The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Structure of Matter, SSP

Lectures	Tue. 8:00 - 9:45 Fri. 12:00-13:45	Auditorium II
Tutorials	Thu. 14:00-16:00	Auditorium II
Exam	See schedule on web	See schedule on web

Tutorials

Thursday 2PM, H II

Dr. Thomas Koethe (koethe@ph2.uni-koeln.de)

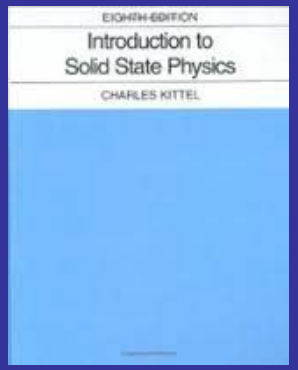
Homework, Tutorials, Grading

- 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)

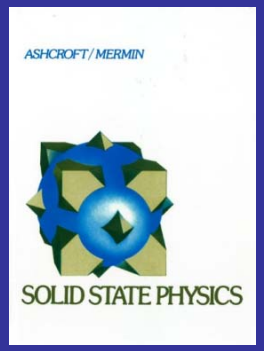
Structure of Matter, SSP

Literature

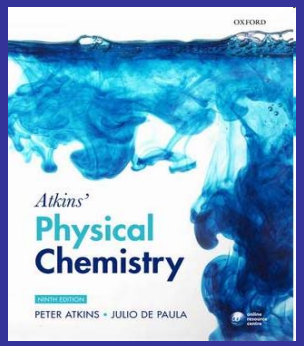
- Introduction to Solid state physics
  Charles Kittel
  = ‘K’



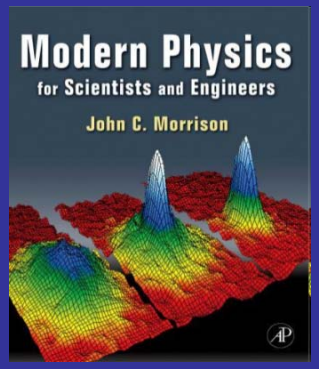
- Solid state physics
  Ashcroft and Mermin



