

# Structure of Matter The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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<http://www.ph2.uni-koeln.de/527.html>

# 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

# Structure of Matter, SSP

## Tutorials

Thursday 2PM, H II

Dr. Thomas Koethe ([koethe@ph2.uni-koeln.de](mailto:koethe@ph2.uni-koeln.de))

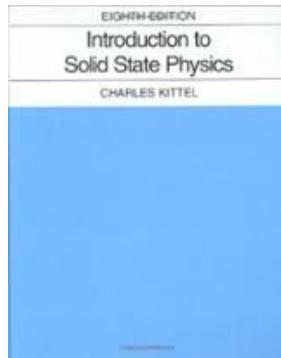
# Homework, Tutorials, Grading

- 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)

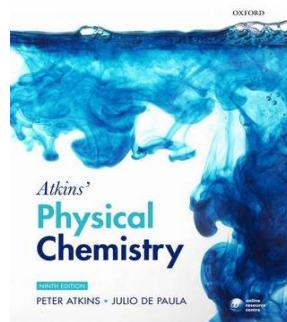
# Structure of Matter, SSP

## Literature

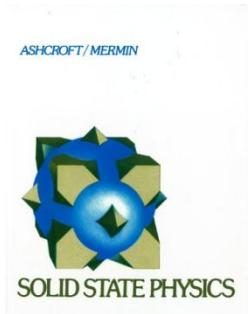
- Introduction to Solid state physics  
Charles Kittel  
= 'K'



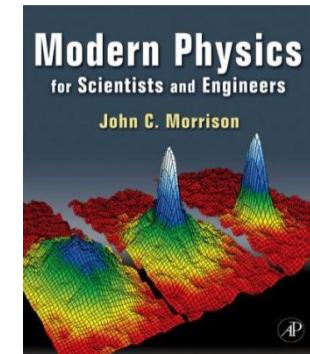
- Physical Chemistry  
Peter Atkins  
Chapter 19



- Solid state physics  
Ashcroft and Mermin

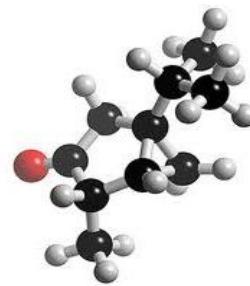
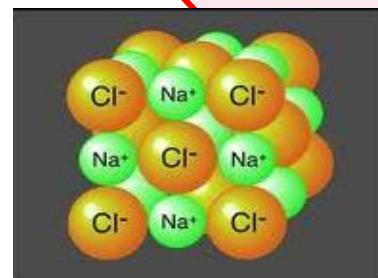
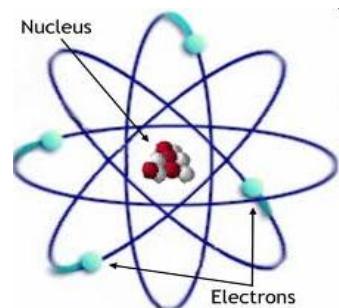
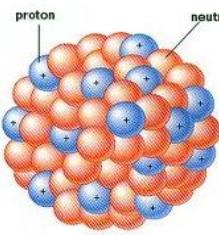
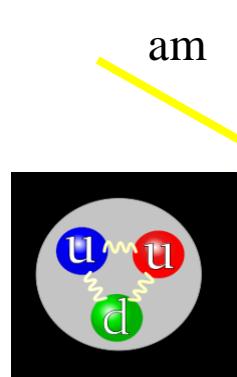


- Modern Physics  
John C. Morrison  
= 'M'



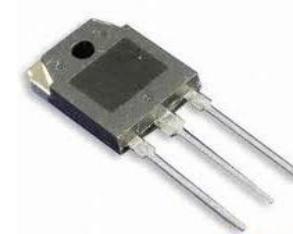
AND MANY OTHERS, see library...

