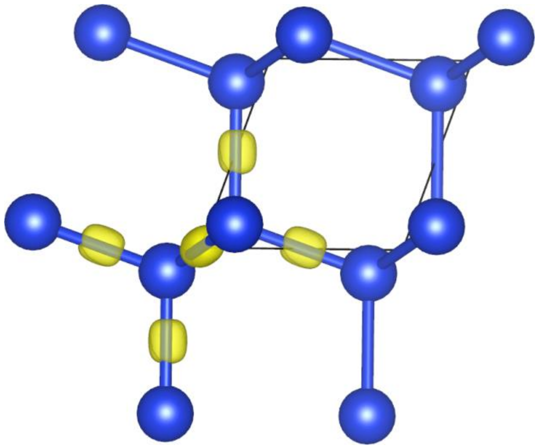
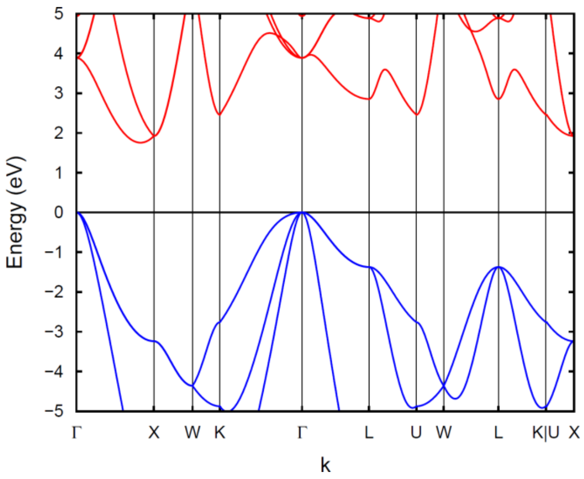
Lecture 4: Band theory

- One-slide introduction to quantum chemical materials modelling
- Band theory of solids
  - Molecules vs. solids
  - Band structures
  - Density of states (DOS) and atom-projected density of states
  - Analysis of chemical bonding in
    - Reciprocal space
    - Real space





Figures: AJK

Quantum chemical materials modelling

- Methods based on **quantum mechanics** (*ab initio* / first principles)
- Two major "branches", which are in fact often combined in practical calculations
  - *Ab initio* molecular orbital theory (MO)
  - Density functional theory (DFT)
- **No system-dependent parametrization** required
  - Only the universal physical constants and the unit cell coordinates of the system are required to predict the properties of the system
  - Choosing the right **level of theory** for a chemical problem is a demanding task
- With the help of powerful computational resources, modern materials modelling techniques can be used to
  - Assist in the interpretation and explanation of experimental results
  - Predict the existence and properties of new materials and molecules
- The predictive power of the modern materials modelling techniques enables **computational materials design**
  - Most effective in close collaboration with experimental work

Molecular orbital theory (1)

Hydrogen molecule H_2

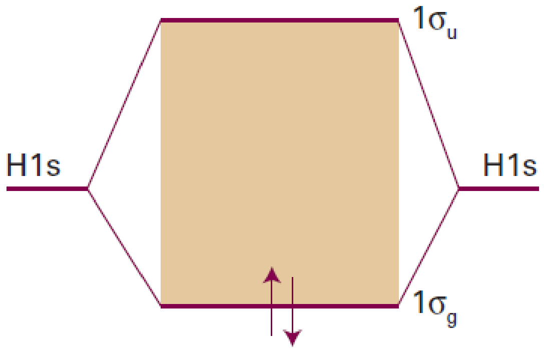


Fig. 10.24 A molecular orbital energy level diagram for orbitals constructed from the overlap of H1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

Oxygen molecule O_2

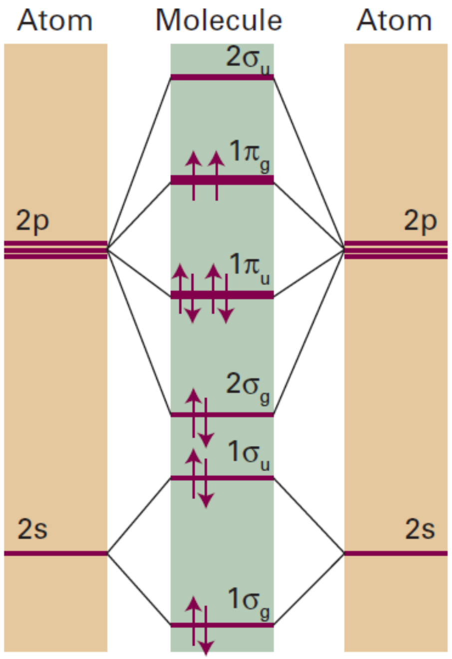


Fig. 10.32 The molecular orbital energy level diagram for homonuclear diatomic molecules. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. As remarked in the text, this diagram should be used for O_2 (the configuration shown) and F_2.

Ref: Atkins' Physical Chemistry, 9th ed. p. 383

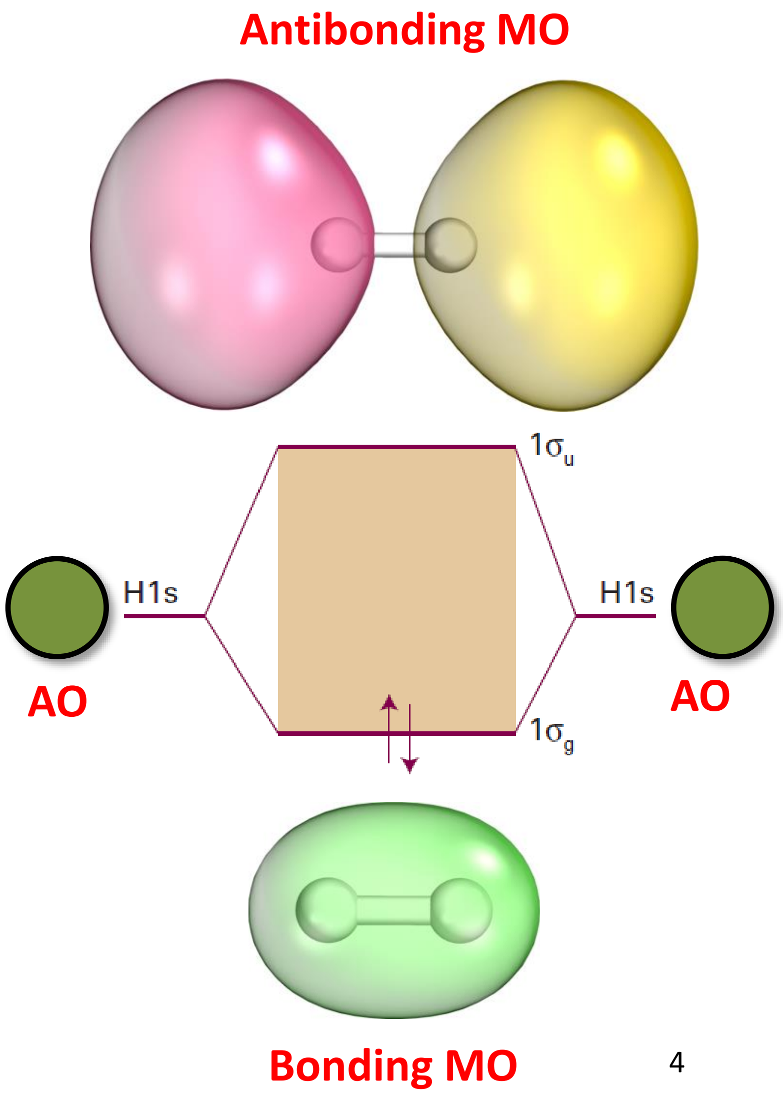
Molecular orbital theory (2)

