Fundamentals of heterogeneous catalysis

The very basics
of “band structure” for electronic structure description

R. Schlögl

www.fhi-berlin.mpg.de

Disclaimer

- This lecture is a qualitative introduction into the concept of electronic structure descriptions different from “chemical bonds”.
- No mathematics, unfortunately not rigorous.
- For real understanding read texts on solid state physics.
- Hellwege, Marfunin, Ibach+Lüth
- The intention is to give an impression about concepts of electronic structure theory of solids.

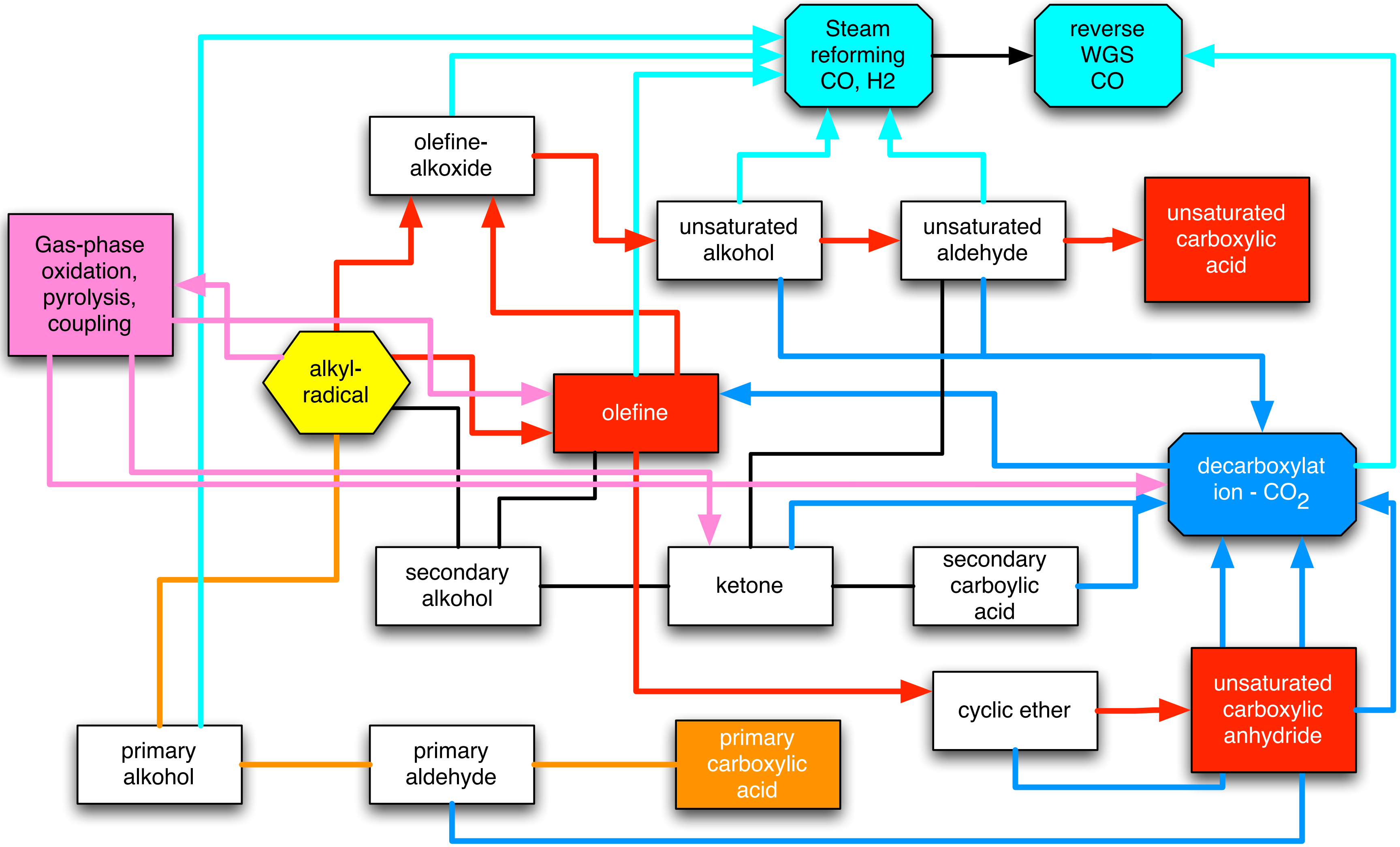
Electronic structure

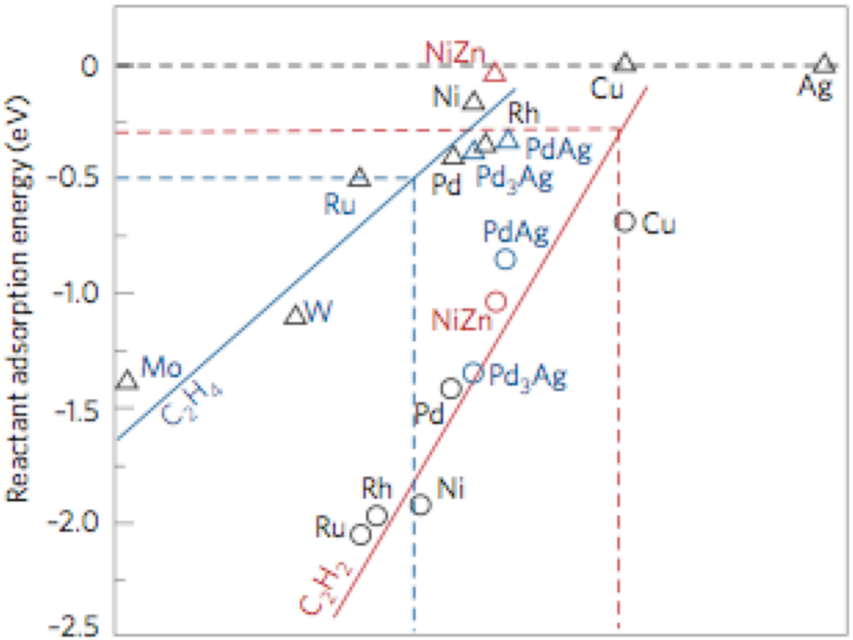
- For chemists well described by Lewis formalism.
- “chemical bonds”.
- Theorists derive chemical bonding from interaction of atoms with all their electrons.
- Quantum chemistry with fundamentally different approaches:
  - DFT (density functional theory), see introduction in this series