# Structure of Matter, SSP



nm

μm



m

# States of matter

Plasma

Gas

Liquid

Liquid crystals

glasses

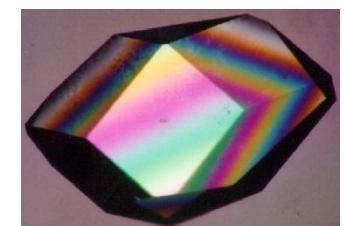
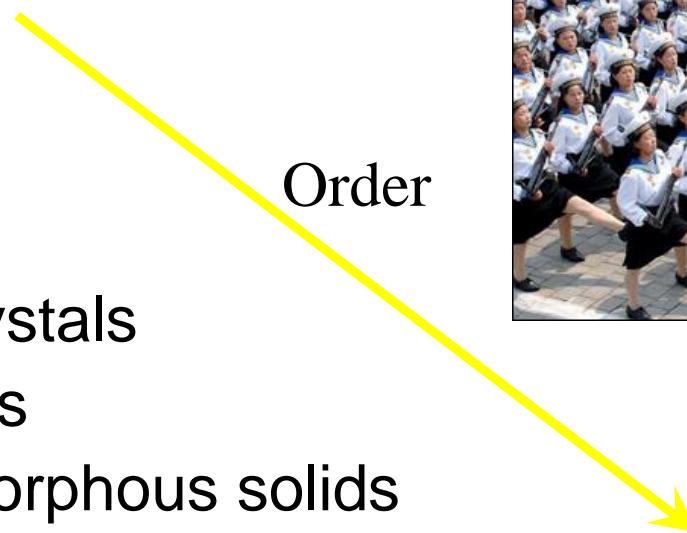
SOLIDS