- Physical Chemistry
  Peter Atkins
  Chapter 19

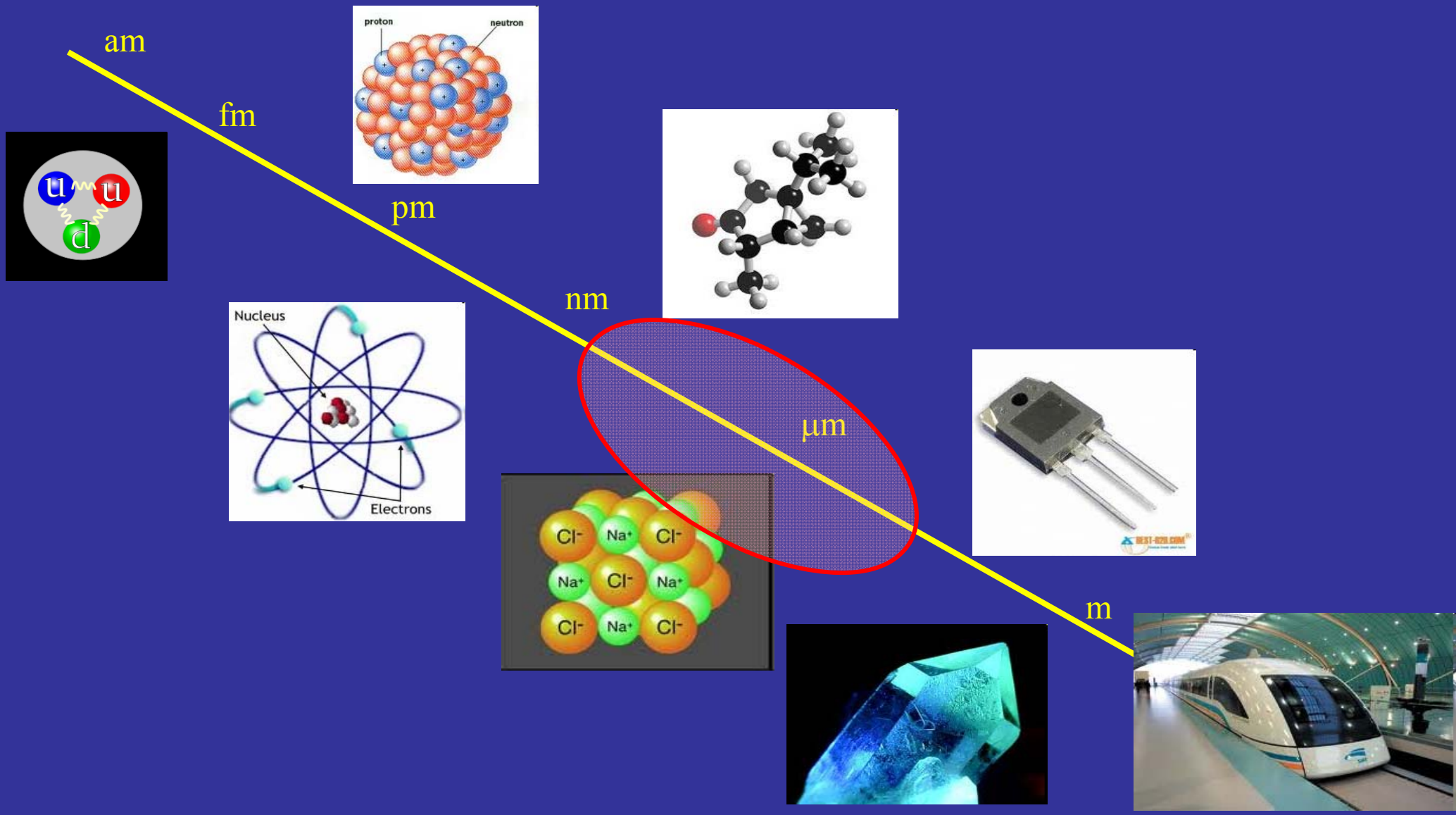


- Modern Physics
  John C. Morrison
  = ‘M’