  - Wavefunction-based (many variants).
- All solve the Schrödinger equation.
- Arrive at description of energetics and geometry of atomic arrangements; “molecules” or unit cells.

Catalysis and energy structure

- The surface of a solid is traditionally not described by electronic structure theory:
- No periodicity with the bulk: cluster or slab models.
- Bulk structure infinite periodically and defect-free.
- Surface electronic structure theory independent field of research with similar basics.
- Never assume to explain reactivity with bulk electronic structure: accuracy, model assumptions, termination issue.
- But: electronic structure fully determines all chemical reactivity.

Alkane activation
many reactions over one catalyst





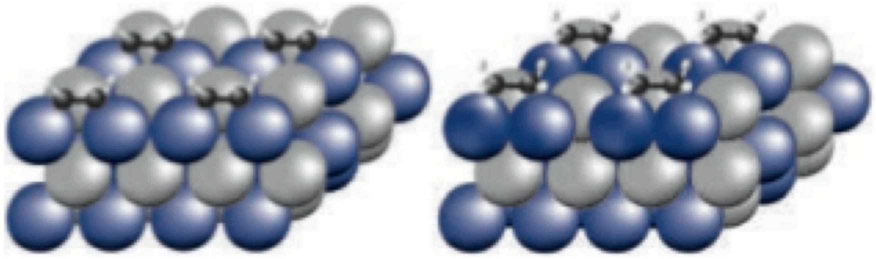

nature chemistry

REVIEW ARTICLE

| DOI: 10.1038/NCHEM.121

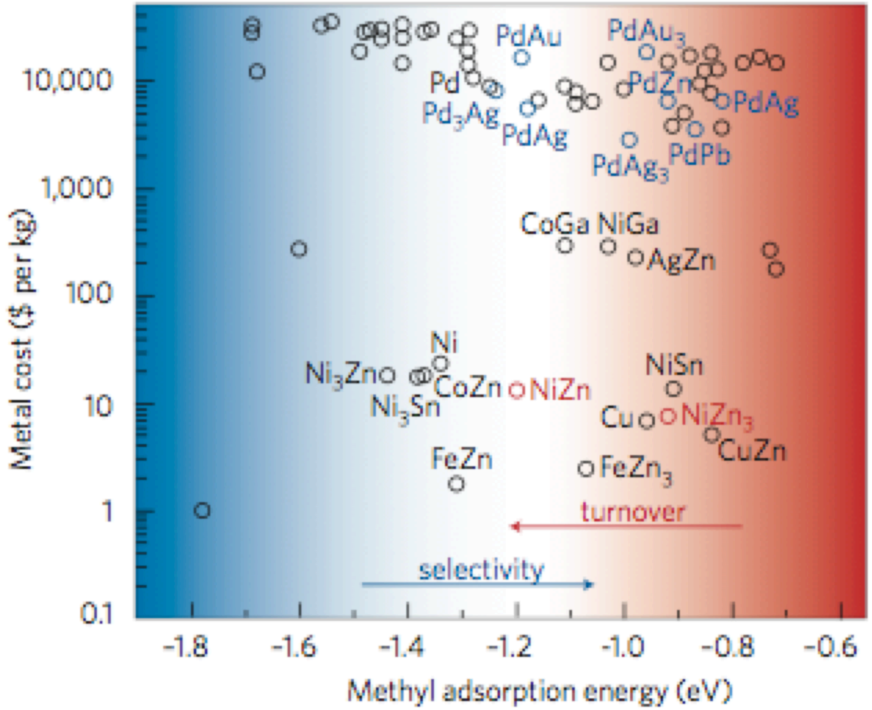
Towards the computational design of solid catalysts

