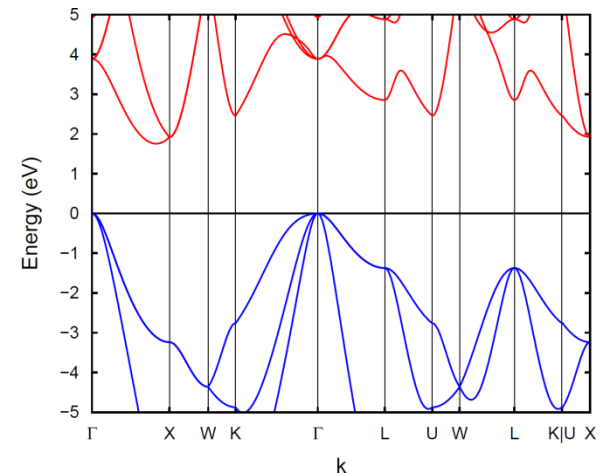
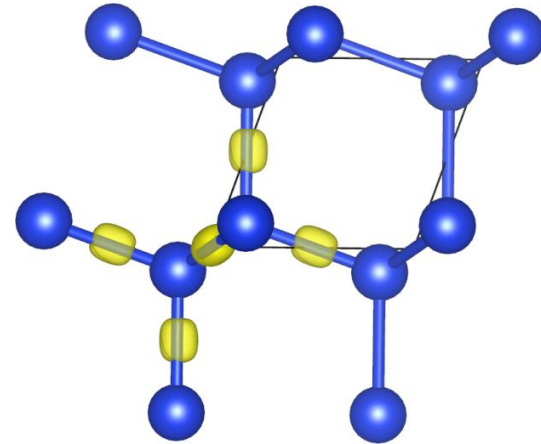


Lecture 4: Band theory

- Very short introduction to modern computational solid state chemistry
- Band theory of solids
 - Molecules vs. solids
 - Band structures
 - Analysis of chemical bonding in
 - Reciprocal space
 - Real space



Figures: AJK

Ab initio 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

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

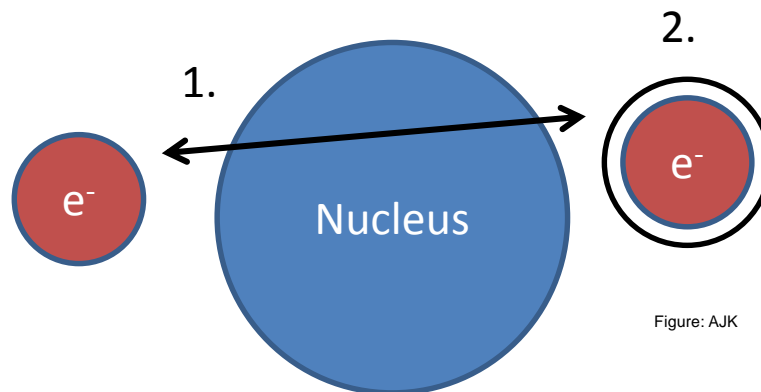


Figure: AJK

Few historical perspectives (1)

- 1920s - 1930s: Quantum mechanics, beginning of the ***ab initio* Molecular Orbital** (MO) theory (Hartree, Fock, etc.)
- Paul Dirac in his year 1929 review article "Quantum Mechanics of Many-Electron Systems" (P. A. M. Dirac, *Proc. R. Soc. London, Ser. A* **1929**, 123, 714-733):
 - "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"
 - "It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems..."
 - "...without too much computation."



Figure: [Wikipedia](#)

Few historical perspectives (2)

- 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

Molecular orbital theory

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

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

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

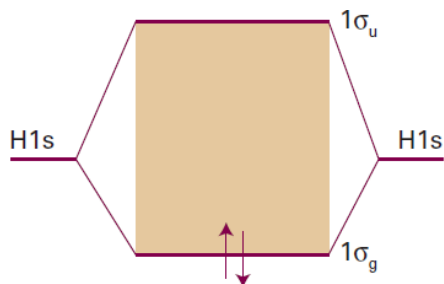


Fig. 10.24 A molecular orbital energy level diagram for orbitals constructed from the overlap of H1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H₂ is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

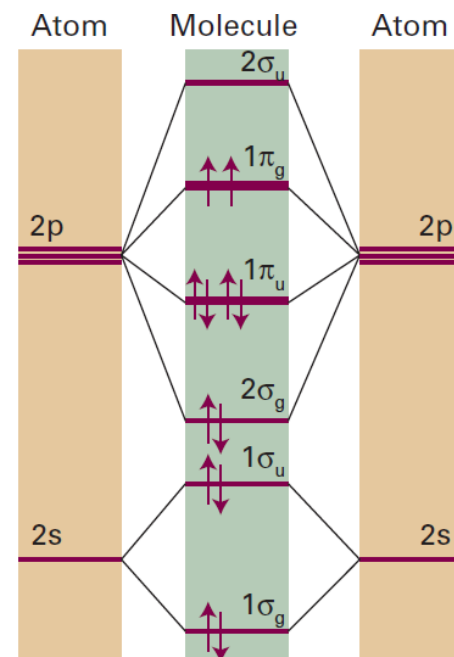


Fig. 10.32 The molecular orbital energy level diagram for homonuclear diatomic molecules. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. As remarked in the text, this diagram should be used for O₂ (the configuration shown) and F₂.

Bonding in Extended Structures

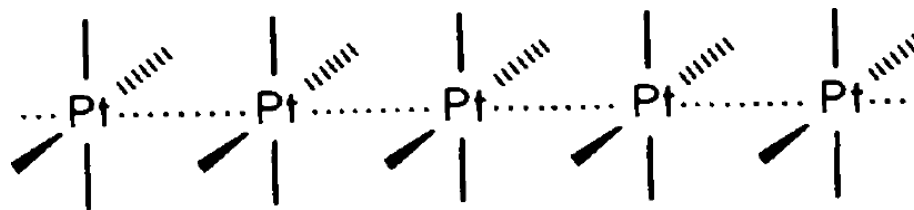
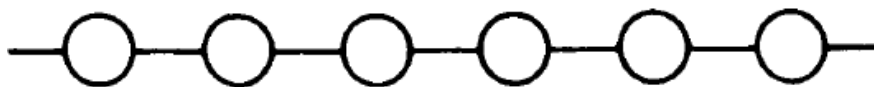
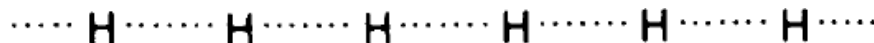
SOLIDS and SURFACES