AND MANY OTHERS, see library…

Structure of Matter, SSP



States of matter

Plasma

Gas

Liquid

Liquid crystals

Solids

glasses

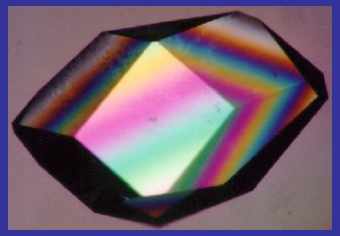
Amorphous solids

quasi periodic crystals

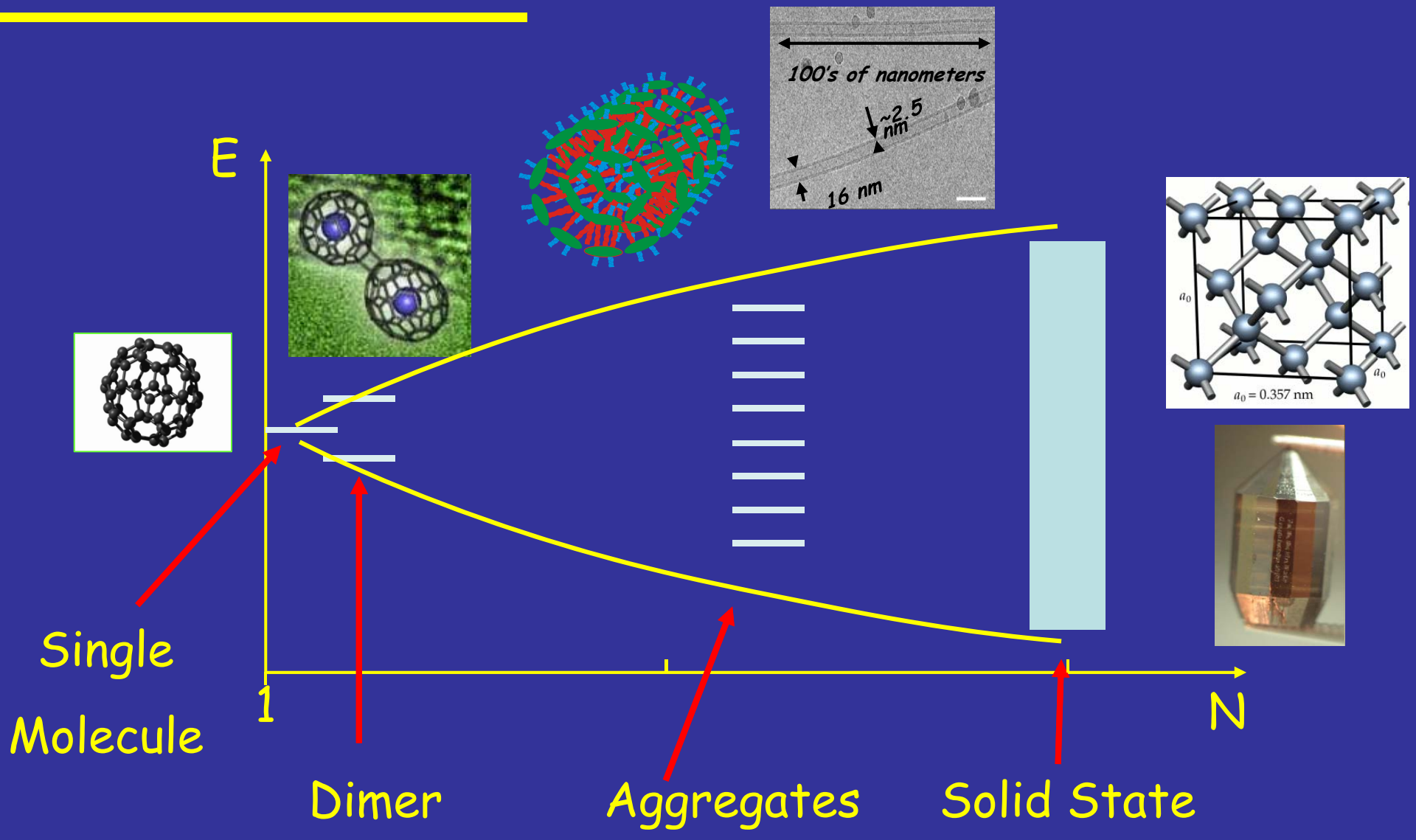
nearly periodic crystals

PERIODIC CRYSTALS

Order



From molecules to solids: electronic bands



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

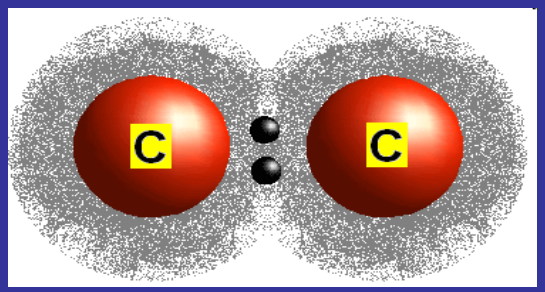
- Topics
  - Bonding, Symmetry and Crystal structure (K-1&3; M-8)
  - Diffraction and Reciprocal space (K-2; M-8)
  - Lattice vibrations (phonons) and thermodynamical properties (K-4&5)
  - Electronic structure of solids and transport; metals, insulators and semiconductors (K-6&7;M-7.7,8 & 9.1)
  - Special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