Molecular orbitals (MO) are constructed from a Linear Combination of Atomic Orbitals (LCAO):

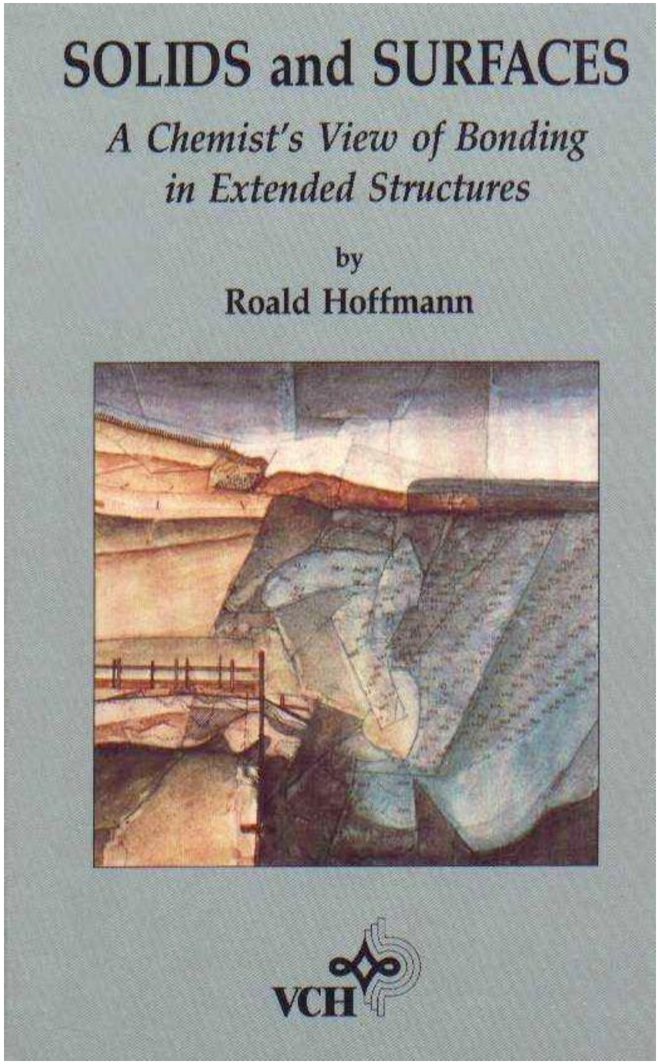
$$\underset{\text{MO}}{\phi_i} = \sum_r c_{ri} \underset{\text{AO}}{\chi_r}$$

The MO coefficients c_{ri} and the energies of the MOs can be calculated with **quantum chemical methods**.

For a longer introduction on MO theory, see for example Atkins' Physical Chemistry or LibreTexts.



Bonding in Extended Structures



SOLIDS and SURFACES

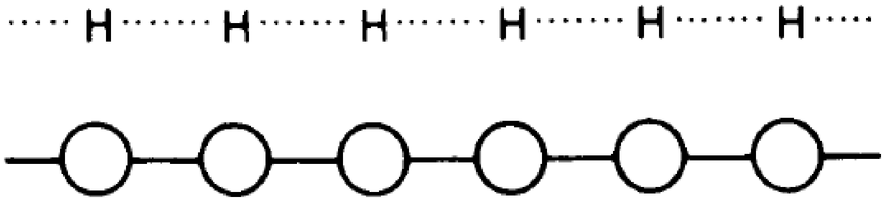
A Chemist's View of Bonding in Extended Structures

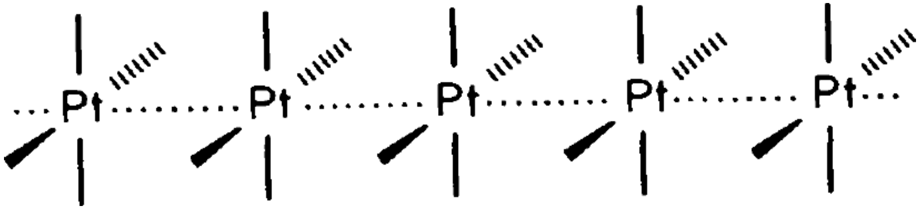
by

Roald Hoffmann

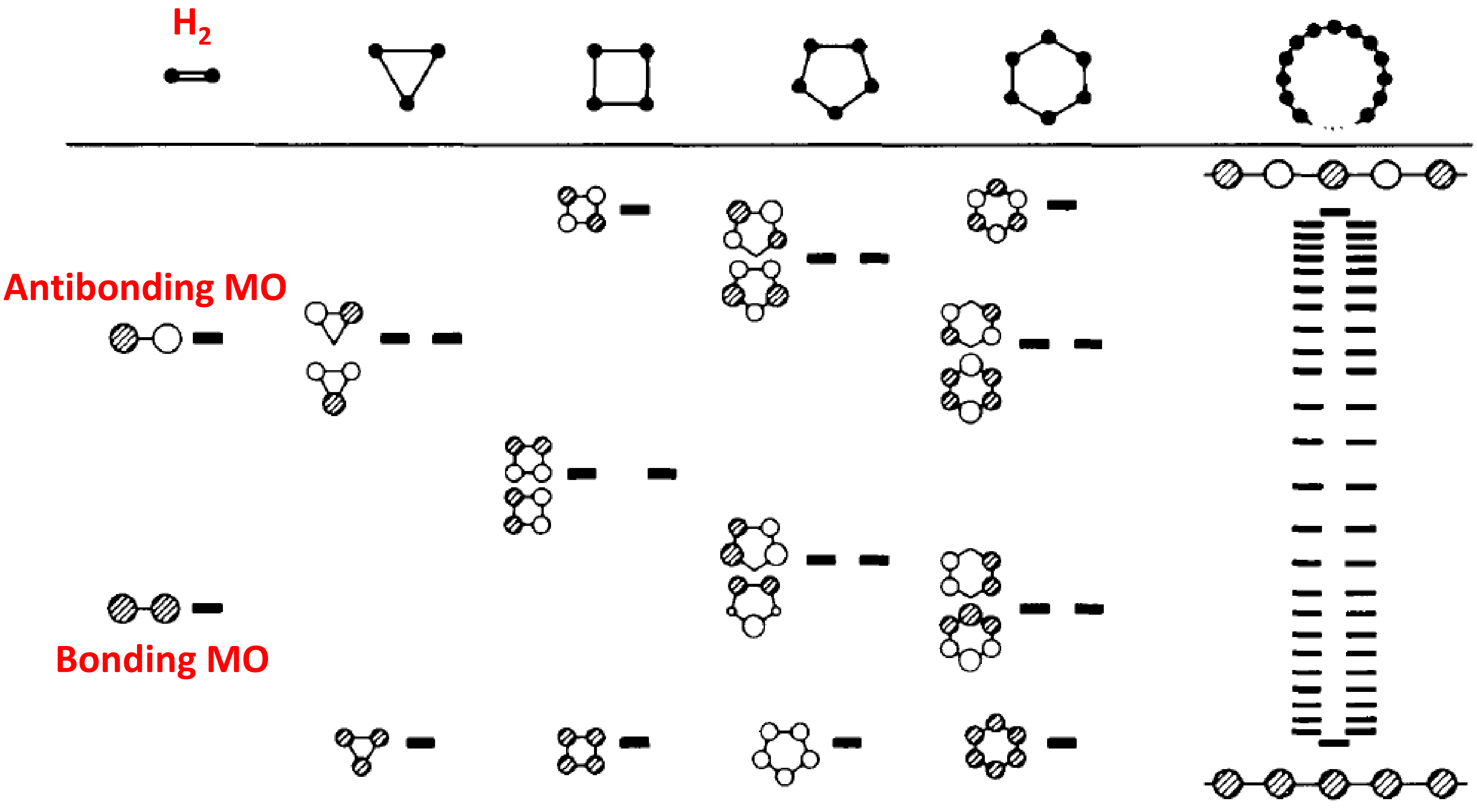
VCH

- Short introduction to band structures using two 1D model structures (infinite chains):
  - Equally spaced H atoms
  - Stack of square planar PtH_4^{2-}