Amorphous solids

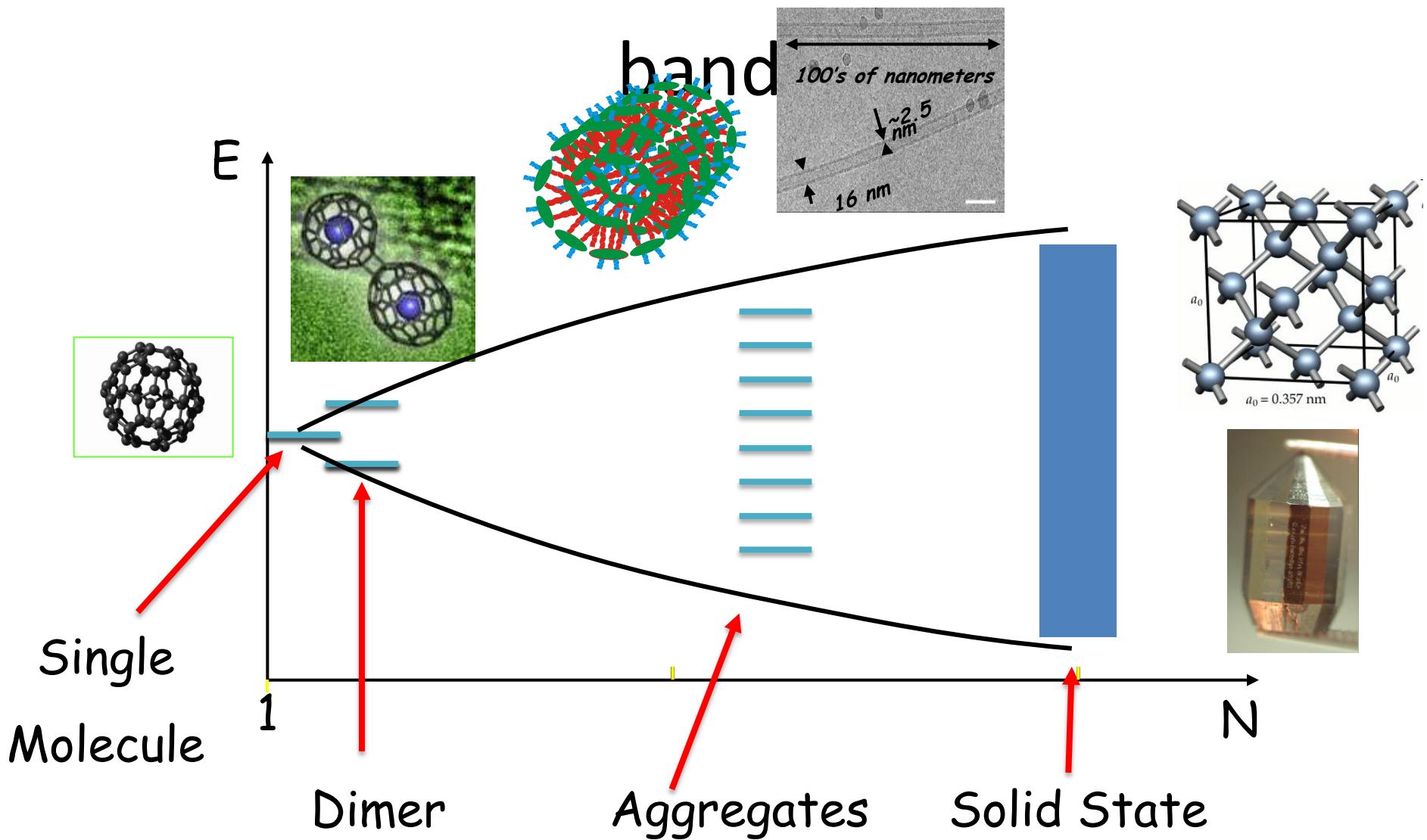
quasi periodic crystals

nearly periodic crystals

PERIODIC CRYSTALS



# From molecules to solids: electronic band



# 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

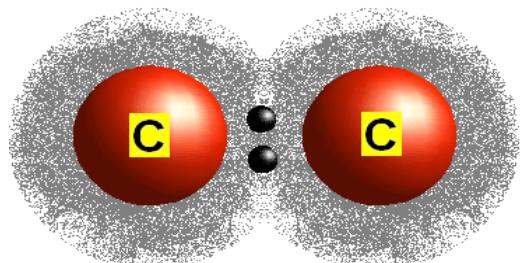
- Topics
  - Bonding, Symmetry and Crystal structure (K-1&3; M-8)
  - Diffraction and Reciprocal space (K-2; M-8)
  - Lattice vibrations (phonons) and thermodynamical properties (K-4&5)
  - Electronic structure of solids and transport; metals, insulators and semiconductors (K-6&7;M-7.7,8 & 9.1)
  - Special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