Today

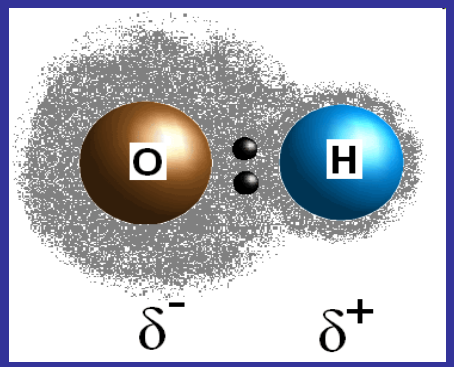
- Bonding
- Crystal structure

Bonding in molecules and solids

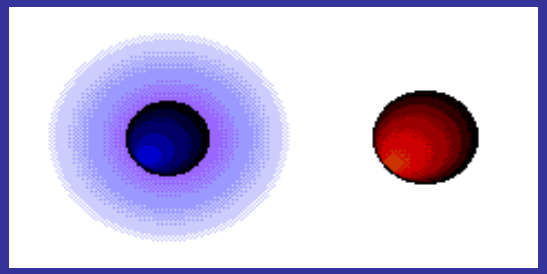
Covalent



Polar

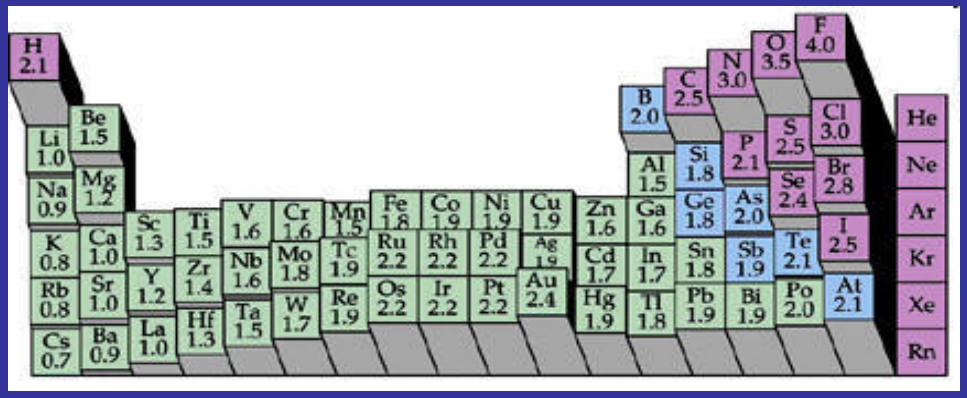


Ionic



Electronegativity difference

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

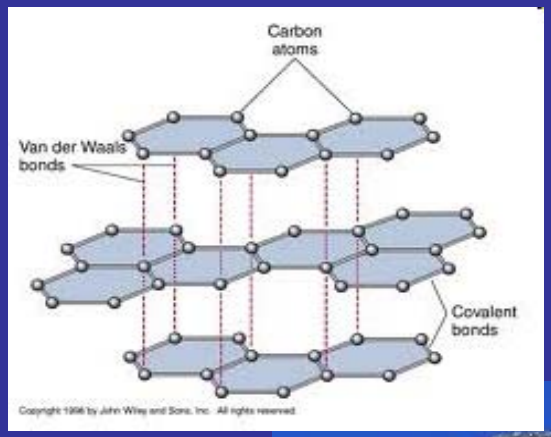


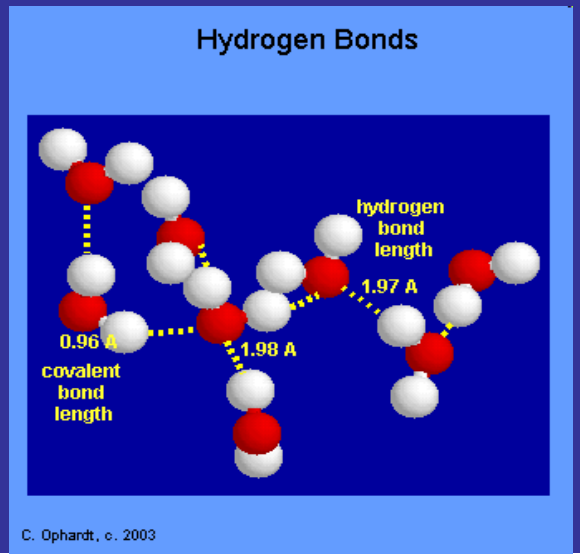
Bonding in molecules and solids

- Covalent bonding
  - Two atoms sharing electrons equally
    Example: H_2, CH_4, CO_2
- Ionic bonding
  - One atom donating electron to partner
    Example: NaCl
- Polar covalent bond
  - In between situation
    Example: H_2O

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

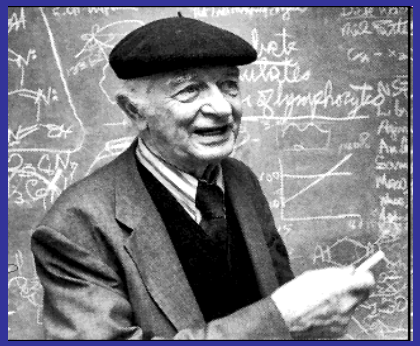
- Valence Bond Theory
  - Originates from Heitler, London. 1927
  - First proposal ‘sharing electrons’: Lewis 1916
  - Strong electron correlations
  - QM approach, incorporating exchange

$$\Psi(1,2) = \left(A(1)B(2) + A(2)B(1)\right)\left\{\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle\right\}$$