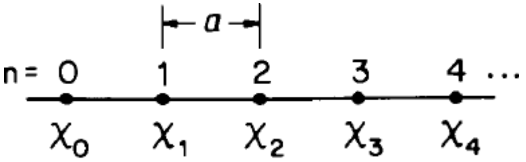
From H_2 to a large ring of H atoms



Ref: Hoffmann

Bloch functions for the H atom chain

Use translational symmetry and write the wave function ψ of the H atom chain as a linear combination of the H(1s) orbitals $\boldsymbol{\chi_n}$



$$\psi_k = \sum_n \underline{e^{ikna}}\ \chi_n$$

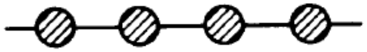
Bloch function

Phase factor (translation)

The resulting wave functions for two *k*:

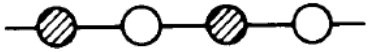
$$k = 0 \qquad \psi_0 = \sum_n e^0\ \chi_n = \sum_n \chi_n$$

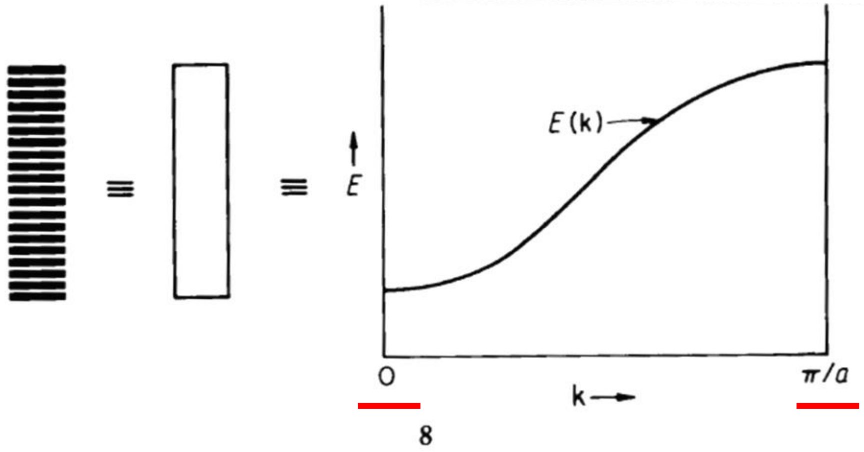
$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$



$$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n}\ \chi_n = \sum_n (-1)^n\ \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$

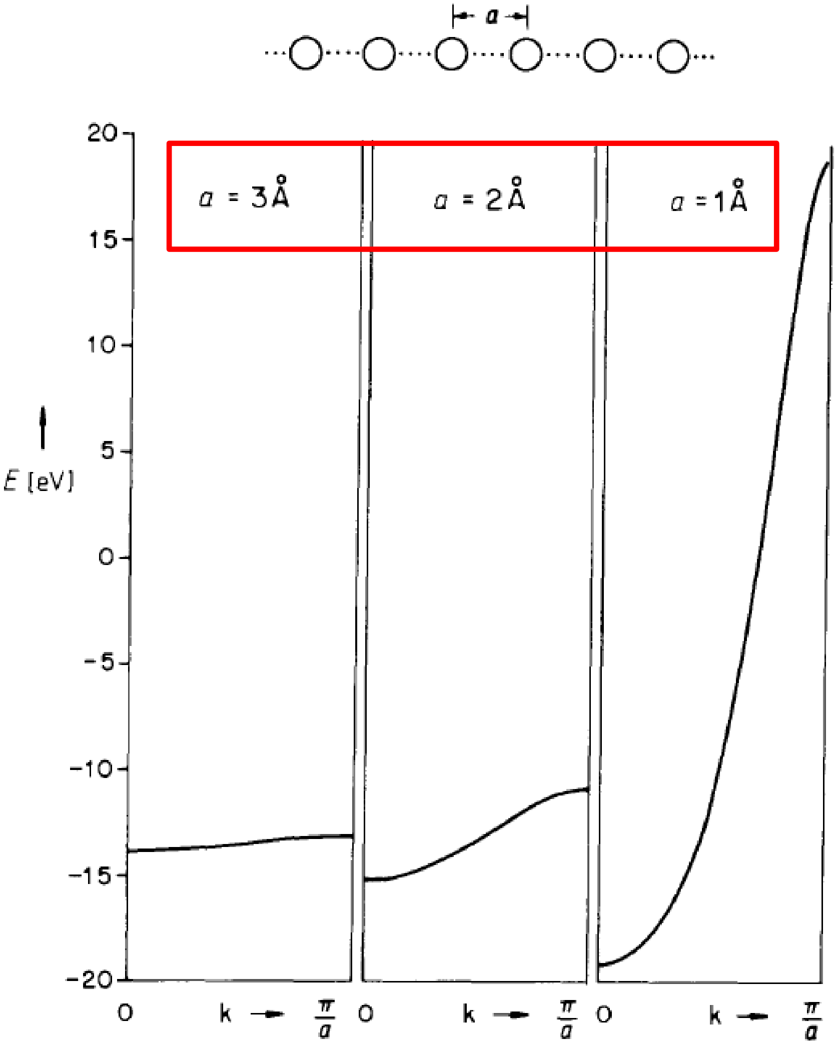




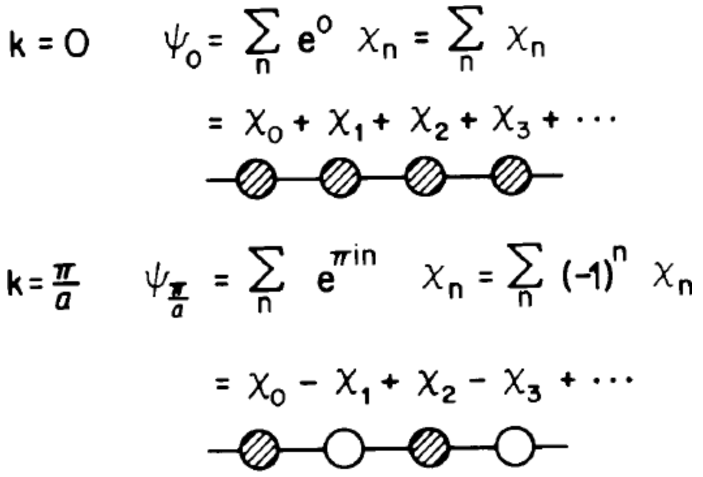
Graphs of $E(k)$ vs. k are called band structures. You can be sure that they can be much more complicated than this simple one. However, no matter how complicated they are, they can still be understood.

Ref: Hoffmann

Band width or *dispersion*



The band structure of a chain of hydrogen atoms spaced 3, 2, and 1 Å apart.