# Today

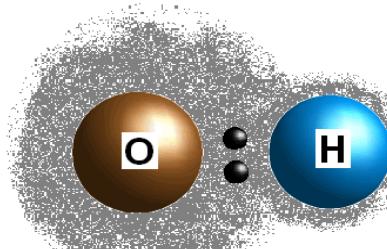
- Bonding
- Crystal structure

# Bonding in molecules and solids

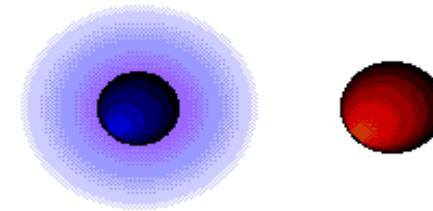
Covalent



Polar



Ionic



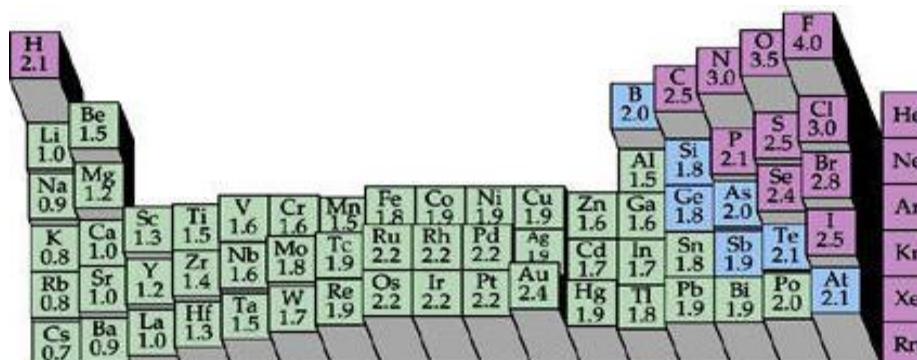
$\delta^-$        $\delta^+$

Electronegativity difference

$A - A$

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

$A^- - B^+$

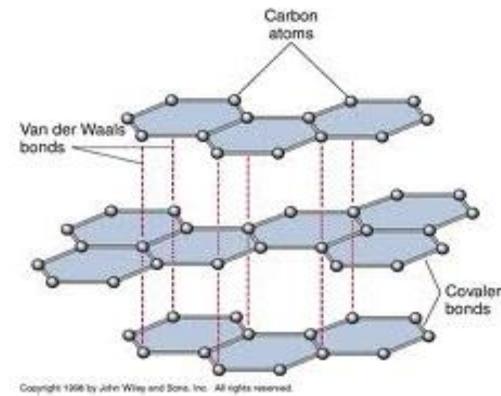


# Bonding in molecules and solids

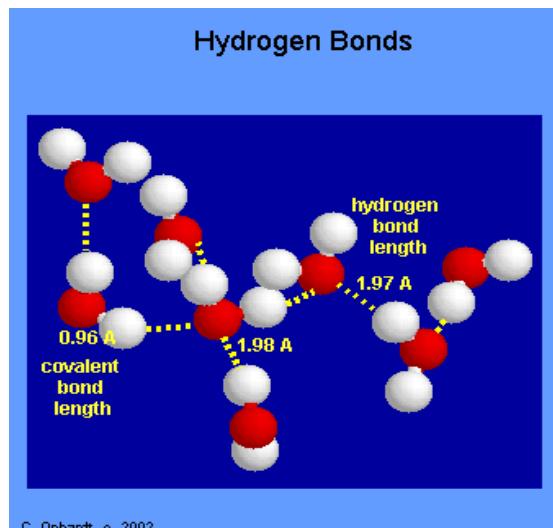
- Covalent bonding
  - Two atoms sharing electrons equally  
Example:  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$
- Ionic bonding
  - One atom donating electron to partner  
Example: NaCl
- Polar covalent bond
  - In between situation  
Example:  $\text{H}_2\text{O}$

# Bonding in molecules and solids

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



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C. Ophardt, c. 2003



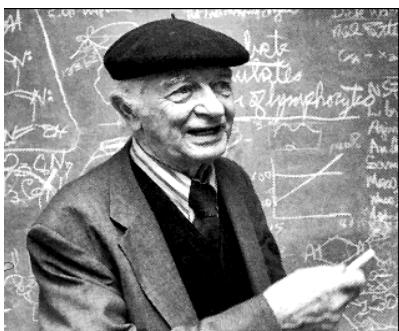
# Molecular theories for bonding

- Valence Bond Theory

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

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

- Later extended (Pauling) to include hybridization



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



Walter Heitler



Fritz London

# 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  $P$ :

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

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

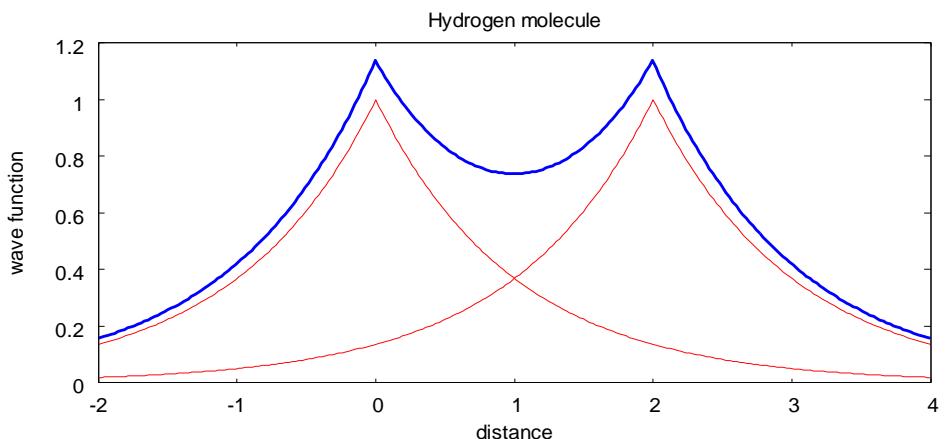
# $H_2$ bonding, orbital part

Bonding orbital

Symmetric orbital part

Anti-symmetric spin part (singlet)