  - Later extended (Pauling) to include hybridization

Walter Heitler

Fritz London



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

Valence Bond Theory

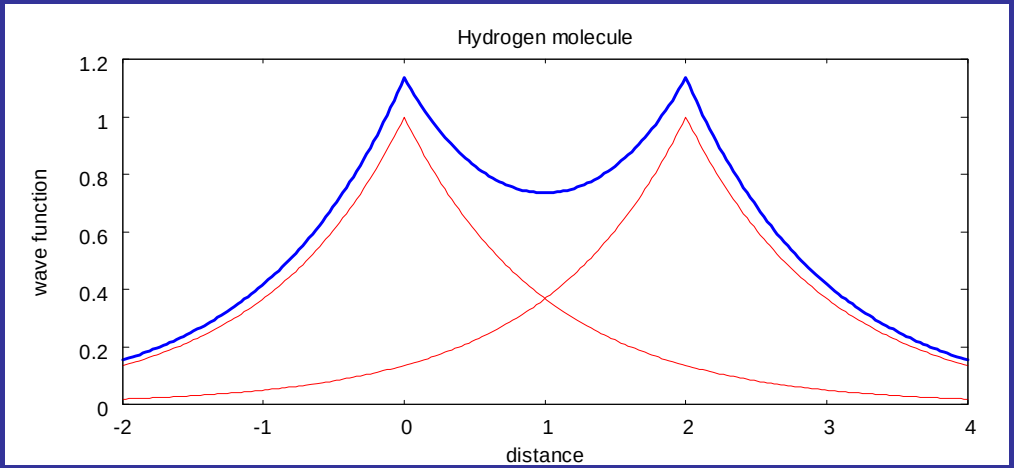
- Heitler-London approach to H_2
- Fermions
  → total wavefunction is antisymmetric
- Wavefunction = orbital + spin part
- Either symm. Spin /Antisymm. Orbit or vice versa.
  → Use this property to construct wvfncts
- Exchange parity operator P:

$$P\Psi = \Psi \text{ if } \Psi \text{ symmetric}$$
$$P\Psi = -\Psi \text{ if } \Psi \text{ antisymmetric}$$

H_2 bonding, orbital part

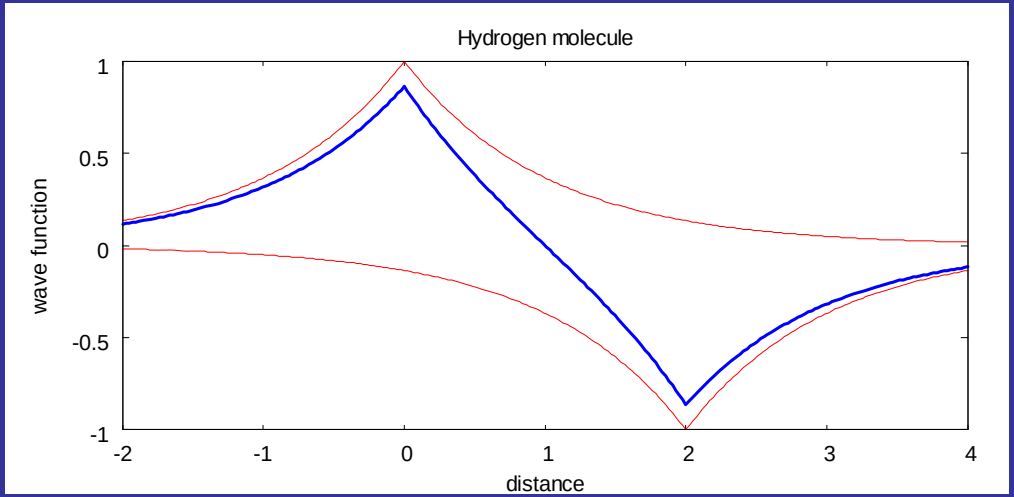
Bonding orbital
- Symmetric orbital part
- Anti-symmetric spin part (singlet)

Electron density on bond



Anti-Bonding orbital
- Anti-symmetric orbital part
- Symmetric spin part (triplet)