$k = 0$ $\quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$

$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$

$k = \frac{\pi}{a}$ $\quad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n$

$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$

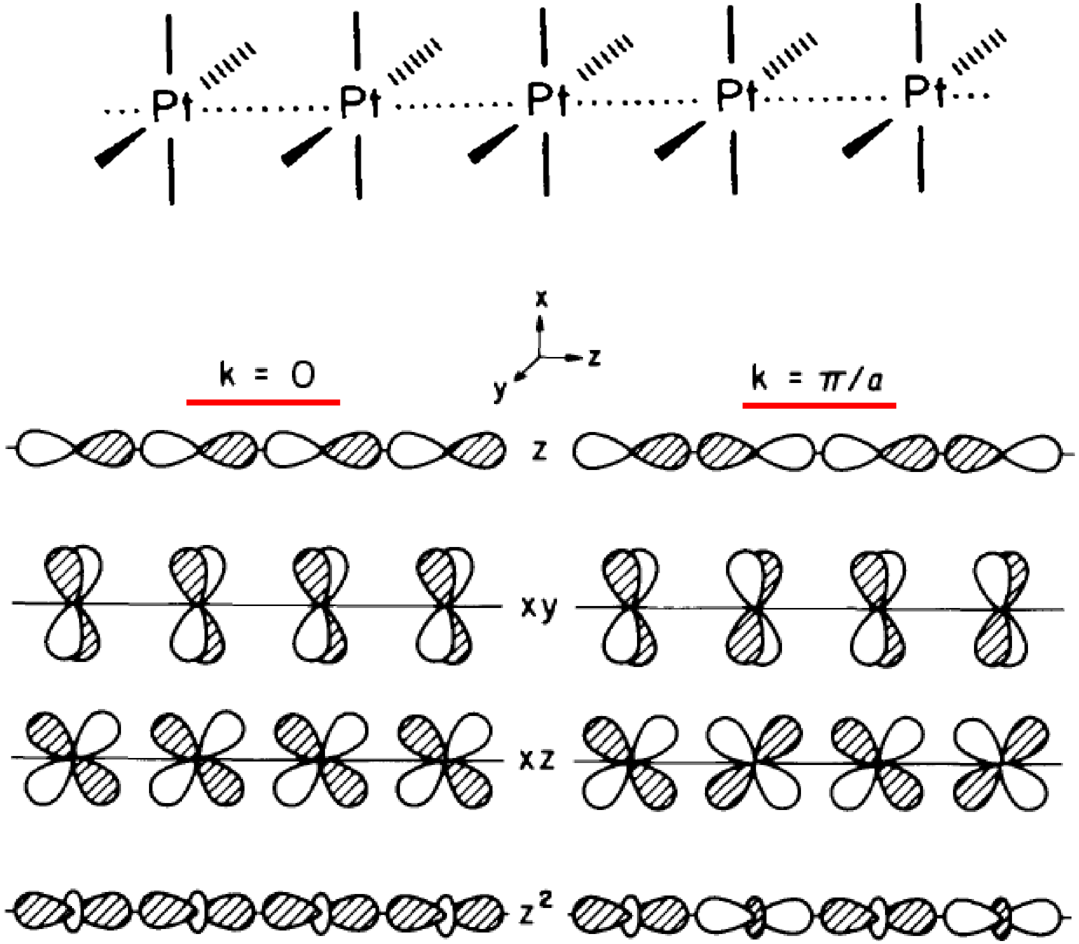
The band width is set by **inter- unit cell** overlap! Band width = ***dispersion***

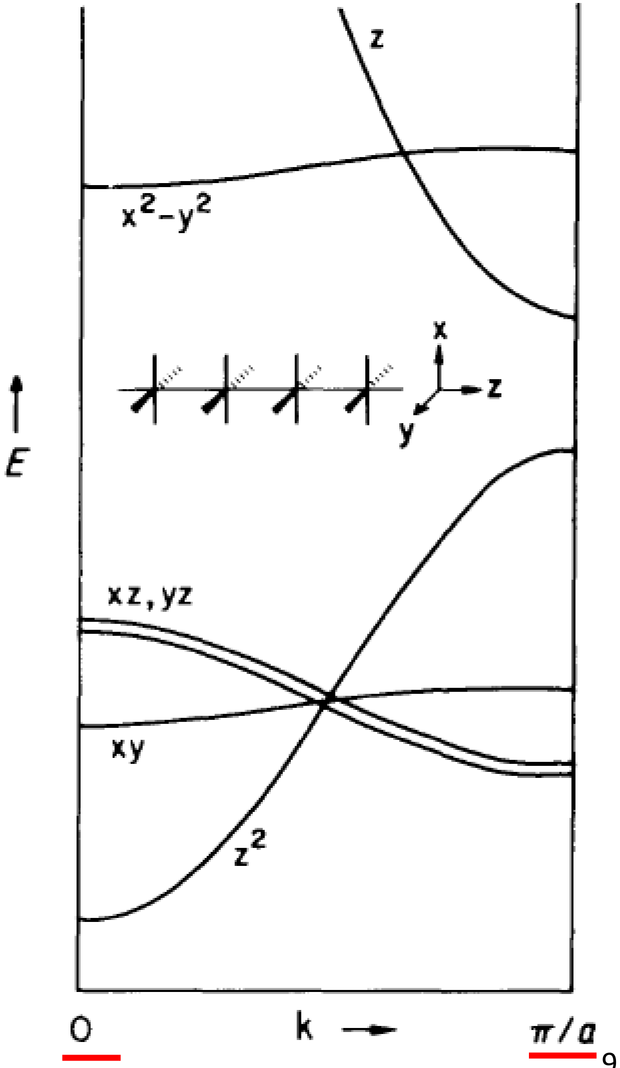
Large band width means that the atoms in a unit cell are interacting with the atoms in neighboring unit cells

Small band width (flat band) means that the atoms in a unit cell are not interacting with the neighboring unit cells

Ref: Hoffmann

Stack of square planar PtH_4^{2-}

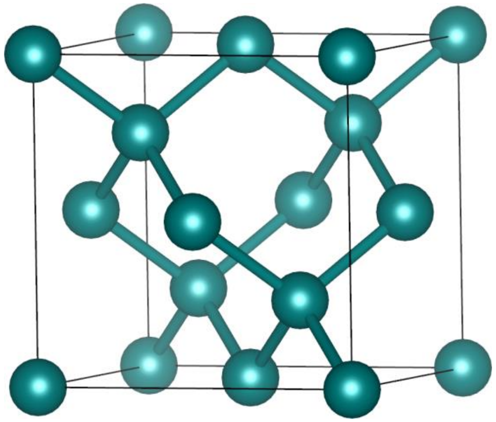




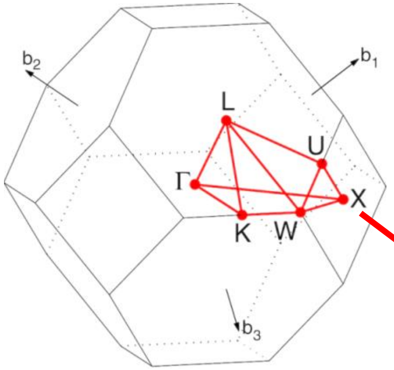
Ref: Hoffmann

Band structures in real solids

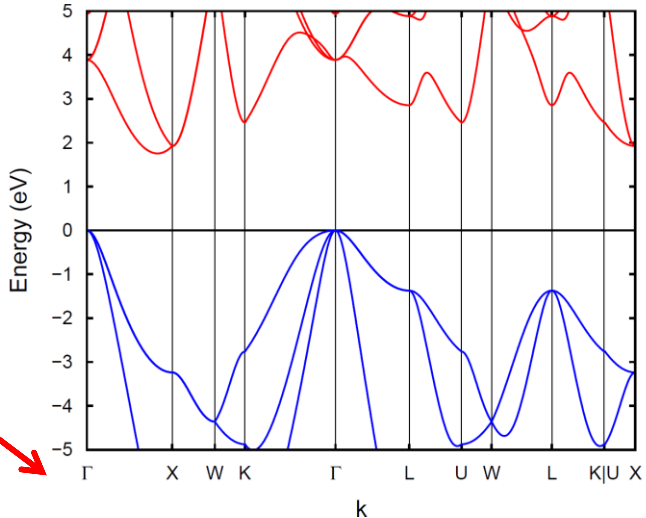
- In the 1D chains discussed above, it was enough to consider the band dispersion curves *E*(*k*) for one line (0 -> *π*/*a*)
- In 3D solids, *k* is called the ***wave vector*** and has three components (k_x, k_y, k_z)
- *E*(*k*) needs to be considered for several lines within the first ***Brillouin zone***
  - Primitive cell in reciprocal space, uniquely defined for all Bravais lattices
- Where do the band energies come from?
  - Quantum chemical calculations (usually ***density functional theory,*** **DFT**)
  - They can be measured also experimentally with e.g. electron cyclotron resonance (not that easily, though)