*A Chemist's View of Bonding
in Extended Structures*

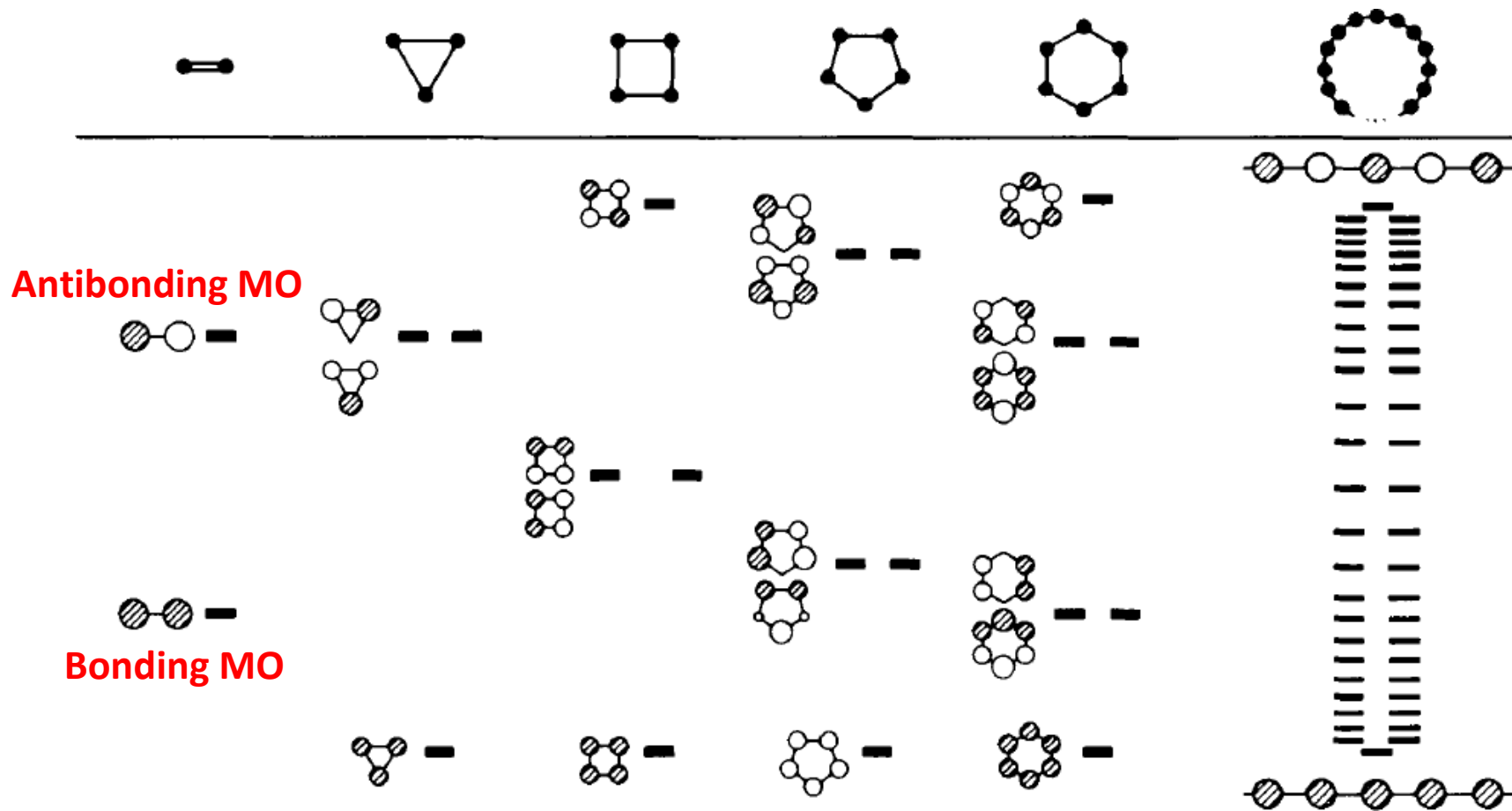
by
Roald Hoffmann



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

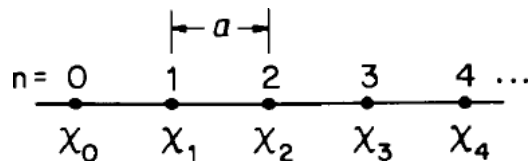


From H₂ to a large ring of H atoms



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 χ_n



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

Phase factor (translation)

The resulting wave functions for two k :

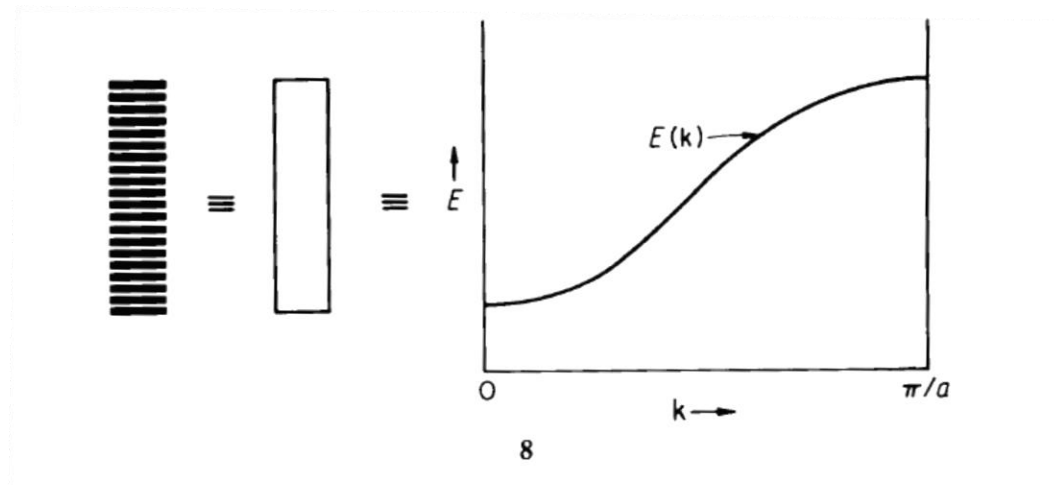
$$k=0 \quad \psi_0 = \sum_n e^{i0} \chi_n = \sum_n \chi_n$$

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

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

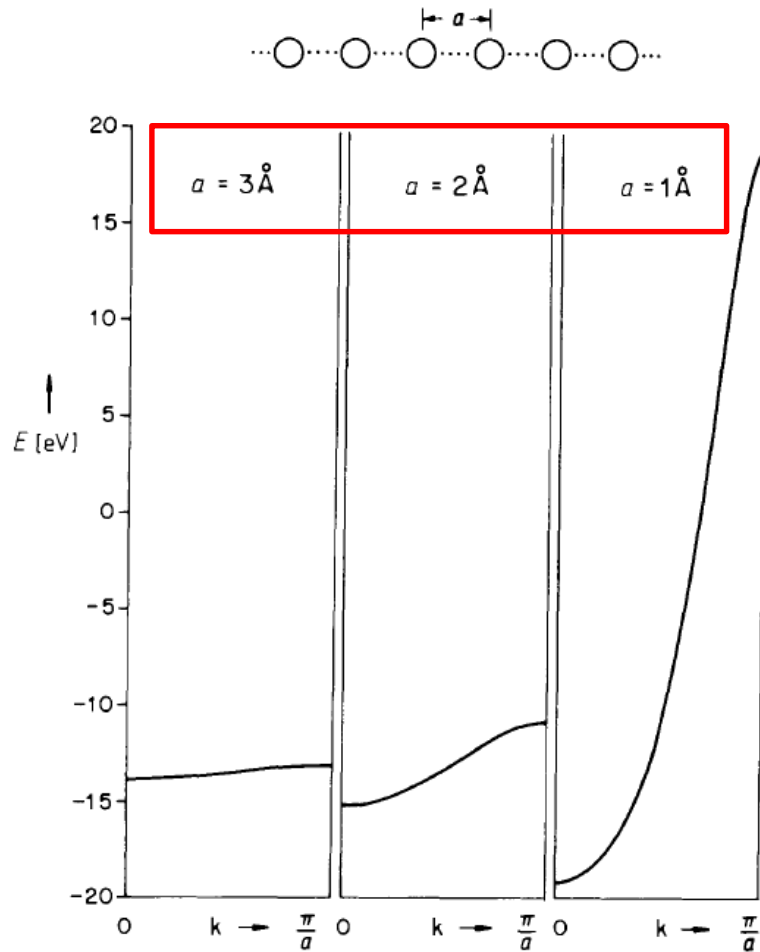
$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

Ref: Hoffmann



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.