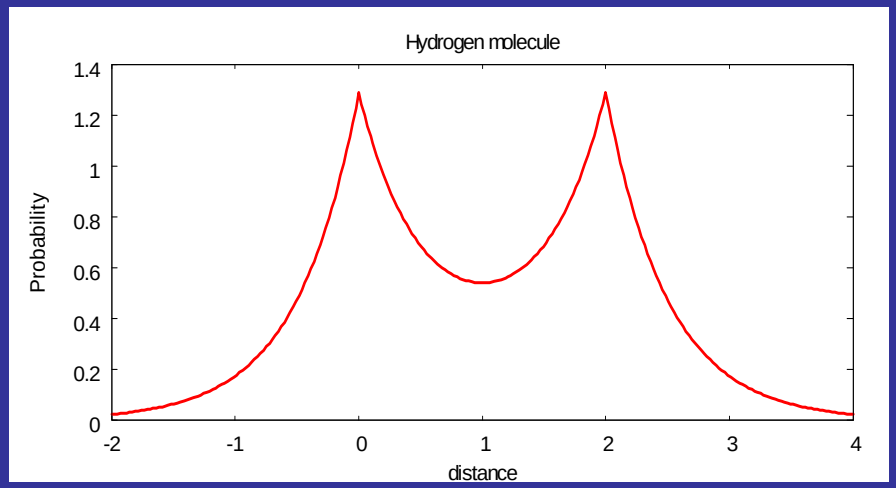
Electron density on atoms



H_2 bonding, orbital part

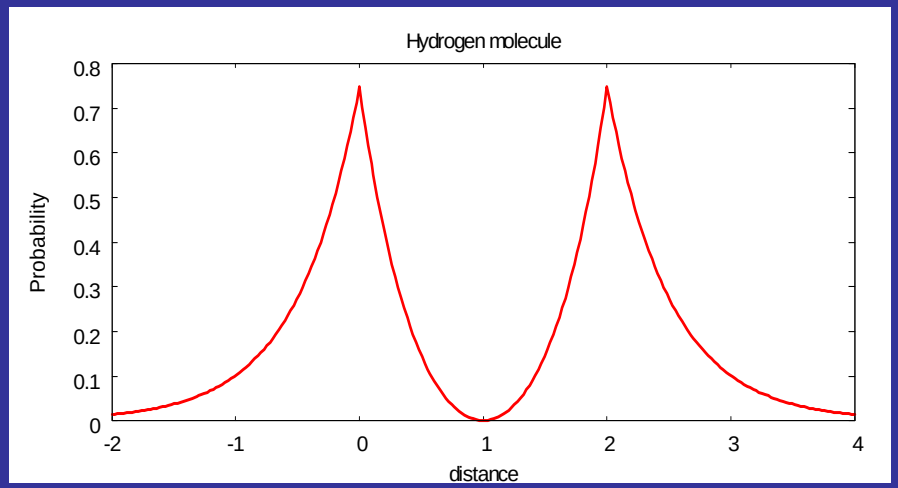
Bonding orbital
- Symmetric orbital part
- Anti-symmetric spin part (singlet)

Electron density on bond due to positive interference wvfncts



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): $\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle$

Symmetric

Triplet (S=1):

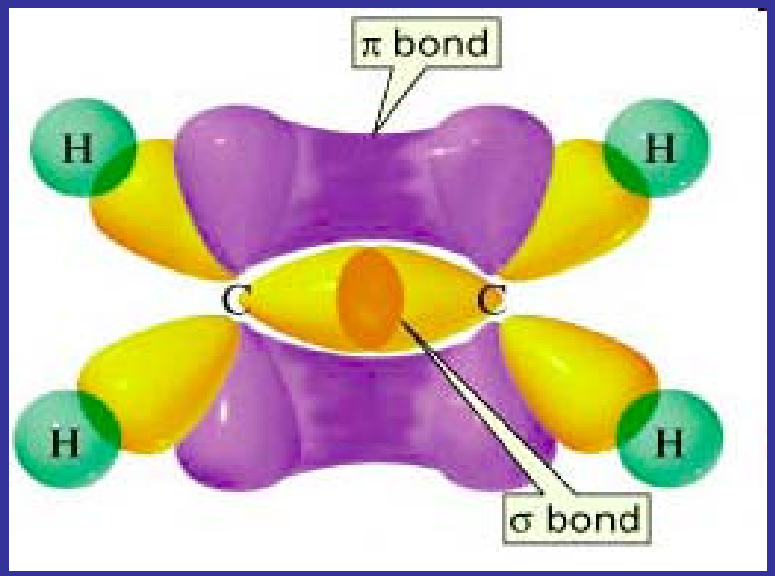
$$m_s = 1 \qquad \left|\uparrow\uparrow\right\rangle$$

$$m_s = 0 \qquad \left|\uparrow\downarrow\right\rangle + \left|\downarrow\uparrow\right\rangle$$