J. K. Nørskov[1]*, T. Bligaard[1], J. Rossmeisl[1] and C. H. Christensen[2]

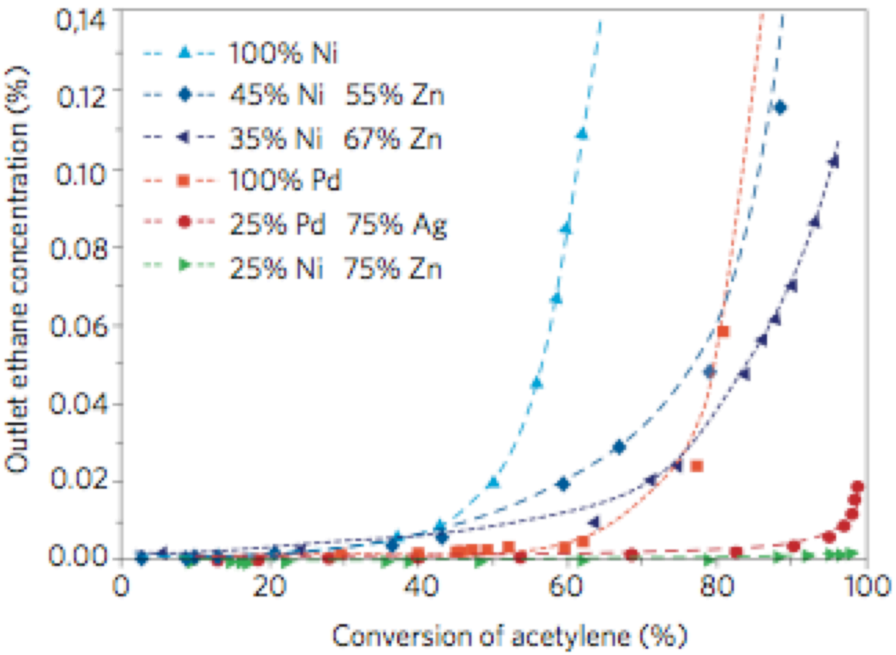


Stability and decomposition kinetics

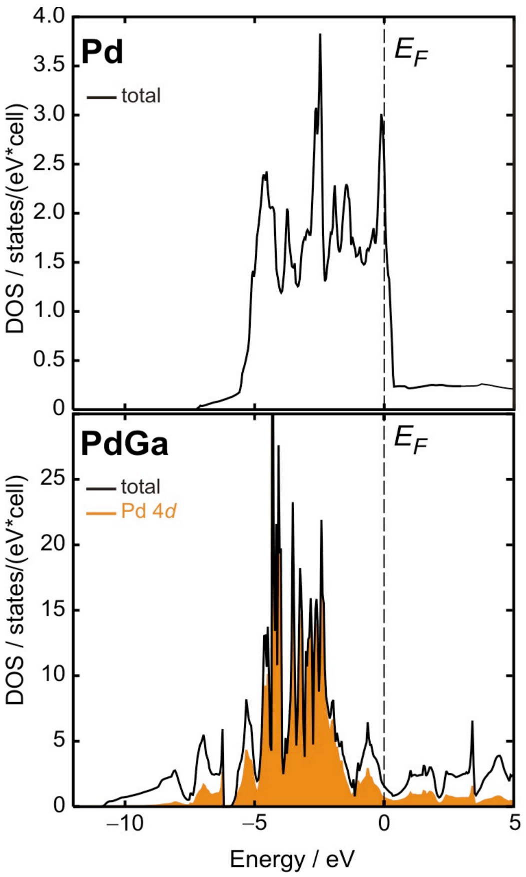