Silicon (*Fd*-3*m*)



Brillouin zone of an ***FCC lattice*** (Si)



Band structure of silicon (DFT)

Figures: AJK

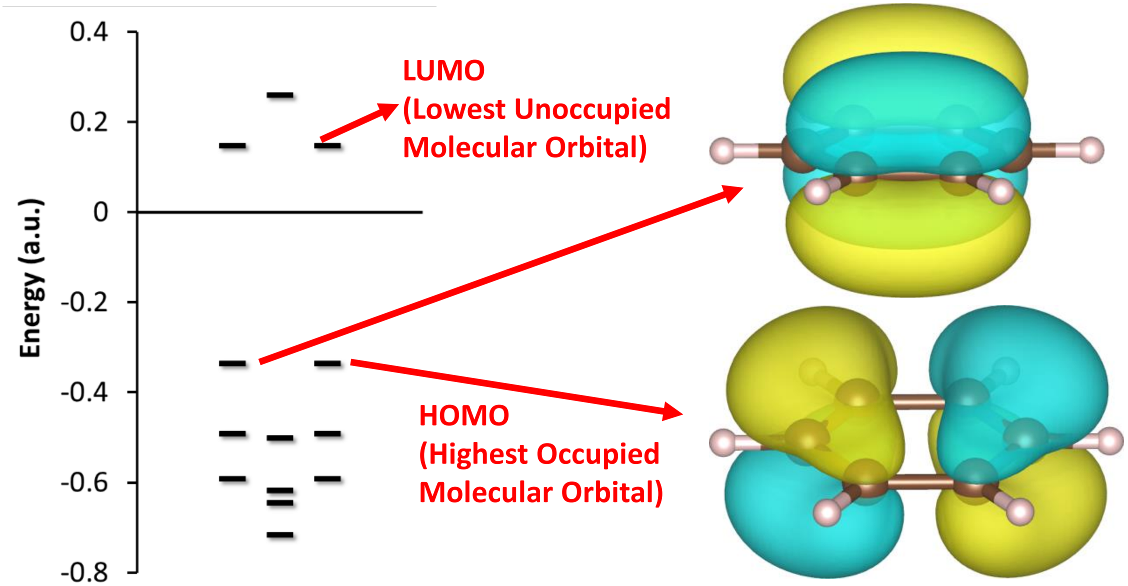
Molecules vs. solids

Molecular orbitals in benzene are shown on the right.

For molecules, we only have *k*=0 (Γ point).

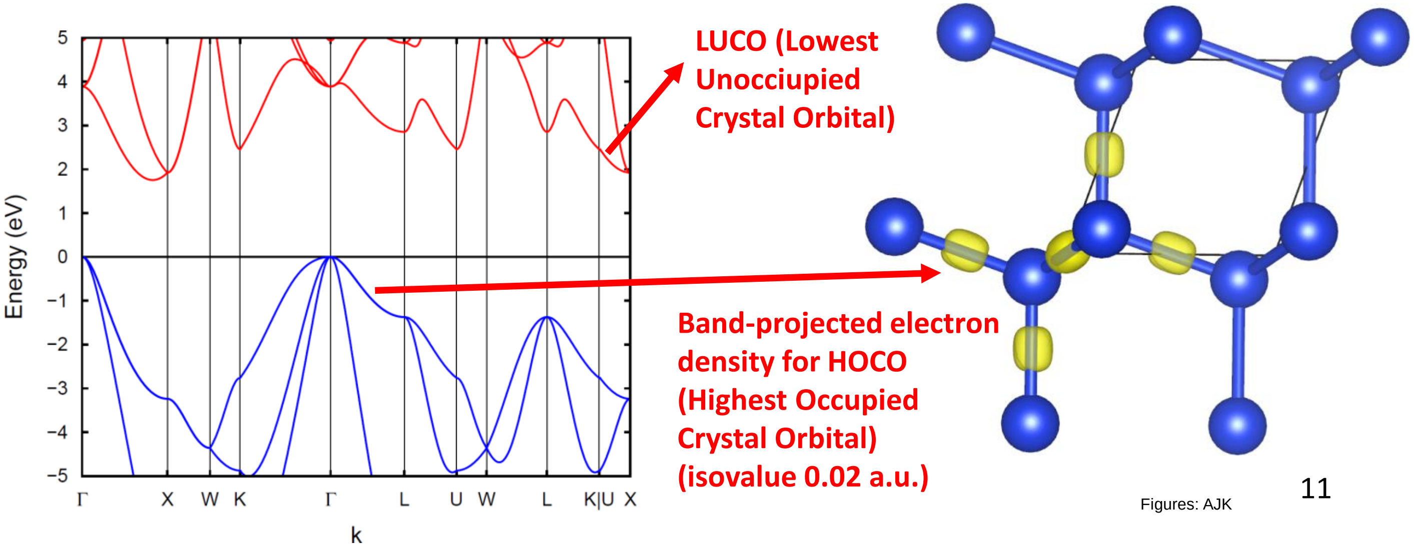
For solids, we take the atoms in the neighboring cells into account by using *E*(*k*)

Figure shows the energy bands in bulk silicon (left) and band-projected electron density for HOCO (right)



LUMO (Lowest Unoccupied Molecular Orbital)

HOMO (Highest Occupied Molecular Orbital)

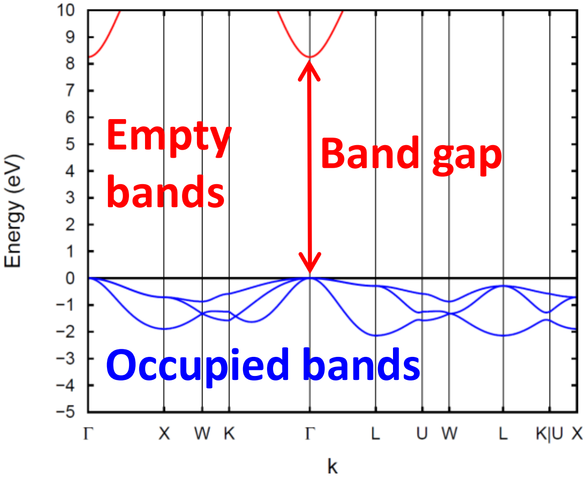


LUCO (Lowest Unocciupied Crystal Orbital)

Band-projected electron density for HOCO (Highest Occupied Crystal Orbital) (isovalue 0.02 a.u.)