Electron density on bond

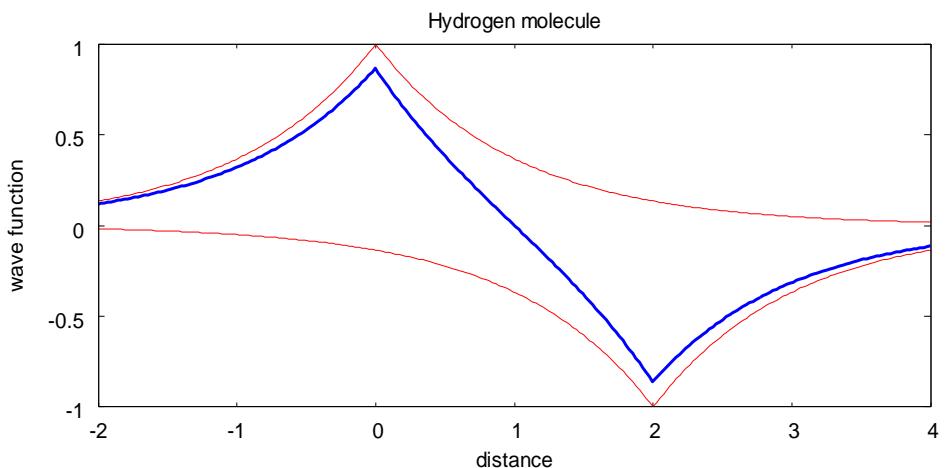


Anti-Bonding orbital

Anti-symmetric orbital part

Symmetric spin part (triplet)

Electron density on atoms



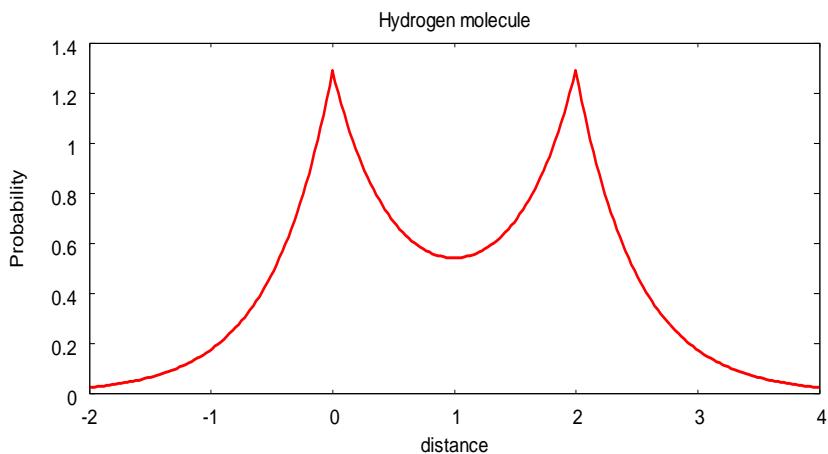
# $H_2$ bonding, orbital part

Bonding orbital

Symmetric orbital part

Anti-symmetric spin part (singlet)

Electron density on bond due to positive  
interference wvfncts

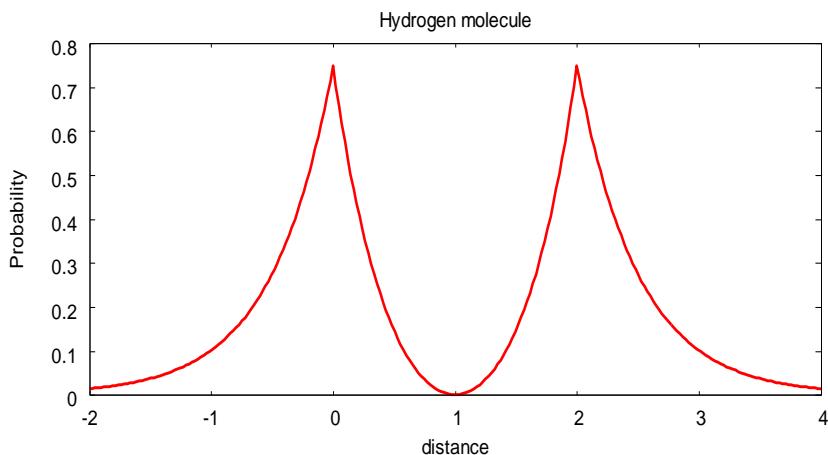


Anti-Bonding orbital

Anti-symmetric orbital part

Symmetric spin part (triplet)