b

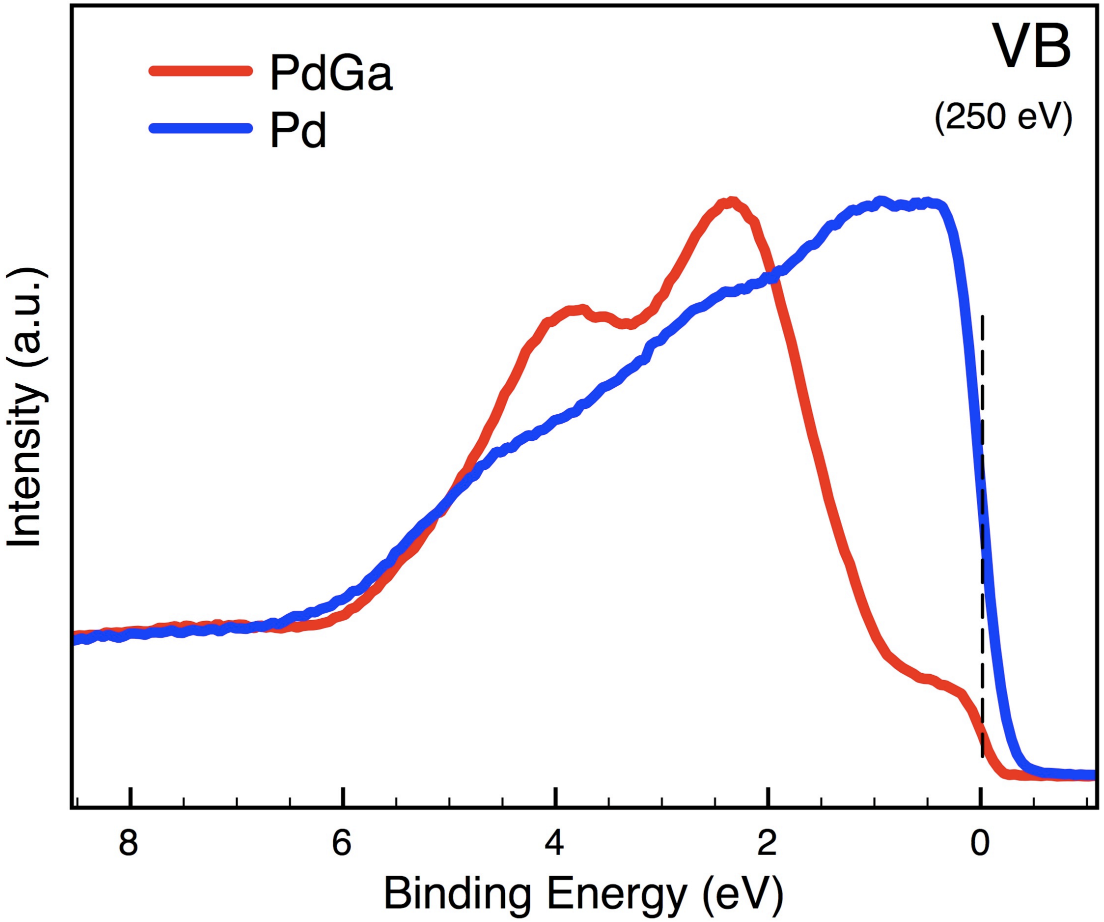


d

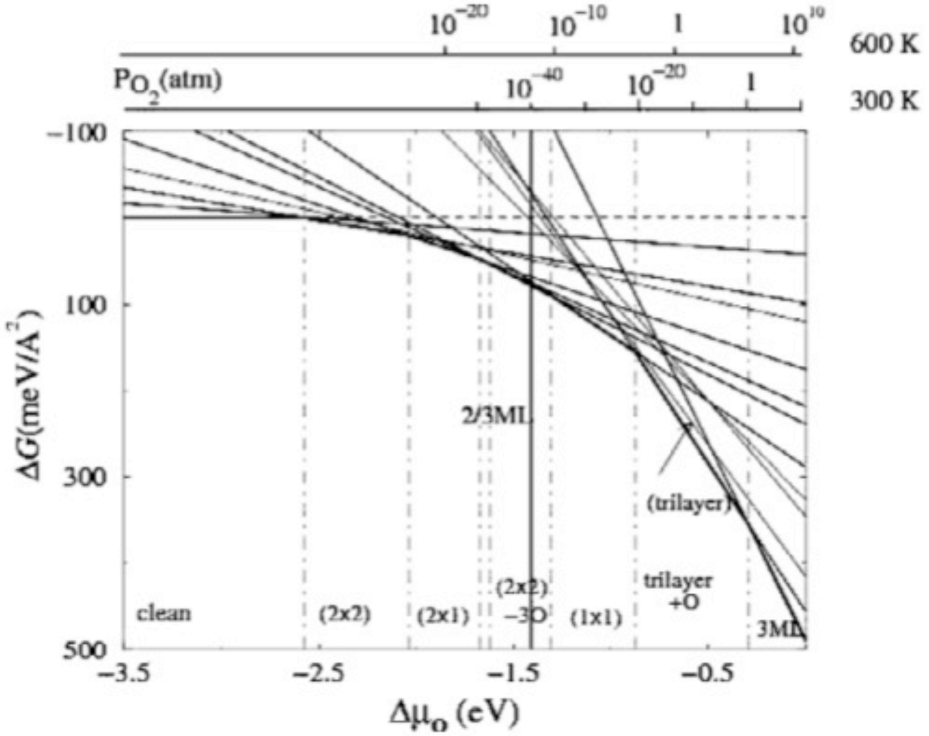


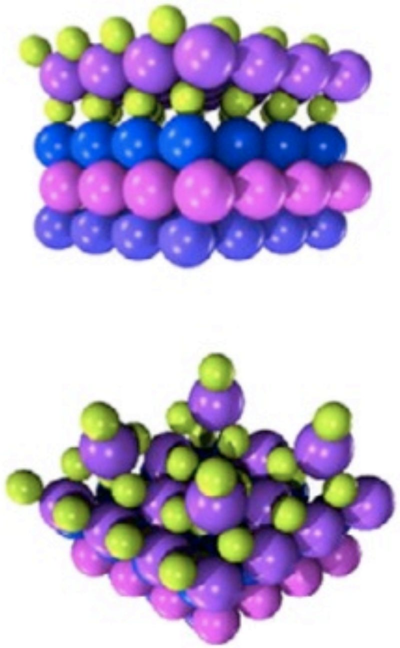
Covalent interaction: good for selectivity