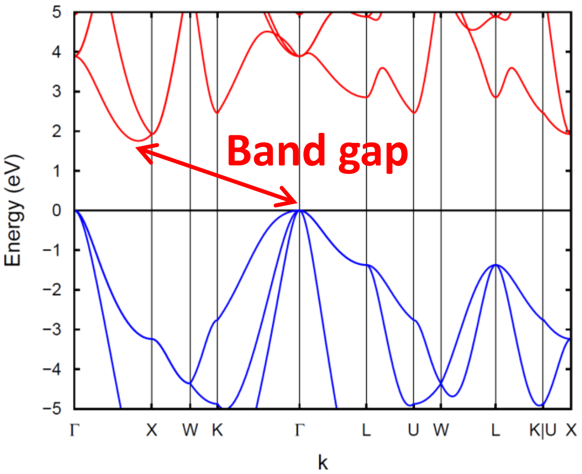
Figures: AJK

Band structure and band gap

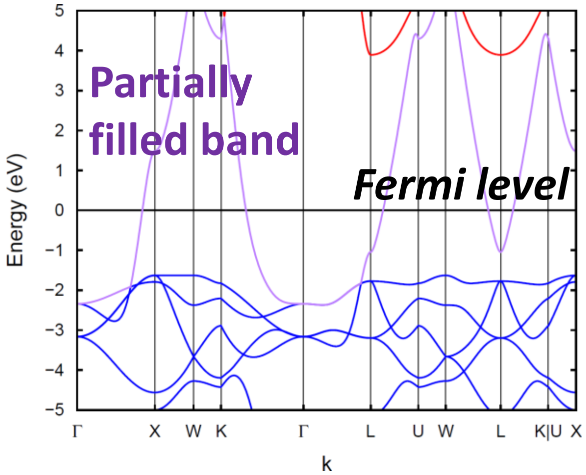


NaCl: **insulator**, large energy gap between occupied and non-occupied bands

Band gap: 8.75 eV (DFT)



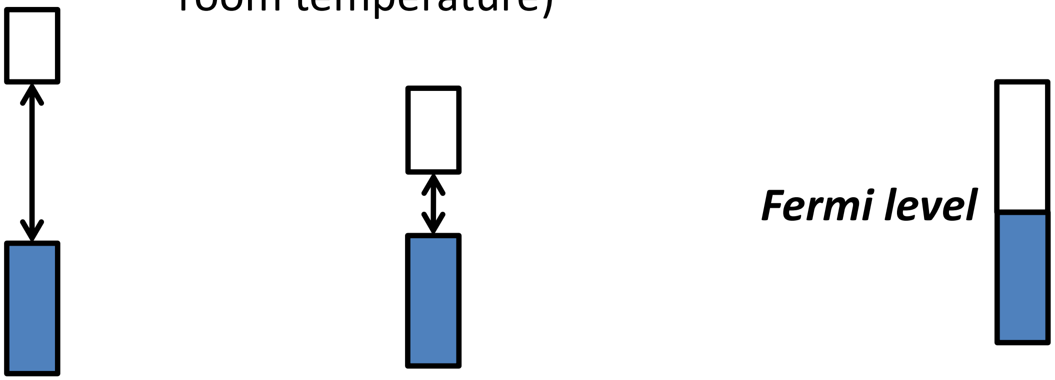
Silicon: **semiconductor**, energy gap between occupied and non-occupied bands. **Indirect** band gap (here ~2 eV in the plot, experimentally ~1.1 eV at room temperature)



Copper: **metal**, partially filled bands

No band gap

Schematic view:



Empty bands:

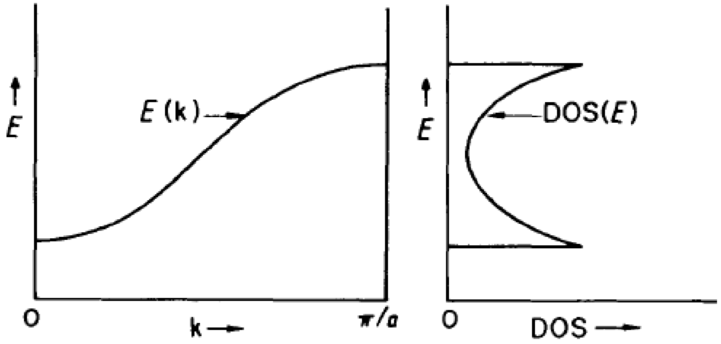
Occupied bands:

Fermi level

Figures:AJK

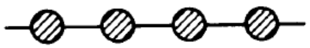
Density of states

- The band structures are a powerful description of the electronic structure of a solid, but often the ”spaghetti diagram” does not immediately tell much more than just the nature of the band gap
- A more ”chemical” look at the band structure can be obtained with Density of States diagrams (DOS)
- DOS(*E*)*dE* = number of levels between *E* and *E* + *dE*
- DOS(*E*) is proportional to the inverse of the slope of *E*(*k*) vs. *k*
  - The flatter the band, the greater the density of states at that energy
  - “Molecular bands” lead into very sharp features in DOS(*E*)



$k = 0$ $\quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$

$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$



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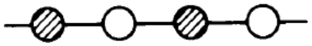
$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$



Ref: Hoffmann

Density of states for PtH_4^{2-} stack

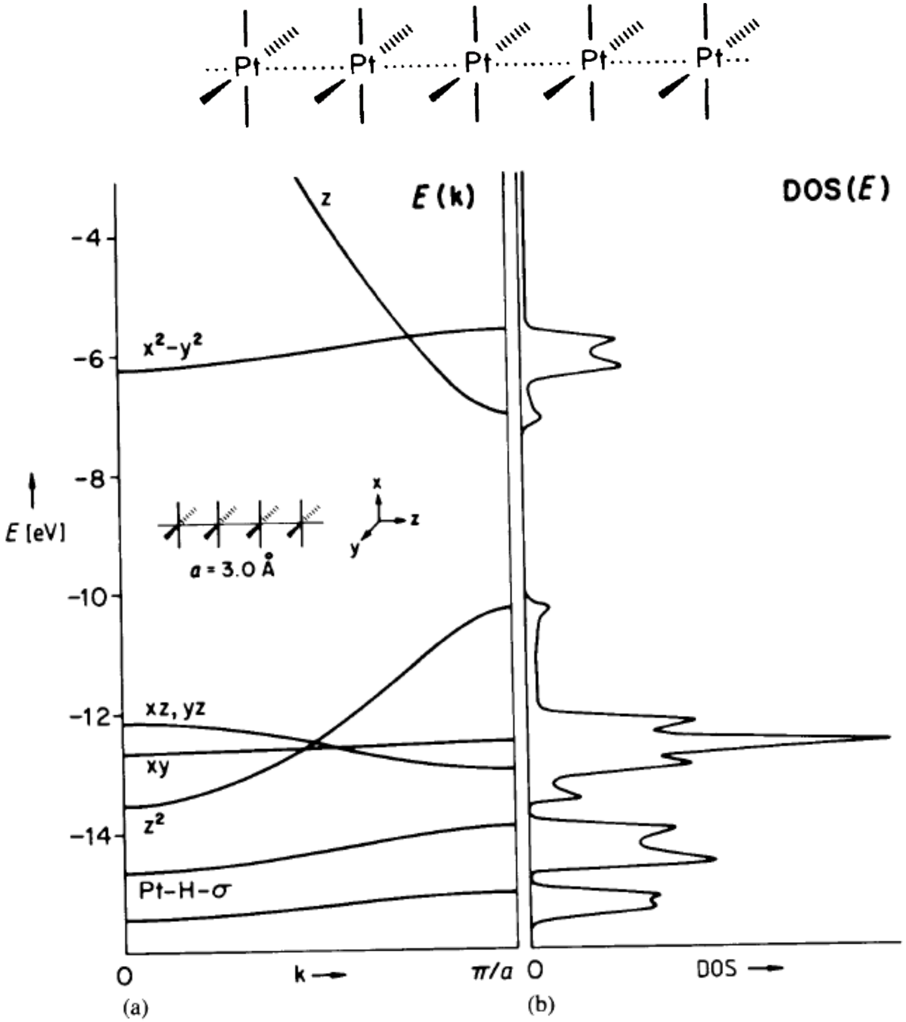
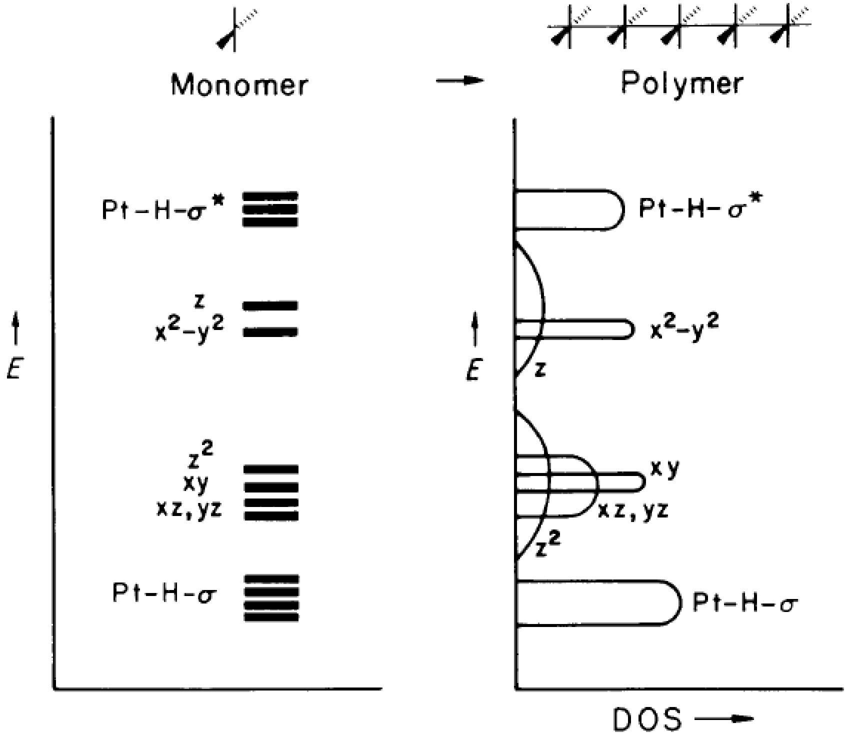