Band width or *dispersion*



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

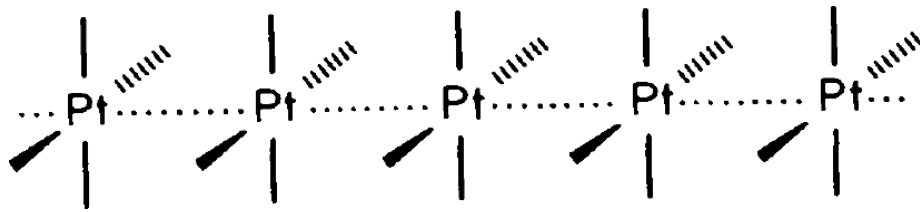
Small band width (flat band) means that the atoms in a unit cell are not interacting with the neighboring unit cells

$$\begin{aligned}
 k=0 \quad \psi_0 &= \sum_n e^{i0n} \chi_n = \sum_n \chi_n \\
 &= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots
 \end{aligned}$$

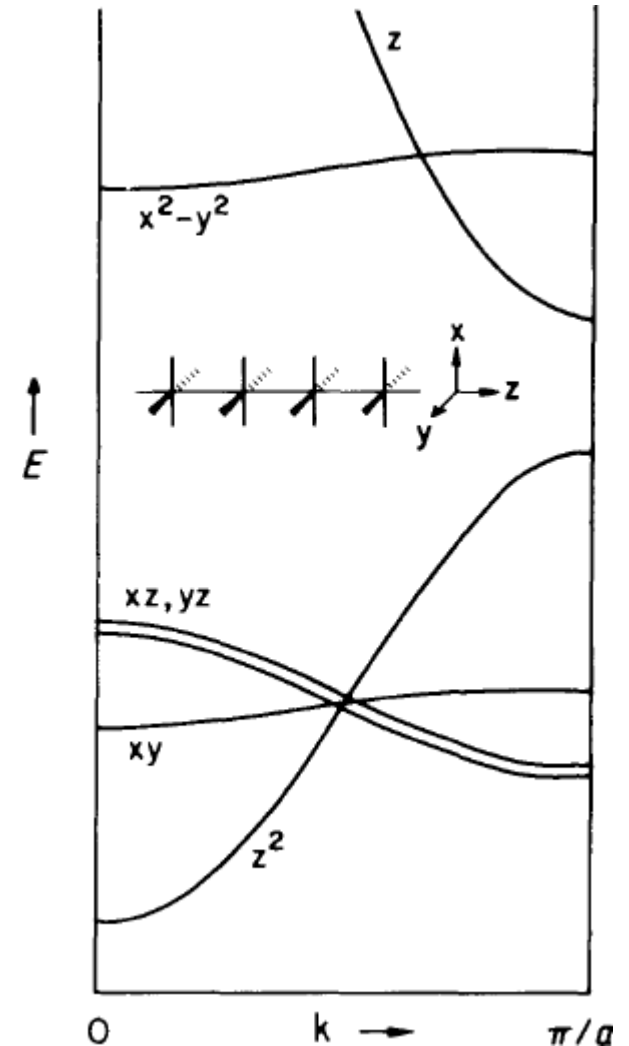
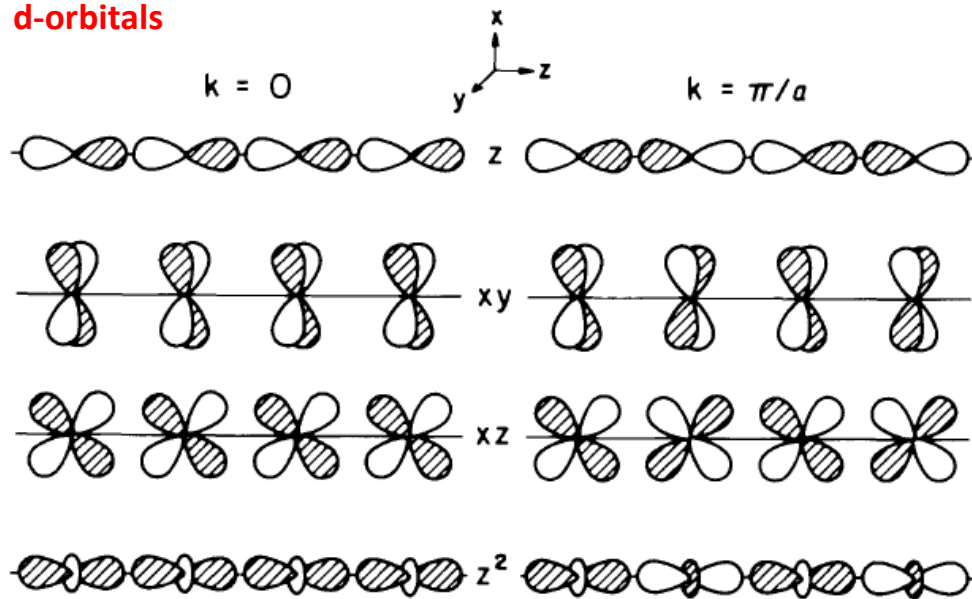
$$\begin{aligned}
 k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} &= \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n \\
 &= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots
 \end{aligned}$$

Figure 1 The band structure of a chain of hydrogen atoms spaced 3, 2, and 1 Å apart. The energy of an isolated H atom is -13.6 eV.