Ru/O_2: Surface thermodynamics





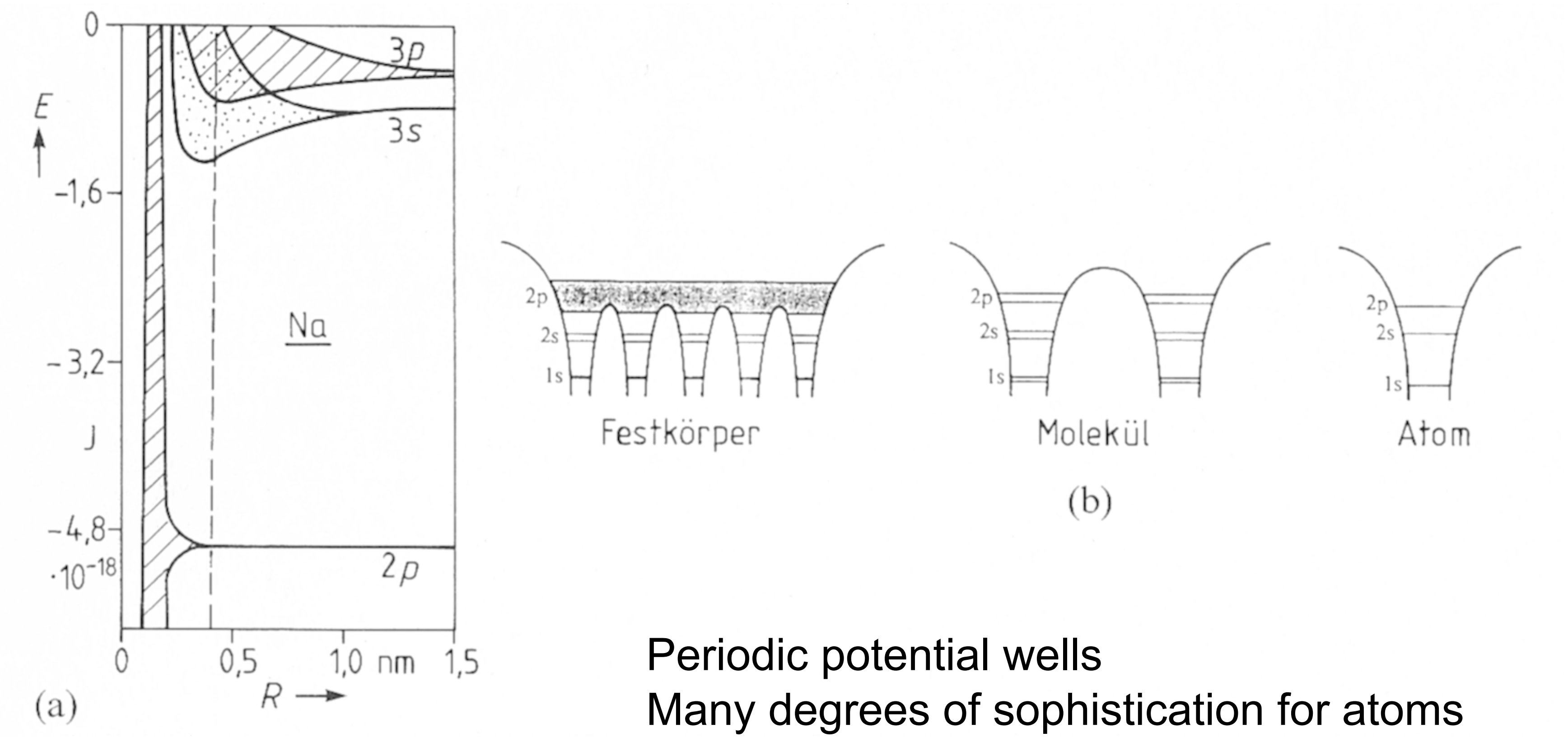
C. Stampfl et al.
J. Phys. C, 2008
K. Reuter,
M. Scheffler

With increasing oxidation potential:
adsorbates,
adsorbates on surface oxide (sub-surface),
surface oxide,
bulk oxide (may be more stable than surface oxide)

Energy conventions

- 1 eV = 1.6 10^{-19} J
- 1K = 1.38 10^{-23} J, 8.61 10^{-5} eV
- Energy is counted negative for “binding” and positive for “antibinding”.
- Atoms contain electrons with a vast range of binding energies: 0 - 20.000 eV.
- Energy scales often begin with zero on top of graph!