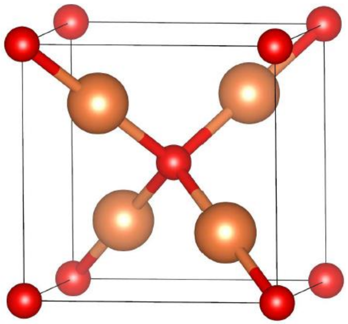
Figure 8 Band structure and density of states for an eclipsed PtH_4^{2-} stack. The DOS curves are broadened so that the two-peaked shape of the xy peak in the DOS is not resolved.



The DOS is almost like a molecular orbital diagram!

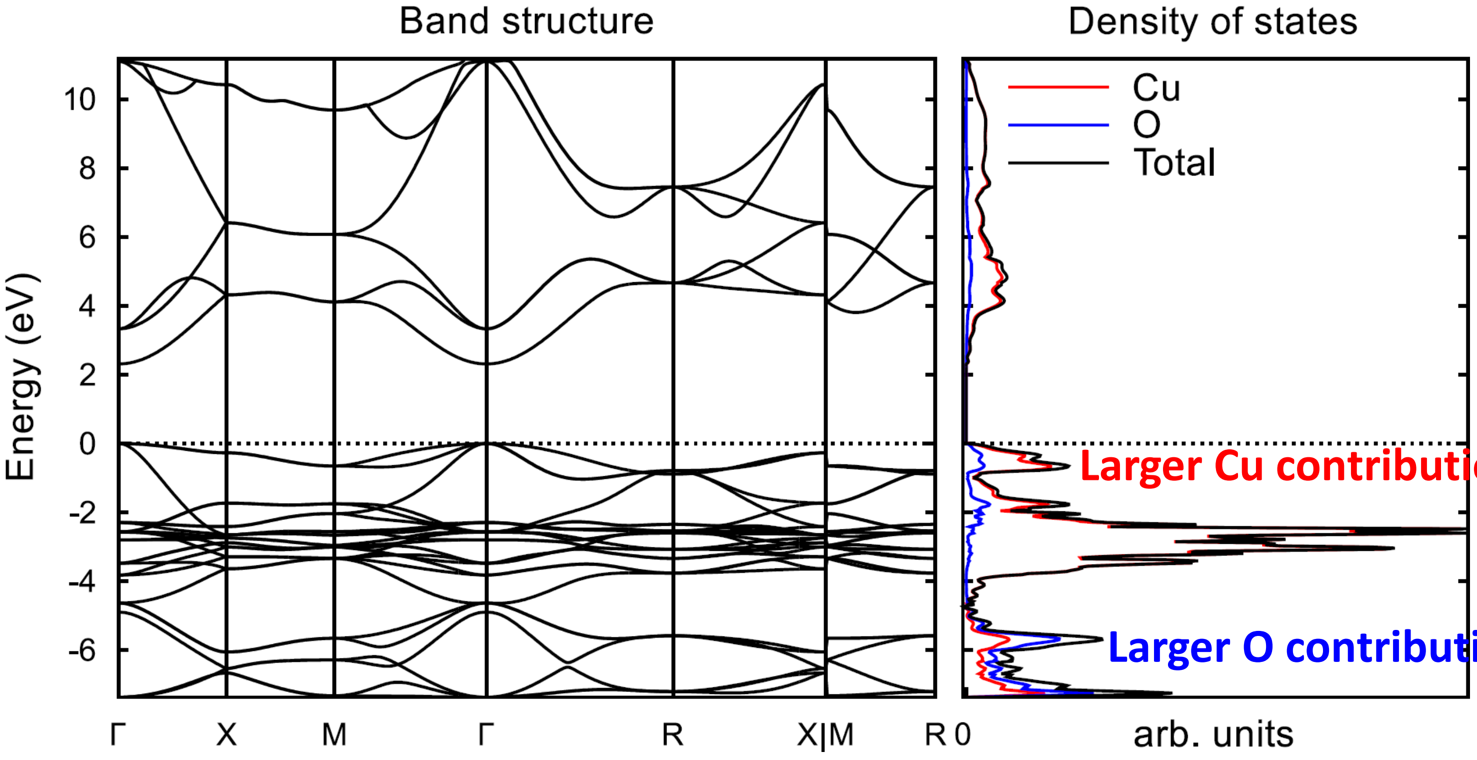
Atom-projected DOS

Figures: Jarno Linnera



Cu$_2$O (*Pn*-3*m*)

- It is also possible to create atom-projected DOS plots that tell how different atoms are contributing to the band structure at certain energies



