ME 4875/MTE 575 - C18

Introduction to Nanomaterials and Nanotechnology

Lecture 3 - Atomic Structure and Bonding
Atomic Structure and Bonding

• It’s important to know about atomic structure and bonding to understand how properties change at the nanoscale

• What are materials composed of?

• Where are these components in a material?

• How are they held together?

• What accounts for the different properties of materials?

• Goals:
  – Qualitative picture of electrons, atoms, binding between atoms, behavior of atoms and electrons in materials (mostly modern physics and chemistry)
  – Give you enough background to read papers about nanomaterials
Basic Structure of Atoms

- Discovery of the electron (1896, J. J. Thompson)
- Discovery of atomic nucleus (1911, Rutherford)

Alpha particles are He$^{2+}$
(two protons and two neutrons)

- Positively charged nucleus containing positively charged protons and neutral neutrons (both very heavy)
- Negatively charged electrons (very light) moving around the nucleus

Uniform distribution of charge
Wave-Particle Duality of Electrons

- Mass-energy equivalence, $E = mc^2$
- Planck’s equation $E = h\nu = \frac{hc}{\lambda}$
- de Broglie relationship $\lambda = \frac{h}{mu}$ (1924)
- Wavelength of the electrons in a 200 kV TEM is 2.5 pm ($2.5 \times 10^{-12}$ m)
Electron Diffraction

- Typical electron **wavelength** is comparable to atomic spacing in crystal, leading to diffraction

constructive interference

\[ 2d \sin \theta = n\lambda \]

destructive interference
Isolated Atoms

• Bohr Model - electron ‘orbits’
  (1913)

  \[ 2\pi r = n\lambda = \frac{nh}{m_e u} \rightarrow r = \frac{nh}{2\pi m_e u} \]
  (each orbit has integer number of wavelengths)

  \[ \frac{m_e u^2}{r} = \frac{Zke^2}{r^2} \rightarrow u = \sqrt{\frac{Zke^2}{rm_e}} \]
  (centripetal force = electrostatic force)

  \[ E = \frac{1}{2} m_e u^2 - \frac{Zke^2}{r} = -\frac{Zke^2}{2r} \]
  (total energy = kinetic energy + electrical potential energy)

  \[ E = -\frac{4\pi^2 Z^2 (ke^2)^2 m_e}{2\hbar^2 n^2} \]
  (Final result: energies of orbits are quantized)
Isolated Atoms

- **Schrödinger equation**
  \[ \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U \Psi = E \Psi \]
  (1926)

- Solutions are ‘orbitals’ with quantum numbers \( n, l, m, s \)
  - \( n \) is principal quantum number (which shell)
  - \( l \) is angular momentum quantum number \( l = 0, 1, 2, \ldots (n-1) \) (which shape)
  - \( m \) is magnetic quantum number \( m = 0, \pm 1, \pm 2, \ldots \pm l \) (which orientation)
  - \( s \) is spin quantum number \( \pm \frac{1}{2} \) (two electrons can occupy each orbital)

- Tells us how many electrons can be in each shell (1s\(^2\), 2s\(^2\), 2p\(^6\), etc.)

\[ s \ (l=0) \quad p \ (l=1) \quad d \ (l=2) \quad f \ (l=3) \]
Bonds between Atoms

Ionic Bond (transferred electrons) to make “complete” shells

\[1s^22s^22p^63s^1 \quad 1s^22s^22p^63s^23p^5 \quad 1s^22s^22p^6 \quad 1s^22s^22p^63s^23p^6\]

Gives two oppositely charged ions, which then have an electrostatic attraction (a bond)
Bonds between Atoms

- Covalent Bond (shared electrons) to make “complete” shells
- Electrons are localized between the ion cores

\[ \text{O} + \text{O} \quad 1s^22s^22p^4 \]

\[ \text{O}_2 \quad 1s^22s^22p^6 \]

The positive ion cores of each atom are attracted electrostatically to the shared electrons, resulting in a bond.
Metallic Bonding (shared \textit{delocalized} electrons)
Bonds between Atoms

Van der Waals Bond (attraction between dipoles)

permanent dipoles (Keesom Force)

permanent/induced dipoles (Debye Force)

instantaneous induced dipoles (London Force)
Bonds between Atoms

• What happens to the atomic orbitals when bonds are formed between atoms?

Atomic Orbitals:

- $s\ (l=0)$
- $p\ (l=1)$
- $d\ (l=2)$
- $f\ (l=3)$
Molecular Orbitals

Here, sign means phase, not charge

- When two atomic orbitals combine (by overlapping in space), they form two molecular orbitals with different energies
- Linear combination of atomic orbitals (approximate)
Molecular Orbitals

Bonding

Antibonding
Solids (Giant Molecules)

• What happens when more than two atoms combine into a molecule?

• The final number of molecular orbitals is equal to the number of atoms

![Diagram showing bonding and antibonding orbitals for single, two, four, and many atoms (solid).](approximate picture)
Metals, Semiconductors and Insulators

- **Metal**: High density of states near the Fermi level, allowing easy movement of electrons.
- **Semiconductor**: High density of states near the Fermi level, with a small gap for movement of electrons.
- **Insulator**: States near the Fermi level are fully occupied, preventing movement of electrons.

At 0 K:
- Metal: All states are occupied.
- Semiconductor: States near the Fermi level are partially occupied, with a small gap.
- Insulator: States near the Fermi level are fully occupied.

At > 0 K:
- Metal: States near the Fermi level remain unoccupied due to thermal energy.
- Semiconductor: States near the Fermi level become more occupied due to thermal energy.
- Insulator: States near the Fermi level remain fully occupied, unaffected by thermal energy.
Next Class

• Next class, we’ll look at crystal structures (how atoms are arranged in a solid)

• For students who are waiting for the registrar to add them to the course and do not have access to Canvas, please go to Prof. Rao’s website nanoenergy.wpi.edu, then click on “ME 4875/MTE 575 Content” tab to access the course materials.
Due tonight by 11:59 pm for those students who are doing a group project

1. Solar Cells
2. Batteries
3. Structural Materials
4. Thermoelectrics
5. Computing (transistors)
6. Memory (magnetic, flash, etc)
7. Drug delivery/Nanomedicine
8. Biological Sensing
9. Chemical Sensing
10. Catalysis
11. Energetic Materials
12. Piezoelectrics
13. Robotics
14. Photonics
15. Coatings