Stack of square planar PtH_4^{2-}

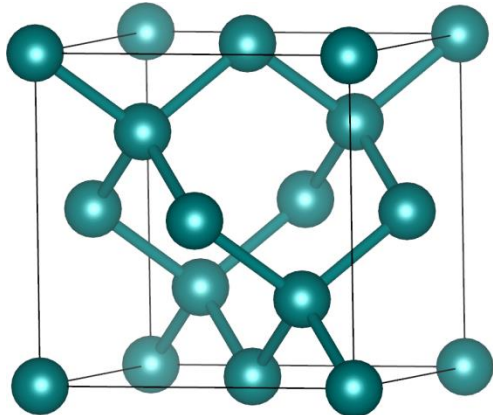


d-orbitals

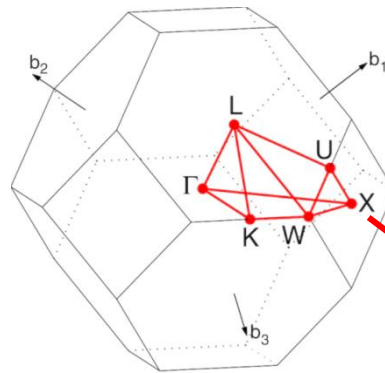


Band structures in real solids

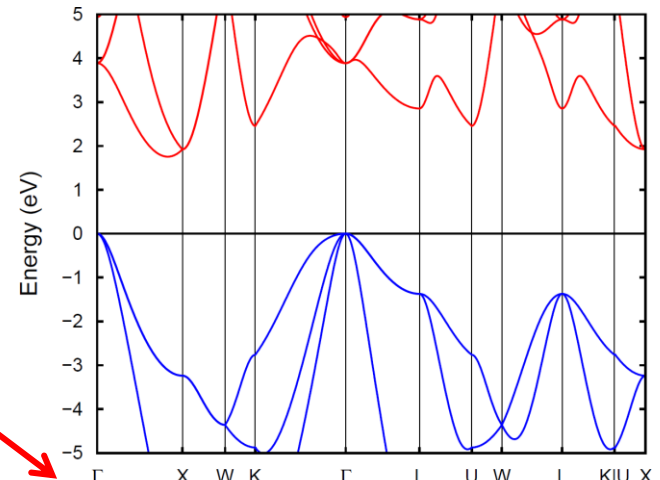
- In the 1D chains discussed above, it was enough to consider the band dispersion curves $E(k)$ for one line ($0 \rightarrow \pi/a$)
- In 3D solids, k is called the **wave vector** and has three components (k_x, k_y, k_z)
- $E(k)$ needs to be considered for several lines within the first **Brillouin 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 ($Fd-3m$)



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



Band structure of silicon (DFT)

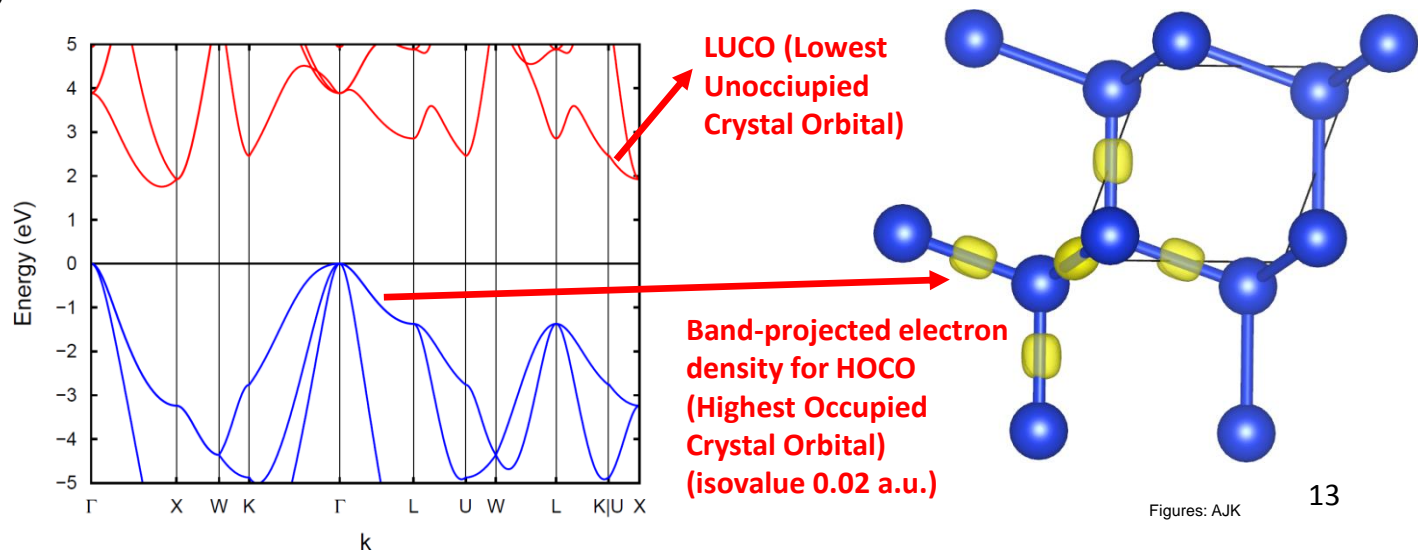
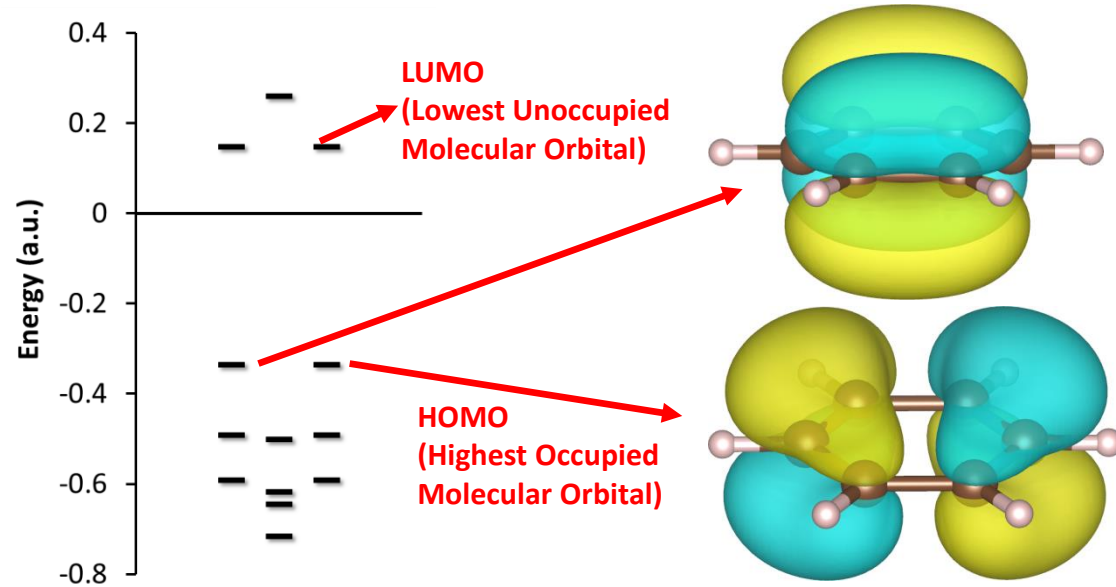
Molecules vs. solids

Molecular orbitals in benzene are shown on the right.

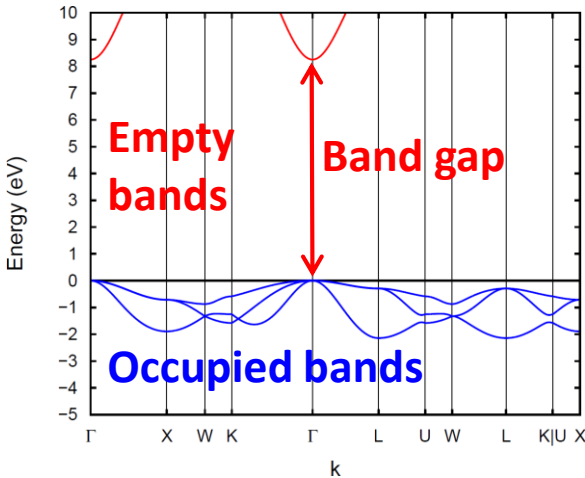
For molecules, we only have $k=0$ (Γ point).