Larger Cu contribution

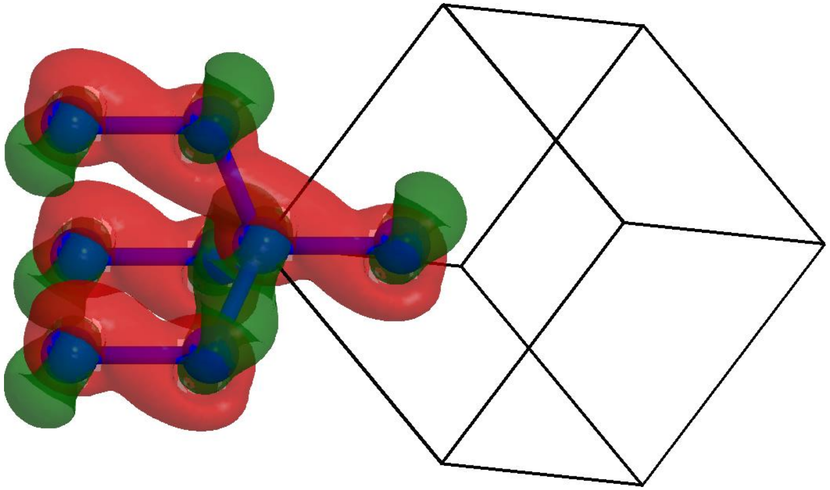
Larger O contribution

The band structure and atom-projected DOS of Cu$_2$O

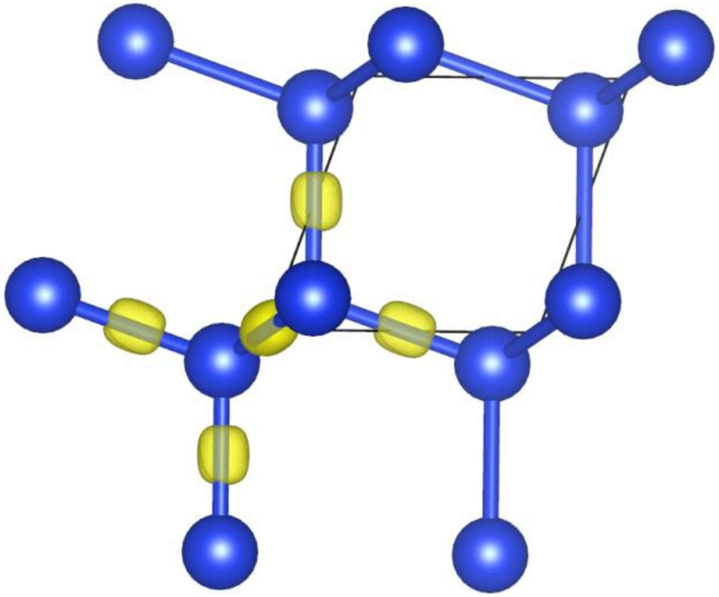
Ref: *Phys. Rev. B* **2017**, *96*, 014304 (DOI).

Real-space representations (1)

- Band structures are reciprocal-space descriptions of the electronic structure
- There are many ways to convert them to the real space. Some examples:
  - Crystal orbital plots (often rather delocalized)
  - Band-projected electron density plots



Silicon, highest occupied crystalline orbital (HOCO) at *k* = 0 (isovalue 0.008 a.u.). Corresponds to highest occupied band at *k* = 0.

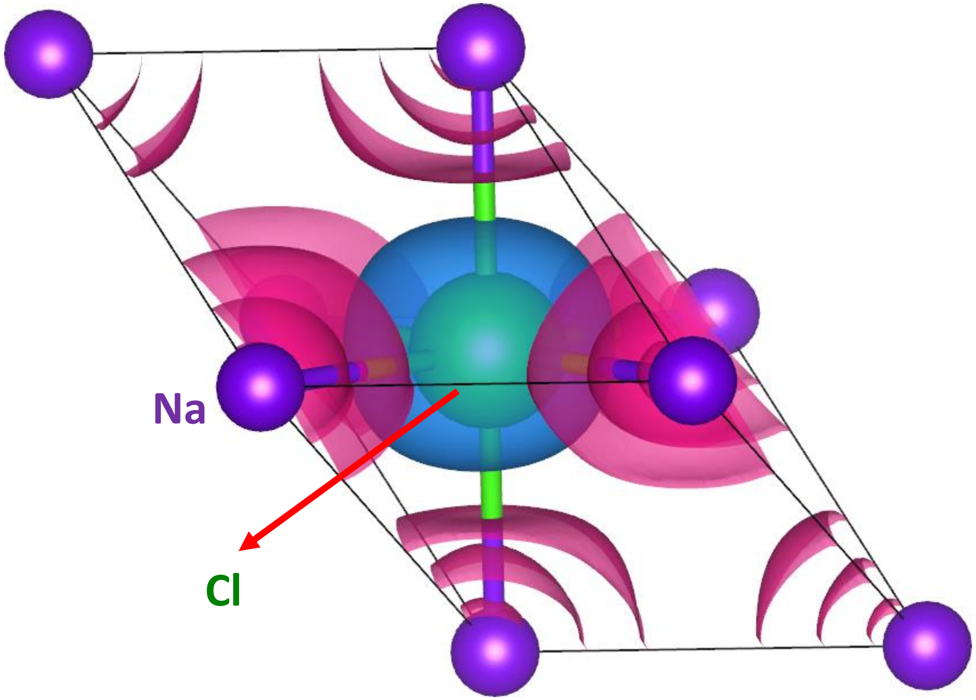


Silicon, band-projected electron density for HOCO (isovalue 0.02 a.u.)

Figures: AJK

Real-space representations (2)

- Electron density (*ρ*) difference plots: *ρ*(solid) – *ρ*(non-interactive isolated atoms).



Electron density difference plot for NaCl (isovalue 0.004 a.u.).

ρ has increased in the blue region an decreased in the red region compared to isolated Na and Cl atoms.

Figures: AJK

Extra slides

“Nice-to-know”-type material that is not needed for completing the exercises

Few historical perspectives

- 1920s - 1930s: Quantum mechanics, beginning of the ***ab initio* Molecular Orbital** (MO) theory (Hartree, Fock, etc.)
- 1950s: Further development of ***ab initio* MO theory** to make it a practical approach for molecular systems; Introduction of computers to quantum chemistry
- 1960s - 1970s: Rapid development of the methodology, algorithms, and computers
  - Early 1960s: The foundations of **Density Functional Theory** (DFT) are developed by Kohn *et al*.
  - 1970: Gaussian70 by Pople *et al.* is a major milestone in usability
- 1980s: The field is maturing and more non-specialists start to use computational methods in their research.
- 1990s: DFT really becomes the new superstar and its ”black-box” nature attracts more and more attention to molecular modelling
  - 1998: Pople and Kohn are awarded the Nobel Prize in Chemistry
- 2000s: Molecular and materials modelling is routinely used in chemical research.
  - Both in collaboration with experiments and in purely computational studies
- Currently: Major emphasis on computational materials design based on high-throughput screening and/or machine learning

Level of theory

- The **level of theory** determines the reliability of the results:
  1. How the electron-electron interactions are described (=”**method**”)
  2. How a single electron is described (=”one electron **basis set**”)
- The computational resource requirements depend on
  - The **level of theory**
  - The size of the **model system** (number of atoms)
  - The type of the **model system** (molecular or periodic in 1D/2D/3D)
- The vast majority of computational solid state chemistry is currently carried out using Density Functional Theory (**DFT**)
  - Currently the most practical computational approach for solids
  - Typically $10^1 - 10^3$ atoms in the unit cell

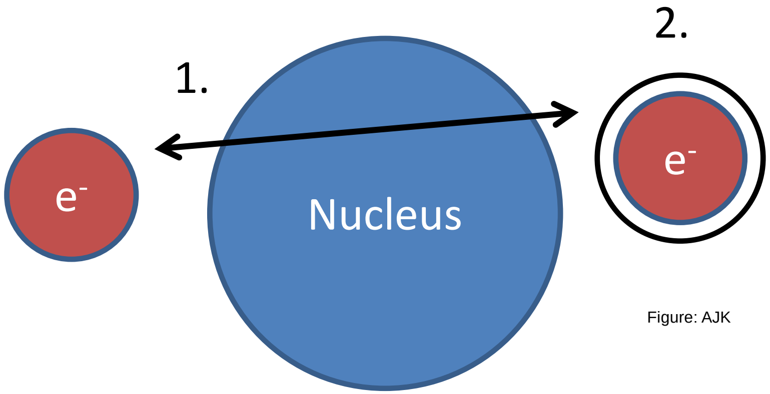


Figure: AJK