The Solid State
WS 2013/14

Lectures (Tuesday & Friday)

Paul van Loosdrecht
Optical Condensed Matter Physics, II. Physikalisches Institut
pvl@ph2.uni-koeln.de

Website II. Physikalisches Institut
www.ph2.uni-koeln.de
http://www.ph2.uni-koeln.de/527.html
## Structure of Matter, SSP

<table>
<thead>
<tr>
<th>Lectures</th>
<th>Tue. 8:00 - 9:45</th>
<th>Auditorium II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fri. 12:00-13:45</td>
<td></td>
</tr>
<tr>
<td>Tutorials</td>
<td>Thu. 14:00-16:00</td>
<td>Auditorium II</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exam</td>
<td>See schedule on web</td>
<td>See schedule on web</td>
</tr>
</tbody>
</table>
Tutorials

Thursday 2PM, H II
Dr. Thomas Koethe (koethe@ph2.uni-koeln.de)
Homework, Tutorials, Grading

• Handout of homework in lecture on Friday. To be discussed on the Thursday after
• Level of questions is partially tutorial, partially on the level of the exam
• Lectures and tutorials are not obligatory, but without them it will be very, very hard to do the exam
• Grading: result of the final exam (covering all Structure of Matter)
Structure of Matter, SSP

Literature

- Introduction to Solid state physics
  Charles Kittel = ‘K’

- Solid state physics
  Ashcroft and Mermin

- Physical Chemistry
  Peter Atkins
  Chapter 19

- Modern Physics
  John C. Morrison = ‘M’

AND MANY OTHERS, see library…
Structure of Matter, SSP

- am
- fm
- pm
- nm
- μm
- m
States of matter

- Plasma
- Gas
- Liquid
  - Liquid crystals
  - Glasses
- Amorphous solids
- Quasi periodic crystals
- Nearly periodic crystals
- Periodic crystals
From molecules to solids: electronic bands

100's of nanometers
Why condensed matter physics

• **World around us**
  – How is information stored
  – Why are metals shiny and diamond transparent
  – Why is it difficult to build a faster computer
  – Why does glass break and metals bend

• **Deep science**
  – Many concepts and methods
  – ~50 or so Nobel prizes over the years
  – Most interesting science where reductionism stops

• **One of the best labs for testing foundational theory**
  – Quantum mechanics
  – Statistical physics
Structure of Matter, SSP

• Topics
  – Bonding, Symmetry and Crystal structure (K-1&3; M-8)
  – Diffraction and Reciprocal space (K-2; M-8)
  – Lattice vibrations (phonons) and thermodynamical properties (K-4&5)
  – Electronic structure of solids and transport; metals, insulators and semiconductors (K-6&7; M-7.7,8 & 9.1)
  – Special topics: Magnetism and/or superconductivity
Today

• Bonding
• Crystal structure
Bonding in molecules and solids

- **Covalent**
  - A - A

- **Polar**
  - $A^{-\delta} - B^{+\delta}$

- ** Ionic**
  - $A^{-} - B^{+}$

Electronegativity difference

- Structure of Matter – WS13/14 – van Loosdrecht – Lecture 1
Bonding in molecules and solids

• **Covalent bonding**
  – Two atoms sharing electrons equally
  Example: H₂, CH₄, CO₂

• **Ionic bonding**
  – One atom donating electron to partner
  Example: NaCl

• **Polar covalent bond**
  – In between situation
  Example: H₂O
Bonding in molecules and solids

- Metallic bonding
  - All atoms sharing their electrons
- van der Waals bonding
  - Example: Graphite
- Hydrogen bonds
  - Example: Water
Molecular theories for bonding

- Valence Bond Theory
  - Originates from Heitler, London. 1927
  - First proposal ‘sharing electrons’: Lewis 1916
  - Strong electron correlations
  - QM approach, incorporating exchange

\[ \Psi(1,2) = (A(1)B(2) + A(2)B(1))\left\{\uparrow\downarrow\right\} - \left\{\downarrow\uparrow\right\} \]

- Later extended (Pauling) to include hybridization

Linus Pauling 1901-1994
1954 Nobel Chem. (bonding)
1962 Nobel Peace (nuclear tests)
Valence Bond Theory

- Heitler-London approach to $H_2$
- Fermions
  - total wavefunction is antisymmetric
- Wavefunction = orbital + spin part
- Either symm. Spin /Antisymmm. Orbit or vice versa.
  - Use this property to construct wvfncats
- Exchange parity operator $P$: 
  
  $P\Psi = \Psi$ if $\Psi$ symmetric
  
  $P\Psi = -\Psi$ if $\Psi$ antisymmetric
H$_2$ bonding, orbital part

Bonding orbital
  Symmetric orbital part
  Anti-symmetric spin part (singlet)
Electron density on bond

Anti-Bonding orbital
  Anti-symmetric orbital part
  Symmetric spin part (triplet)
Electron density on atoms
H$_2$ bonding, orbital part

Bonding orbital
  Symmetric orbital part
  Anti-symmetric spin part (singlet)
Electron density on bond due to positive interference wavefunctions

Anti-Bonding orbital
  Anti-symmetric orbital part
  Symmetric spin part (triplet)
Electron density on atoms
H$_2$ Bonding, spin part

Anti-symmetric

singlet (S=0):

\[ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \]

Symmetric

Triplet (S=1):

\[ m_s = 1 \quad |\uparrow\uparrow\rangle \]
\[ m_s = 0 \quad |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \]
\[ m_s = -1 \quad |\downarrow\downarrow\rangle \]
σ- and π-bonds

- σ-bond: bond between axially (w.r.t. bonding axis) symmetric orbitals
- π-bond: bond between axially non-symmetric orbitals → conjugation, torsional stiffness

Conjugated molecules

Ethene
Molecular electronics

Diarythelene: switching conjugation

BINDING IN SOLIDS

Molecular
Covalent
Ionic
Metallic
Molecular Solids

- Van der Waals bonding (weak interaction)
- Most organic molecules, inert gases
- Low melting point (often below 300 K)
- Soft, easy to deform & compress
- Typically poor conductors

Solid CO₂ (dry ice)

Lysosome crystal (NASA)
Ionic Solids

- NaCl, KCl, etc.
- Ions are ‘closed shell’ → no directional bonding → close packed structures
- Poor electrical conductors
- Strong bonding → hard & high melting points
- To excite electrons requires UV, reasonably transparent in the visible

HCP (ABAB)  FCC (ABCABC)
Covalent Solids

- 3D arrangement of ions bound by shared valence electrons
- difficult to deform because bonds are directional (‘MO`s’)
- Stiff, high melting point
- No free electrons → Insulators or semiconductors
- Diamond, silicon, germanium
Metallic Solids

- Insufficient # of electrons for covalent bonding
- Melting temp. can be low (Hg 234 K)
- Weakly bound outer electrons $\rightarrow$ delocalization
- excellent conductors of heat & electricity
- High reflectivity in IR/VIS range
Energy scales

Length scale atoms, orbitals, interatomic: \( r \sim 1 \, \text{Å} \)

Potential energy: Coulomb

\[
E = \frac{q^2}{r} \sim 14 \, \text{eV} \quad (160,000 \, \text{K})
\]

Kinetic energy: “Particle in a box”:

\[
E = \frac{\hbar^2 \cdot (1/r)^2}{2 \cdot m} \sim 4 \, \text{eV} \quad (45,000 \, \text{K})
\]

Ionic: Coulomb interaction

Metals: e\(^-\) - delocalization