Electron density on atoms



# $H_2$ Bonding, spin part

Anti-symmetric

singlet ( $S=0$ ):

$$|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$$

Symmetric

Triplet ( $S=1$ ):

$$m_s = 1$$

$$|\uparrow\uparrow\rangle$$

$$m_s = 0$$

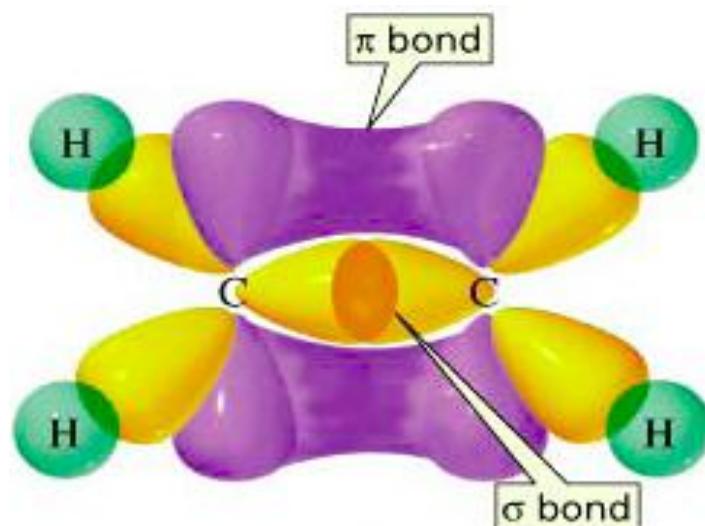
$$|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$$

$$m_s = -1$$

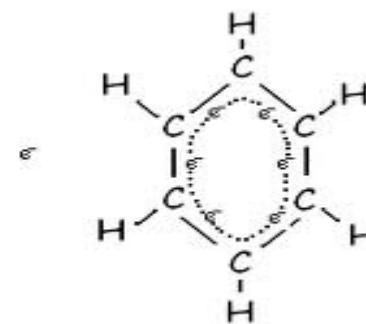
$$|\downarrow\downarrow\rangle$$

# $\sigma$ - and $\pi$ -bonds

- $\sigma$ -bond: bond between axially (w.r.t. bonding axis) symmetric orbitals
- $\pi$ -bond: bond between axially non-symmetric orbitals  
→ conjugation, torsional stiffness

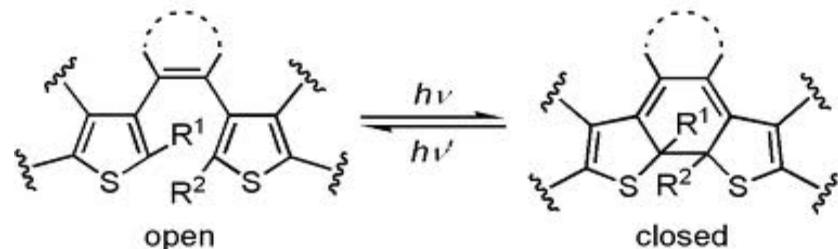
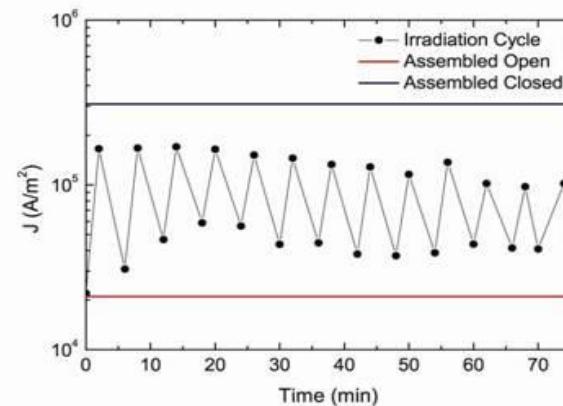
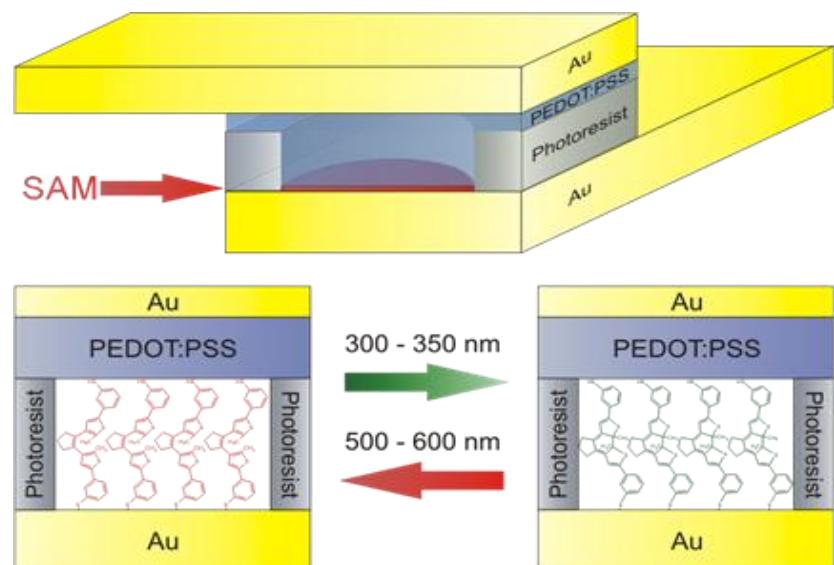