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)



Band structure and band gap

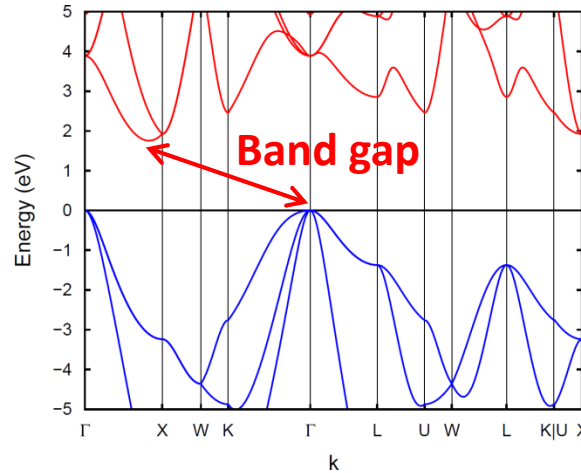


NaCl: **insulator**, large energy gap between occupied and non-occupied bands
 Band gap: 8.75 eV (DFT)

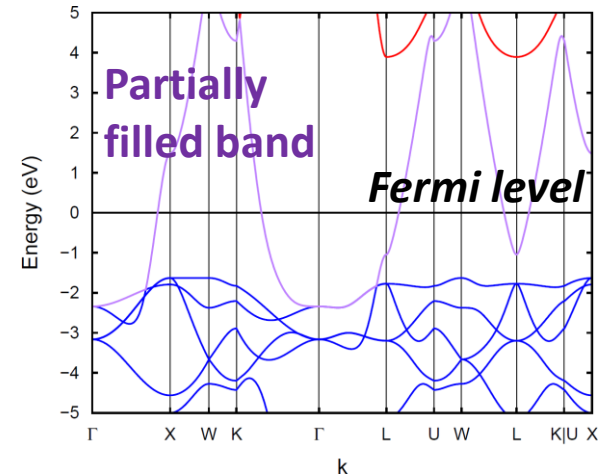
Empty bands: 

Schematic view:

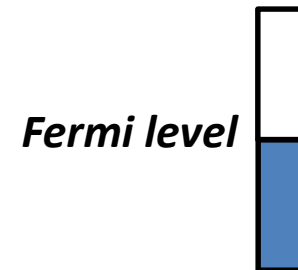
Occupied bands: 



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)

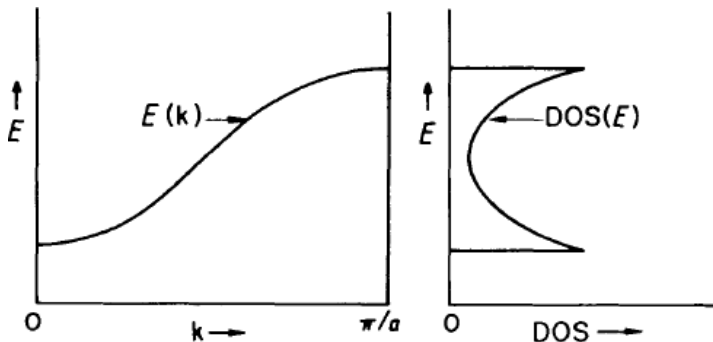


Copper: **metal**, partially filled bands
 No band gap



Density of states (1)

- 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 $DOS(E)$



$$\begin{aligned}
 k=0 \quad \psi_0 &= \sum_n e^{i0n} \chi_n = \sum_n \chi_n \\
 &= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots \\
 &\text{---} \textcircled{\text{shaded}} \text{---} \textcircled{\text{shaded}} \text{---} \textcircled{\text{shaded}} \text{---} \textcircled{\text{shaded}} \text{---} \\
 k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} &= \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n \\
 &= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots \\
 &\text{---} \textcircled{\text{shaded}} \text{---} \textcircled{\text{white}} \text{---} \textcircled{\text{shaded}} \text{---} \textcircled{\text{white}} \text{---}
 \end{aligned}$$

Density of states (2)

