivity, malleability, and ductility in metals.

6   Crystalline Structures

Crystals are solids having, in all three dimensions of space, a regular repeating internal unit of structure. Common crystal structures include:
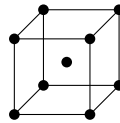
6.1   Simple Cubic (sc)

Atoms are arranged at the corners of a cube. This is the simplest repeating unit in crystalline structures.
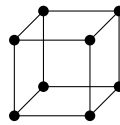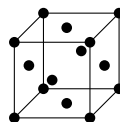
6.2   Body-Centered Cubic (bcc)

Apart from atoms at the corners of the cube, there's also an atom at the cube's center.

6.3   Face-Centered Cubic (fcc)

Atoms are present at the corners and the centers of all the cube faces.

7   Atoms and Quantum Mechanics

7.1   Wave Functions and Orbitals

Atoms and their behavior are fundamentally quantum mechanical in nature. Electrons in an atom don't possess exact trajectories, but rather, they have probability distributions described by wave functions, typically denoted as ψ. The square of the wave function, $|\psi|^2$, gives the probability density of finding an electron at a particular point in space.

8 Time-independent Schrödinger Equation for a Single Electron Atom

The Schrödinger equation for a single electron atom (like hydrogen) is given by:

$$\hat{H}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \tag{1}$$

where:

- $\hat{H}$ is the Hamiltonian operator which represents the total energy of the system. It comprises the kinetic energy of the electron and its potential energy due to the nuclear attraction.

- $\psi(r,\theta,\phi)$ is the wave function of the electron, which is a function of the spherical polar coordinates r (radial distance), θ (polar angle), and ϕ (azimuthal angle).

- E is the total energy of the electron in the atom.

In atomic units (where $\hbar = m_e = e = 1$), the Hamiltonian for the electron in the potential of the nucleus is:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{2}$$

where:

- ∇^2 is the Laplacian operator representing the second spatial derivatives.

- Z is the atomic number of the nucleus, representing the number of protons in the nucleus.

The Schrödinger equation serves as the foundational equation of quantum mechanics, describing the behavior of electrons in atomic and molecular systems.

The general form of the Schrödinger equation for a molecule with multiple atoms is:

$$\hat{H}\Psi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N}) = E\Psi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N}) \tag{3}$$

where:

- $\hat{H}$ is the Hamiltonian operator of the molecular system.

- $\Psi(\mathbf{r_1}, \mathbf{r_2}, ..., \mathbf{r_N})$ is the molecular wave function, which describes the state of all N electrons in the molecule.

- E is the total energy of the molecular system.

The Hamiltonian $\hat{H}$ for such a system can be expressed as:

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 + \sum_{i<j} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{A<B} \frac{Z_A Z_B}{|\mathbf{R_A} - \mathbf{R_B}|} \quad (4)$$

where:

- The first term represents the kinetic energy of all the electrons.

- The second term is the electron-electron repulsion.

- The third term describes the attraction between the electrons and the atomic nuclei.

- The fourth term is the nuclear-nuclear repulsion.

- $\mathbf{r_i}$ denotes the position vector of the ith electron.

- $\mathbf{R_A}$ denotes the position vector of the Ath nucleus.

- Z_A is the charge of the Ath nucleus (number of protons in the nucleus).

- M is the number of nuclei in the molecule.

8.1 Quantum Numbers

Every electron in an atom is described by a set of quantum numbers:

- Principal Quantum Number (n): Describes the main energy level and distance from the nucleus. $n = 1, 2, 3, \ldots$.

- Azimuthal Quantum Number (l): Describes the shape of the orbital. It ranges from 0 to $n - 1$. For a given l, the orbital types are: $l = 0$ (s), $l = 1$ (p), $l = 2$ (d), $l = 3$ (f), and so on.

- Magnetic Quantum Number (m_l): Describes the orientation of the orbital in space. It ranges from $-l$ to $+l$.

- Spin Quantum Number (m_s): Describes the electron's spin. It can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

8.2 Pauli Exclusion Principle

No two electrons in an atom can have the same set of four quantum numbers. This principle explains the electron configuration of atoms.

9 Sample Problem: Quantum Numbers

Given an electron in the $3d$ orbital, identify the possible sets of quantum numbers.

Solution: For a $3d$ orbital:

$$n = 3$$
$$l = 2 \quad (\text{since } d \text{ corresponds to } l = 2)$$
$$m_l = -2, -1, 0, 1, 2 \quad (\text{possible values for a } d \text{ orbital})$$
$$m_s = +\frac{1}{2} \text{ or } -\frac{1}{2} \quad (\text{two possible spins})$$

Hence, the sets of quantum numbers for electrons in a $3d$ orbital are:

$$(n, l, m_l, m_s) = (3, 2, -2, \pm\frac{1}{2}), (3, 2, -1, \pm\frac{1}{2}), (3, 2, 0, \pm\frac{1}{2}), (3, 2, 1, \pm\frac{1}{2}), (3, 2, 2, \pm\frac{1}{2})$$

10 Conclusion

The mathematical framework behind the structure of atoms and molecules is deeply rooted in quantum mechanics. These principles serve as a foundation for understanding molecular behavior, reactivity, and bond formation.