Ethene



Conjugated molecules

# Molecular electronics



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

Diarythene: switching conjugation

# BINDING IN SOLIDS

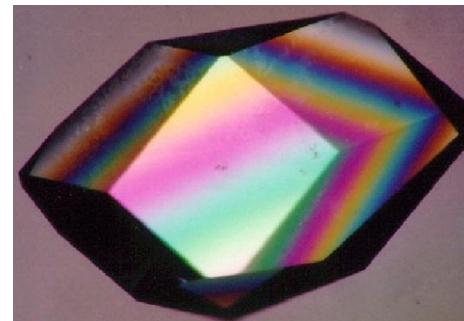
Molecular  
Covalent  
Ionic  
Metallic

# 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 CO<sub>2</sub> (dry ice)

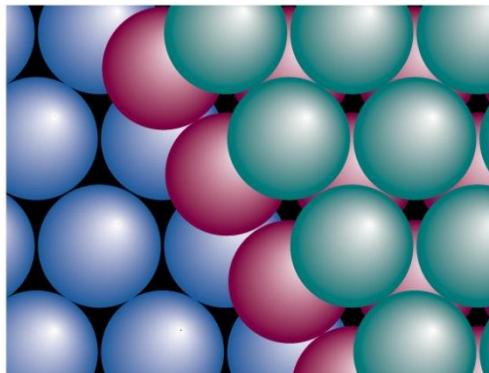


Lysosome crystal (NASA)

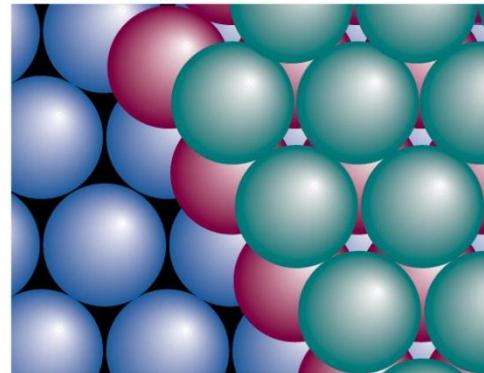
# Ionic Solids



- 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)

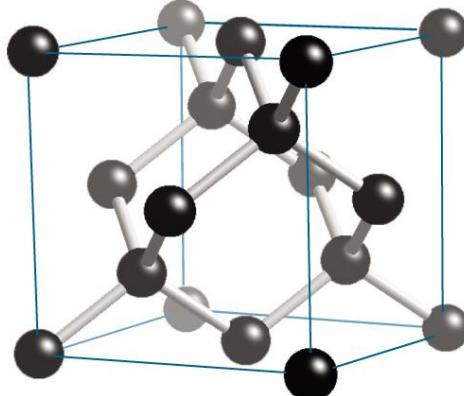


FCC (ABCABC)



# 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



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:  $r \sim 1 \text{ \AA}$

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