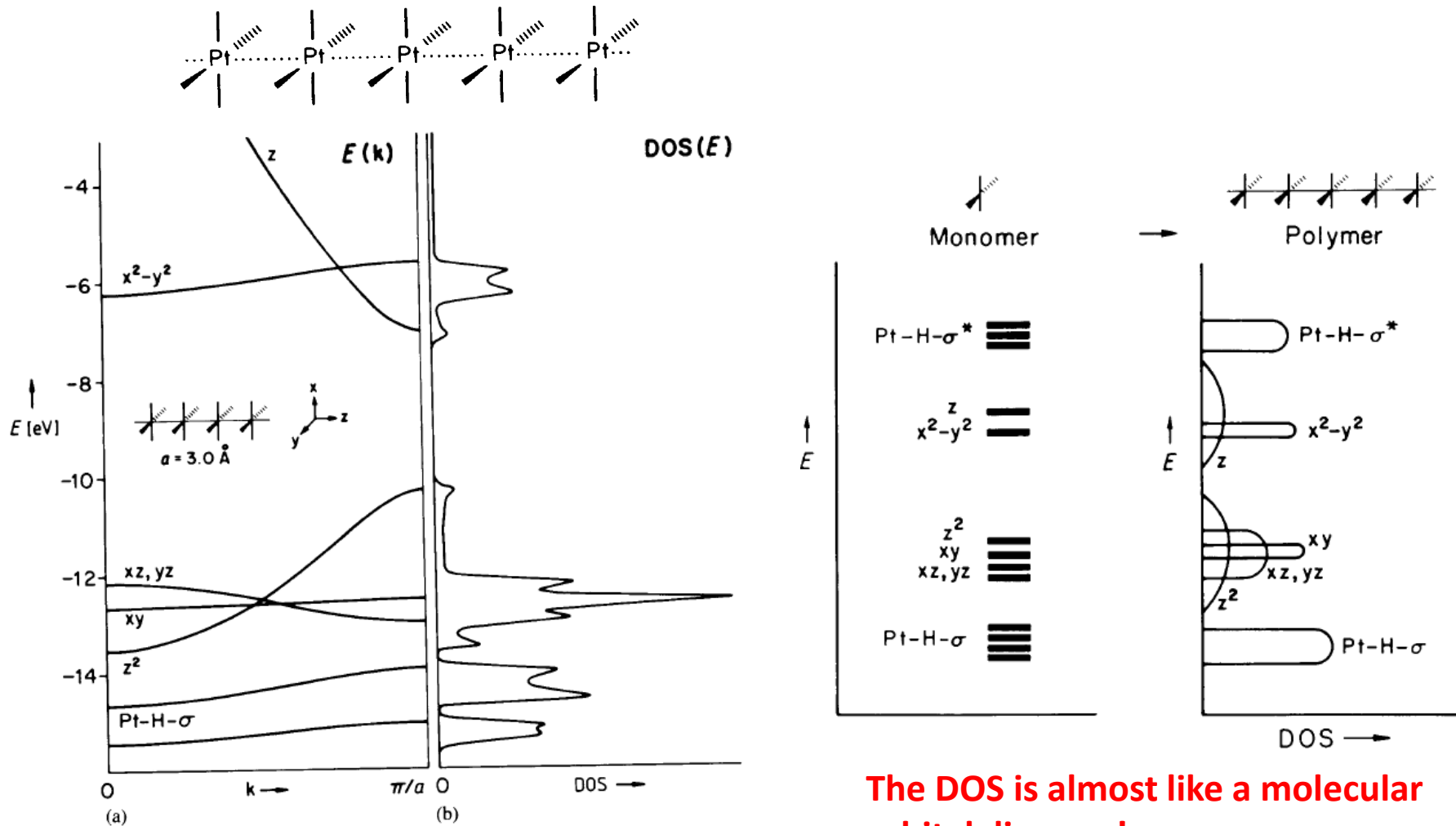


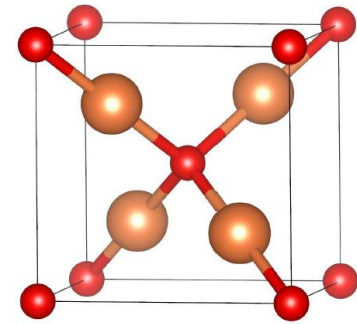
Figure 8 Band structure and density of states for an eclipsed PtH_4^{2-} stack. The DOS curves are broadened so that the two-peaked shape of the xy peak in the DOS is not resolved.

The DOS is almost like a molecular orbital diagram!

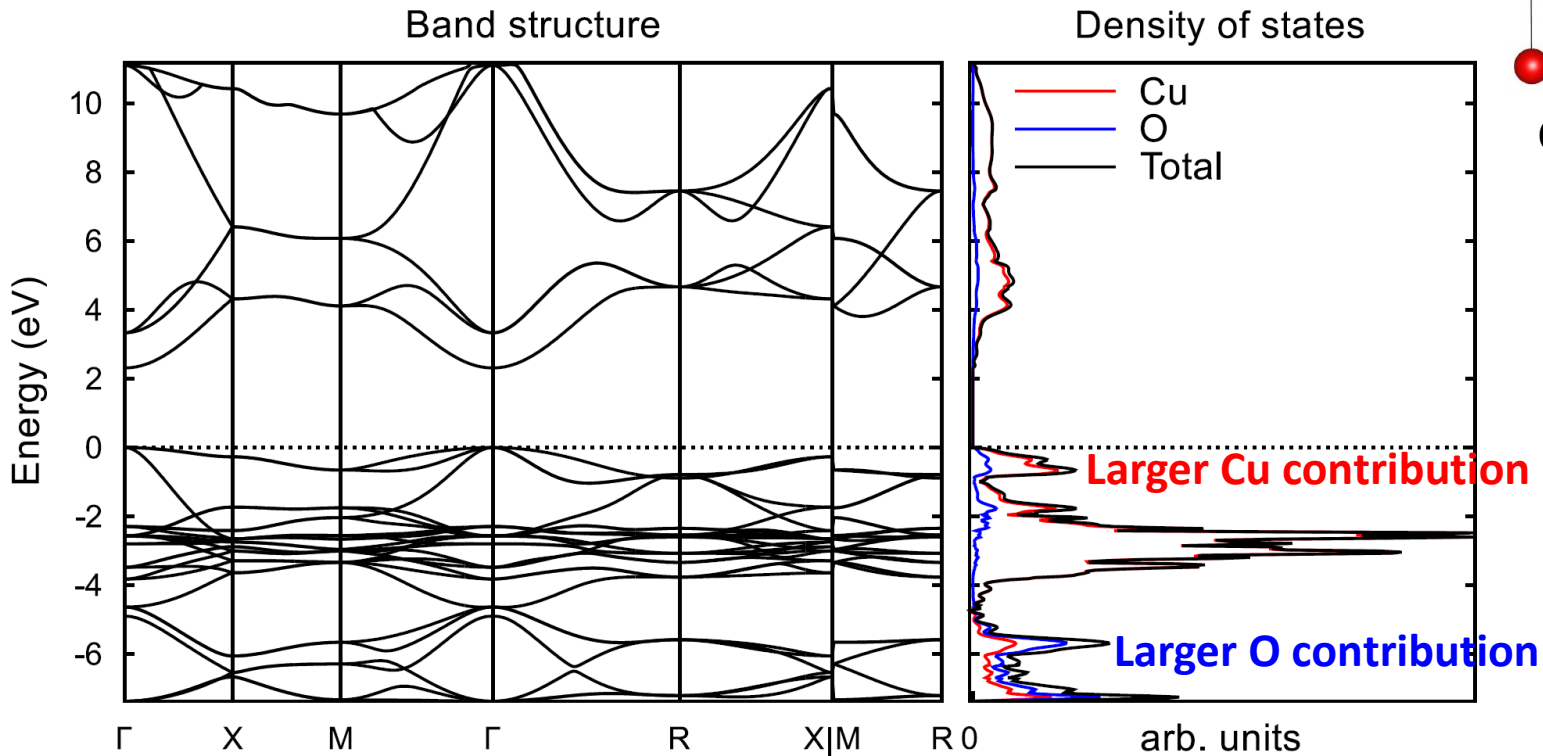
Density of states (3)

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

Figures: Jarno Linnera



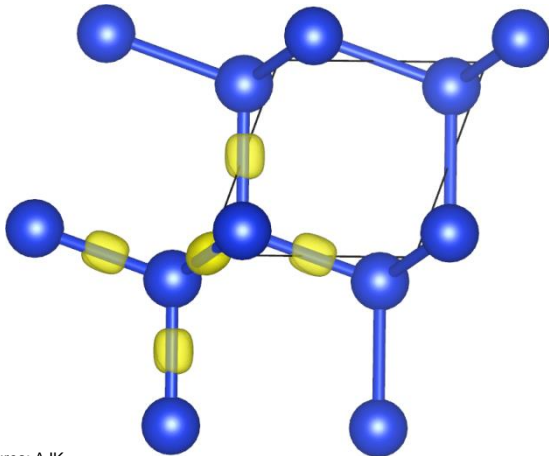
Cu_2O ($Pn-3m$)



The band structure and atom-projected DOS of Cu_2O

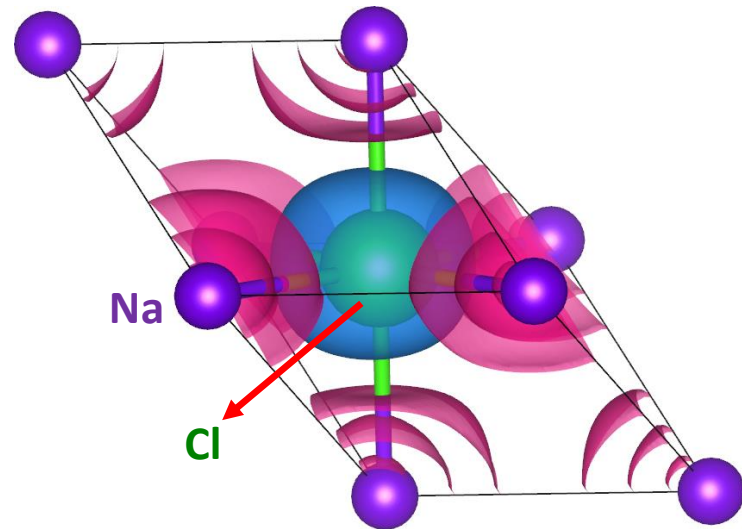
Real-space representations

- Band structures are reciprocal-space descriptions of the electronic structure
- There are many ways to convert them to the real space. Some examples:
 - Band-projected electron density plots and crystal orbital plots
 - Electron density (ρ) difference plots: $\rho(\text{solid}) - \rho(\text{non-interactive isolated atoms})$.
 - Bond Overlap populations (see discussion on $\text{K}_2[\text{Zr}(\text{NH}_2)_6]$)



Figures: AJK

Band-projected electron density in silicon (HOCO, isovalue 0.02 a.u.)