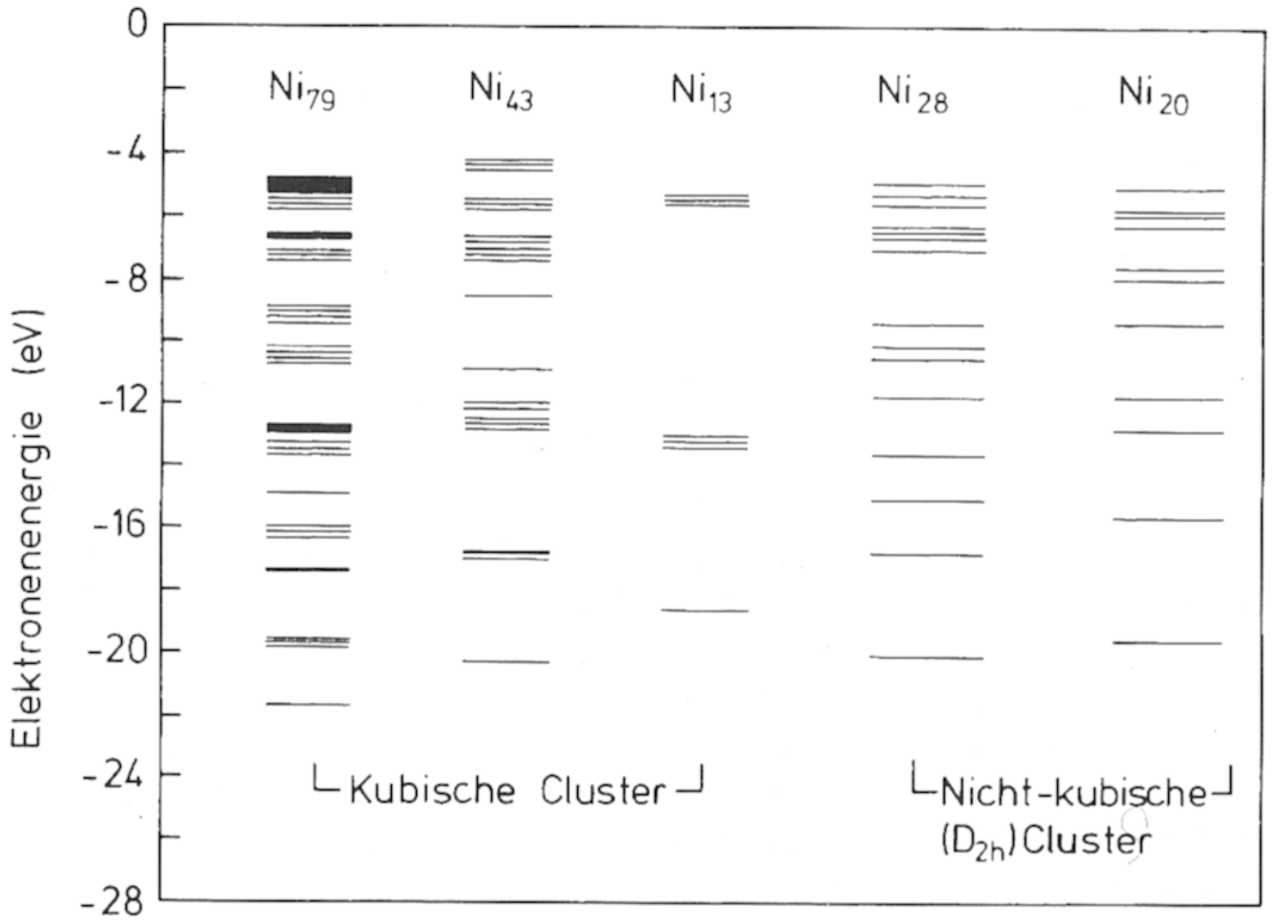
Energy representations



Periodic potential wells
Many degrees of sophistication for atoms

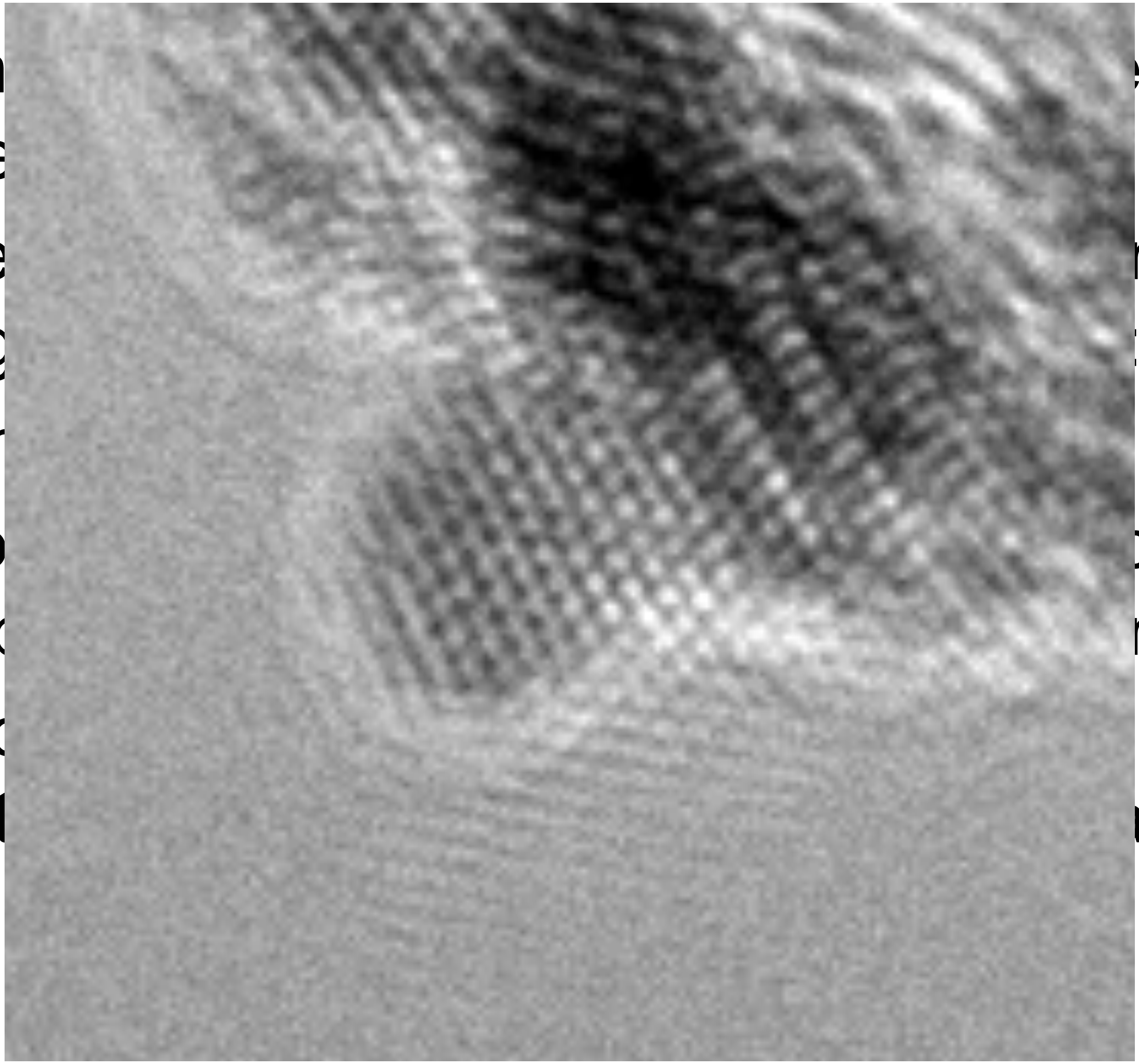
After: Slater, 1936

The chemist´s view of “bands”