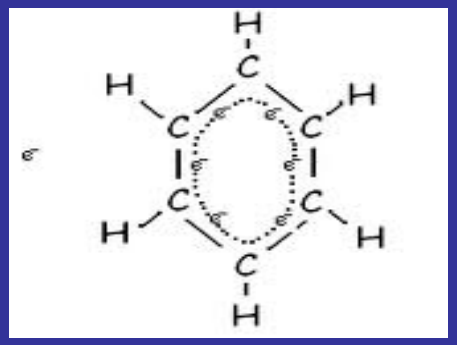
$$m_s = -1 \qquad \left|\downarrow\downarrow\right\rangle$$

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

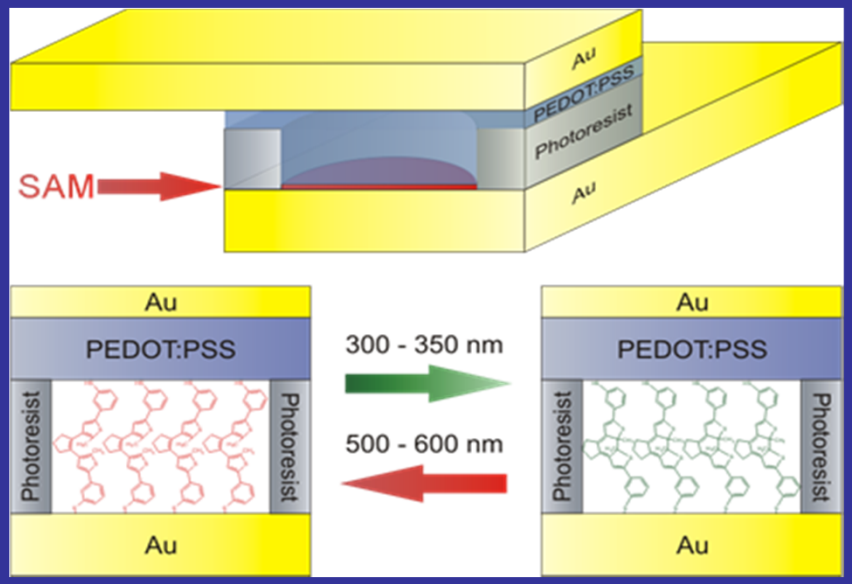


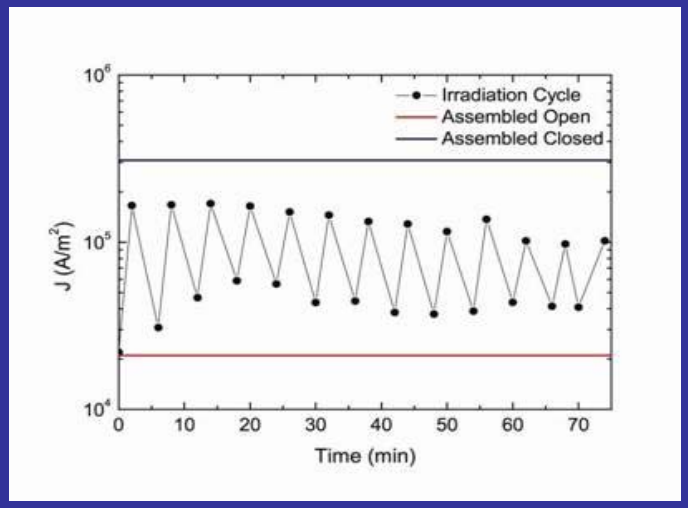
Ethene

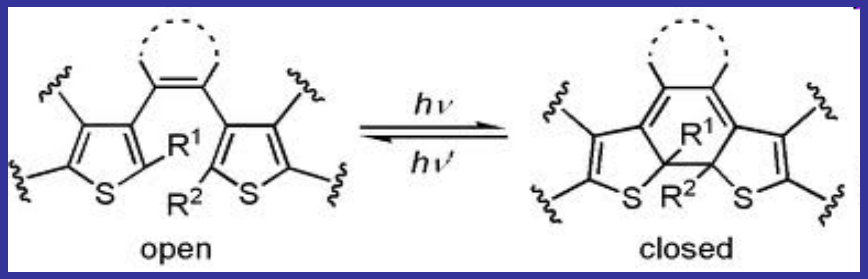


Conjugated molecules

Molecular electronics







Diarythelene: switching conjugation

De Boer, Blom, *et al.*, Nature 2006
Kronemeijer *et al.* Adv. Mat. 2008

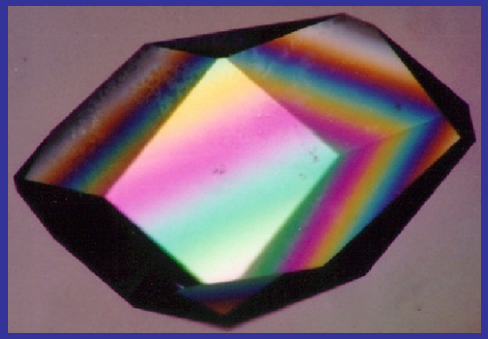
BINDING IN SOLIDS

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

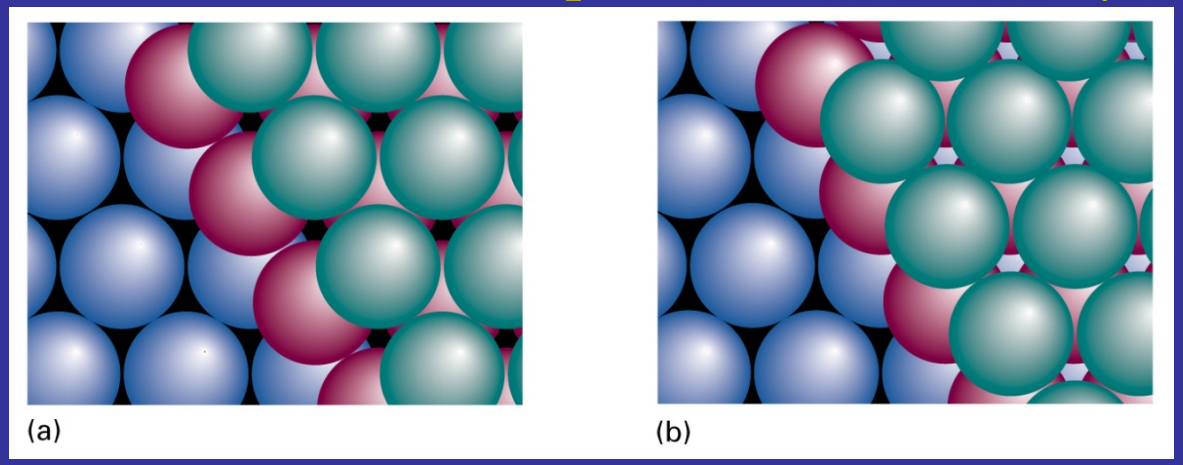
Solid CO_2 (dry ice)



Lysosome crystal (NASA)

Ionic Solids

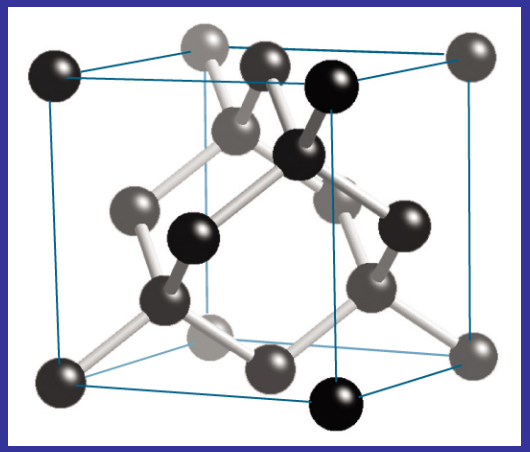
- NaCl, KCl, etc.
- Ions are 'closed shell' → no directional bonding → close packed structures
- Poor electrical conductors
- Strong bonding → hard & high melting points
- To excite electrons requires UV, reasonably transparent in the visible



HCP (ABAB) FCC (ABCABC)

Covalent Solids

- 3D arrangment 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



Diamond lattice

Metallic Solids

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

Ag Single Xtal

Energy scales

Length scale atoms, orbitals, interatomic: $r \sim 1$ Å

<u>Potential energy</u>: Coulomb

$$E = \frac{q^2}{r} \sim 14 \text{ eV} \quad (160.000 \text{ K})$$

<u>Kinetic energy</u>: “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