Electron density difference plot for NaCl (isovalue 0.004 a.u.). ρ has increased in the blue region and decreased in the red region

Molecular calculations for solid state structures: $K_2[Zr(NH_2)_6]$

The Complex Amide $K_2[Zr(NH_2)_6]$

Florian Kraus,^{*[a]} Sebastian A. Baer,^[a] and Antti J. Karttunen^[b]

Dedicated to Professor Hanskarl Müller-Buschbaum on the Occasion of His 80th Birthday

Z. Anorg. Allg. Chem. **2011**, 637, 1122–1130

Abstract. We present the low-temperature synthesis of potassium hexamido zirconate(IV) from the transition metal tetrafluoride and the alkali metal dissolved in liquid ammonia at $-40\text{ }^\circ\text{C}$. Potassium hexamido zirconate(IV) $K_2[Zr(NH_2)_6]$ is the first ternary amide reported for elements of group 4 of the periodic table. It crystallizes with a novel structure type in the trigonal space group $R\bar{3}c$ with $a = 6.5422(2)\text{ \AA}$, $c = 32.824(2)\text{ \AA}$, $V = 1216.66(9)\text{ \AA}^3$, $Z = 6$ and $c/a = 5.017$. The structure can be derived from the K_2PtCl_6 type. The compound contains discrete D_3 -symmetric $[Zr(NH_2)_6]^{2-}$ anions which differ significantly from octahedral shape. Quantum chemical calculations show the distortion to arise from a splitting of degenerate d-orbitals on the zirconium atom leading to a significant gain in energy.

$\text{K}_2[\text{Zr}(\text{NH}_2)_6] \cdot (2)$

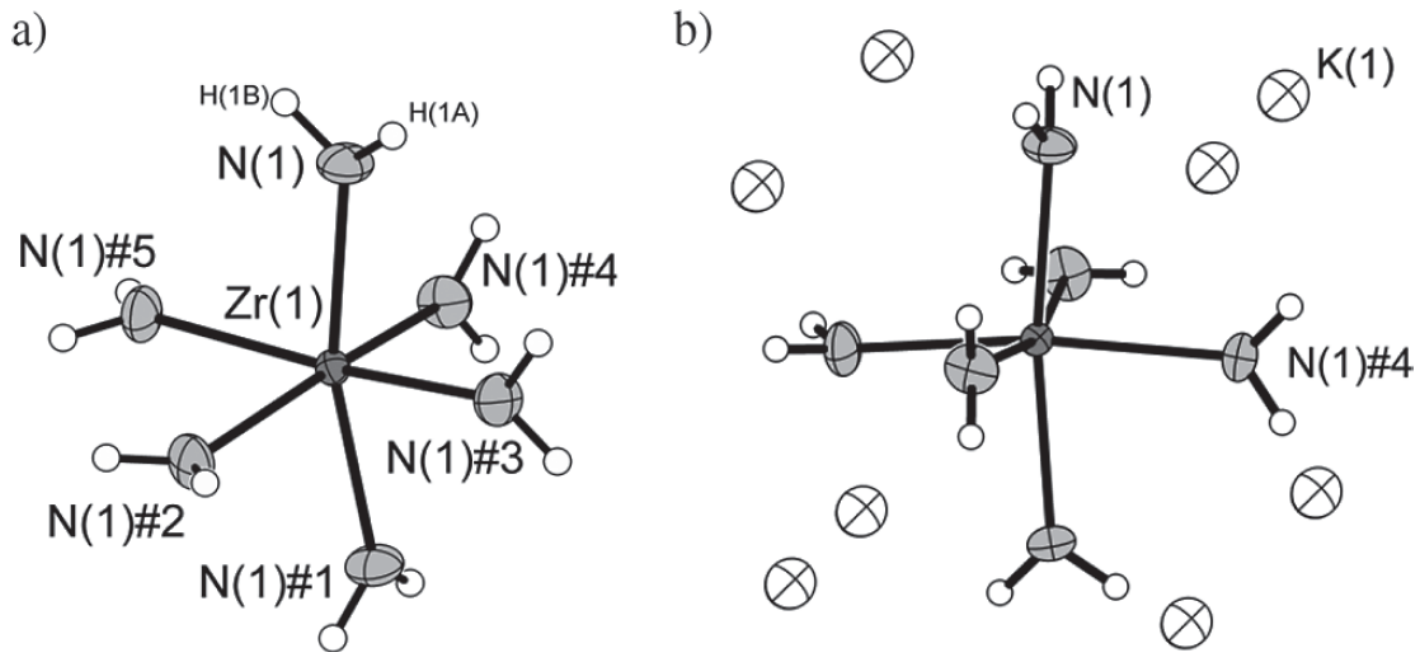
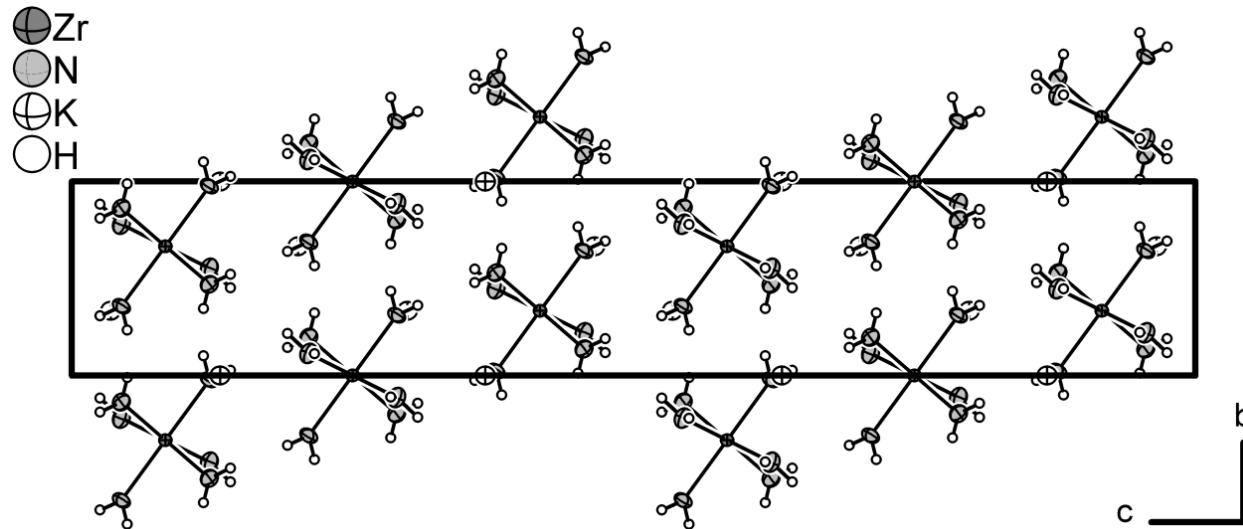


Figure 1. a) Projection of the $[\text{Zr}(\text{NH}_2)_6]^{2-}$ anion of compound **1**. b) Projection of the coordination sphere of the $[\text{Zr}(\text{NH}_2)_6]^{2-}$ anion by potassium ions of compound **1**. Thermal displacement parameters are shown at 70 % probability level at 123 K. Symmetry transformations for the generation of equivalent atoms: #1 $-x, -x+y, -z+1/2$; #2 $x-y, -y, -z+1/2$; #3 $y, x, -z+1/2$; #4 $-y, x-y, z$; #5 $-x+y, -x, z$.