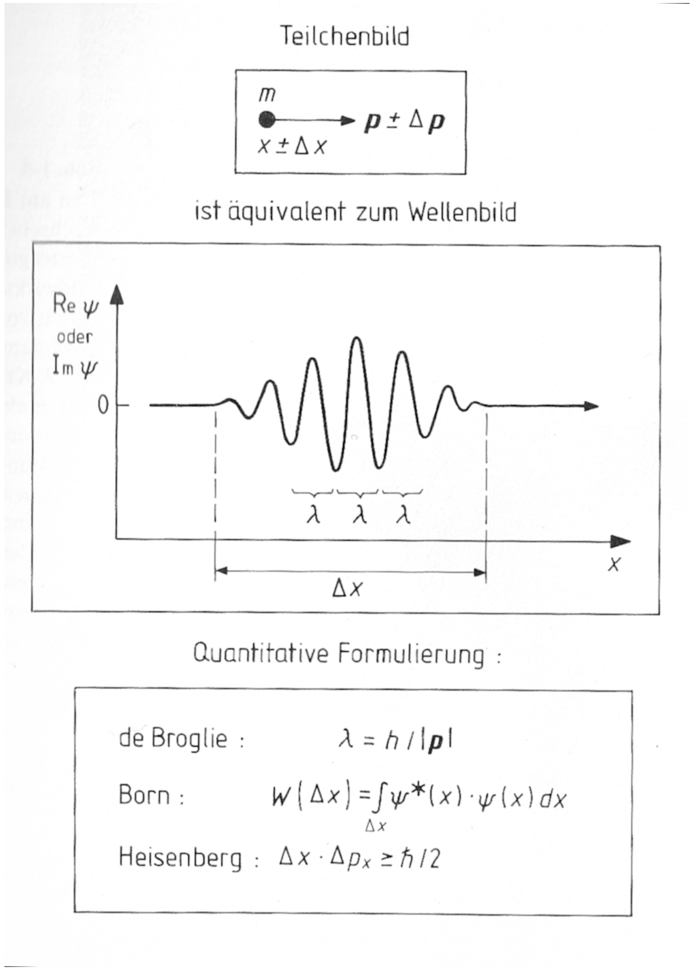
Remember: valence band, conduction band, Fermi energy

Band structure theory



- The ph with a comple
- No che ns moving
- A kiner
- Develo bonds and orb n space.
- Transf procal lattice t ce