Understanding the basics of atomic and molecular structures and the types of bonds gives insights into the properties of materials. Crystalline structures further provide a view of how atoms or molecules are periodically arranged in materials, leading to their unique properties.

11 Hands-on Session: Introduction to Avogadro

11.1 Objectives

- Understand the basic user interface of Avogadro.

- Learn how to build, visualize, and manipulate molecular structures.

- Explore some of the basic computational tools available.

11.2 Prerequisites

- Avogadro software installed. You can download it from here.

11.3 Steps

Launching Avogadro and Navigating the Interface:

Open Avogadro software. Familiarize yourself with the main toolbar, sidebars, and status bar.

Creating a Simple Molecule:

Click on the "Draw" tool (pencil icon). Choose an element from the periodic table (e.g., Carbon). Left-click in the main window to place atoms. Draw bonds by clicking and dragging between atoms. Double or triple click for double or triple bonds, respectively.

Manipulating Molecules:

Use the "Selection" tool (arrow icon) to select atoms or bonds. Right-click on an atom to change its element type. Use the "Manipulate" tool (hand icon) to move atoms or rotate the molecule.

Building a Known Compound:

From the main menu, select Build ¿ Insert, and choose a molecule from the list (e.g., benzene). Rotate, zoom in/out, and explore the structure.

Optimizing Geometry:

With your molecule built, click on the Extensions menu. Choose Optimize Geometry. This will use a force field to adjust the molecule to a more energetically favorable conformation.

Visualizing Molecular Orbitals:

After building your molecule, click on the Extensions menu. Choose Molecular Orbitals. (Note: This may require a calculation to determine the orbitals.)

Exploring Surface Calculations:

Under the Extensions menu, find and select Surfaces. Experiment with different surface types, such as electron density or molecular orbitals.

Saving Your Work:

Click File – Save As to save your molecular structure in various formats.

12   Avogadro Exploration Homework

12.1   Objective

To familiarize yourself with the Avogadro molecular editor and visualization tool, understanding its various features, and applying it to study molecular structures and their properties.

12.2   Instructions

1. **Getting Started**:

   - Install Avogadro.
   - Launch the application and familiarize yourself with the main interface.

2. **Drawing and Understanding Basic Molecules**:

   - Using the "Draw" tool, create a simple molecule, such as Methane (CH_4).
   - Add a double bond, and convert it into Ethene (C_2H_4).
   - Change one carbon atom to oxygen, creating Ethanal (CH_3CHO).

3. **Manipulation and Visualization**:

   - Rotate, zoom in and out, and pan across your created molecule. Familiarize yourself with the visualization tools.
   - Try out different visualization styles available in Avogadro. For example, wireframe, stick, and space-filling models.

4. **Exploring Predefined Structures**:

   - Load a predefined structure of Benzene from the software's built-in database.
   - Visualize its molecular orbitals through the Extensions menu. Note down any observations.

5. **Molecular Optimization**:

   - Create a random, unoptimized molecule of your choice.
   - Use the Optimize Geometry function to adjust the molecule to a more energetically favorable conformation. Note the changes in bond lengths and angles before and after optimization.

6. **Advanced Visualization**:

   - Take any molecule (e.g., water).
   - Use the Surfaces option in the Extensions menu to visualize electron density around the molecule.
   - Experiment with other surface types like molecular orbitals. Note your observations.

7. **Research and Documentation**:

   - Investigate sigma (σ) and pi (π) bonds in ethene (C_2H_2) and ethyne (C_2H_2) using Avogadro.
   - Capture screenshots or render images of the bond types as visual aids.
   - Write a brief report (around 200-300 words) explaining the difference betweenσ and π bonds using your visual aids.

Submission

1. Save your created molecular structures in .cml format.

2. Combine the saved structures, screenshots, and your written report into a single zipped folder.

3. Submit the zipped folder as per your instructor's guidelines.

Evaluation

Your assignment will be evaluated based on:

- Accuracy and complexity of created molecular structures.

- Quality and clarity of the visual aids (screenshots/renderings).

- Depth of understanding demonstrated in the written report.

Tips

- Explore the Help section in Avogadro if you come across features you're unfamiliar with.

- Ensure your report is concise, clear, and free of jargon so that anyone can understand your explanations.