$K_2[Zr(NH_2)_6]$ (3)



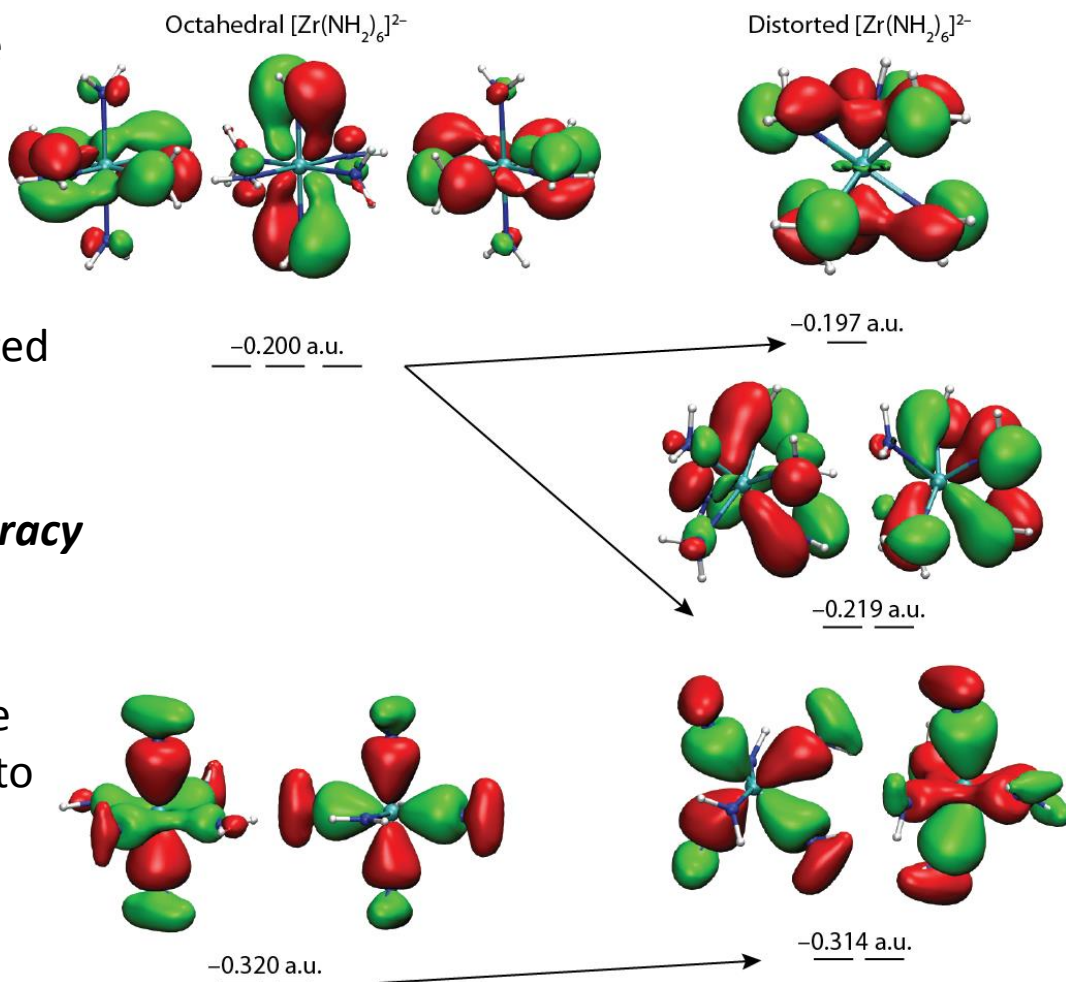
- **The question:** Why are the $[Zr(NH_2)_6]^{2-}$ anions in $K_2[Zr(NH_2)_6]$ distorted from perfect octahedral coordination?
- In analogous compound $K_2[Sn(NH_2)_6]$, the $[Sn(NH_2)_6]^{2-}$ anions have perfect octahedral coordination
- Quantum chemical approach:
 - Solid state DFT calculations for $K_2[Zr(NH_2)_6]$
 - Molecular DFT calculations for $[Zr(NH_2)_6]^{2-}$

$K_2[Zr(NH_2)_6]$ (4)

- First, we tried to explain the structural difference between the $[Zr(NH_2)_6]^{2-}$ and $[Sn(NH_2)_6]^{2-}$ anions by investigating the solid state structures
- Could the distortion of $[Zr(NH_2)_6]^{2-}$ be due to **hydrogen bonding**?
- Compare the **strength** of the hydrogen bonds via **bond overlap analysis**
- Solid ammonia (reference structure which has strong hydrogen bonds):
 - The covalent N–H bonds possess a bond overlap population of $0.337 e^-$
 - The overlap population for the N \cdots H hydrogen bonds is $0.040 e^-$
- In $K_2[Zr(NH_2)_6]$, the overlap populations for the N \cdots H hydrogen bonds are equivalent to those in solid ammonia ($0.044 e^-$ and $0.040 e^-$)
 - Real hydrogen bonding is present in the structure
- In $K_2[Sn(NH_2)_6]$, N \cdots H overlap populations are one order of magnitude smaller
 - N \cdots H hydrogen bonding does not take place.
- However, it is not clear why the hydrogen bonding should distort $[Zr(NH_2)_6]^{2-}$
- We decided to investigate the **electronic structure** of the anions in more detail

$\text{K}_2[\text{Zr}(\text{NH}_2)_6] (5)$

- The **molecular orbitals** of the $[\text{Zr}(\text{NH}_2)_6]^{2-}$ anion involving **bonding Zr–N interactions** (isodensity value 0.04 a.u.).
- The undistorted anion (S_6) is shown on the left, the distorted one (D_3) on the right
- Distortion of the octahedral geometry **breaks the degeneracy** of the three-fold degenerate Zr(d)–N bonding MOs
- The Zr(d)–N bonding MOs are stabilized by ~ 18 kJ/mol due to **improved orbital overlap**





- What about $[Sn(NH_2)_6]^{2-}$?
- Unlike for Zr, Sn has no empty metal d-orbitals available for the Sn–N(sp^3) bonding
- Thus, distortion of the octahedral structure would not lead to additional stabilization of the complex via improved orbital overlap.
- **Conclusion:** The *electronic effects* play a key role in the distortion, the hydrogen bonding network in $K_2[Zr(NH_2)_6]$ might have a minor role
- **Take-home message:** Molecular calculations can also be helpful in understanding solid-state structures, if the solid state structure has molecular building blocks