Nature of electrons



Teilchenbild

ist äquivalent zum Wellenbild

Quantitative Formulierung :

de Broglie : $\lambda = h / |\mathbf{p}|$

Born : $W(\Delta x) = \int_{\Delta x} \psi^*(x) \cdot \psi(x)\, dx$

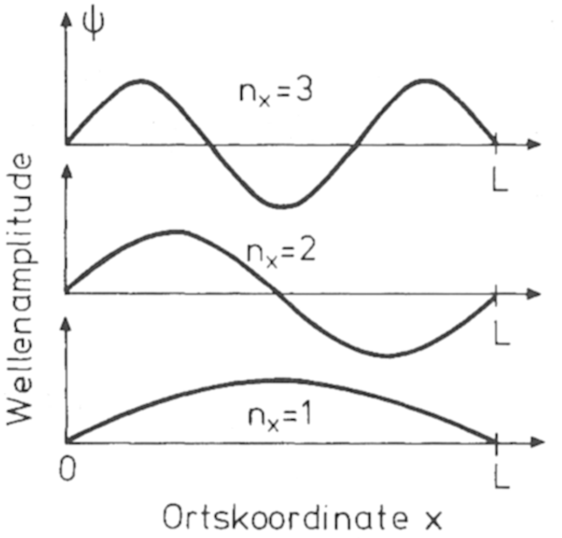
Heisenberg : $\Delta x \cdot \Delta p_x \geq \hbar / 2$

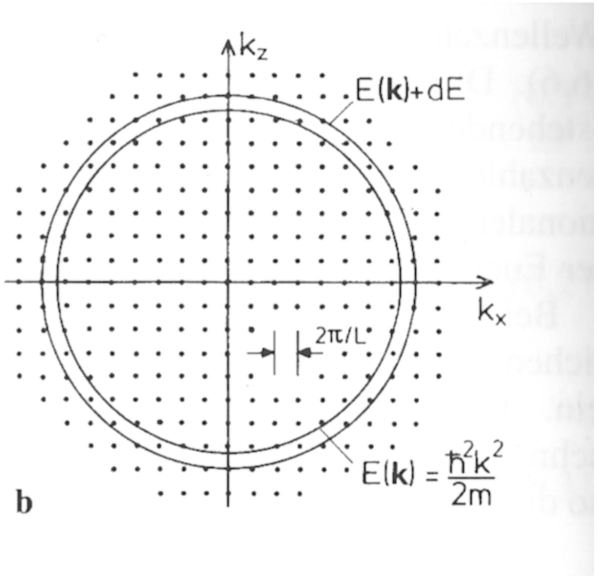
Wavefunctions occur also here for electron movement.

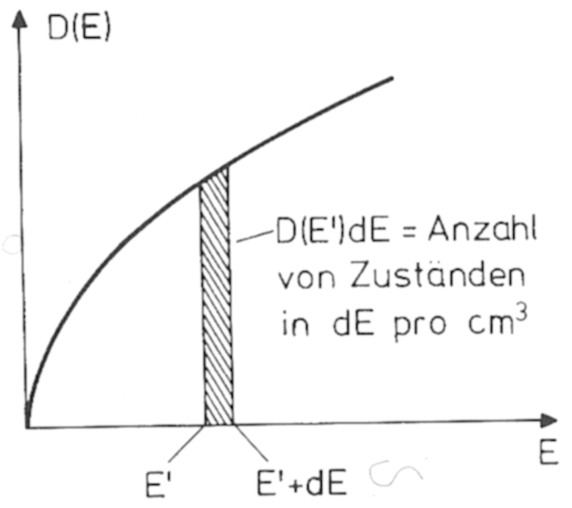
They have different form than the atomic wavefunctions in the initial theory

Today modern computational methods use also “atom-like” functions

Particle in box model







Representations of electrons in 1-D and 2-D descriptions. No need for atoms or solids, a pure model concept.

Descriptions using a “lattice” of wavevector endpoints: conceptual similarity to a solid with atoms forming a lattice (not the same one!!).

The most basic description of electrons in motion

$$E = \frac{1}{2} m v^2$$

$$v = \frac{h}{m \cdot \lambda}$$

$$\lambda = 2L/n$$

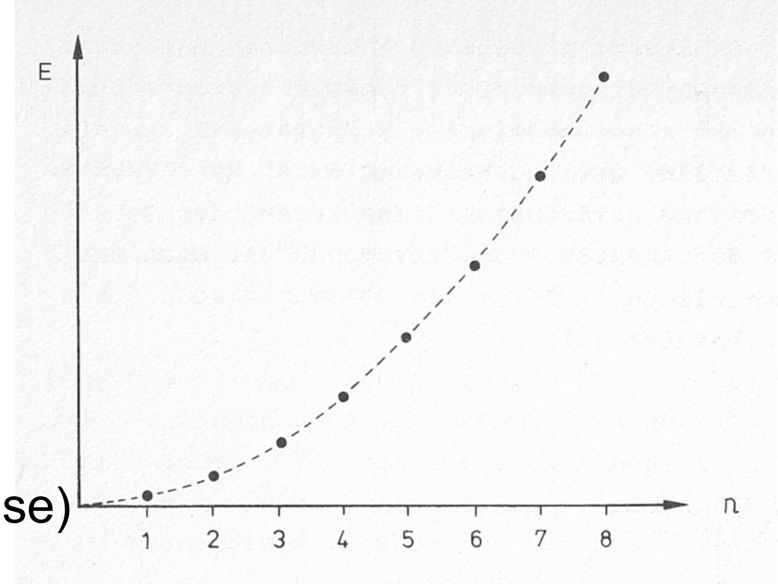
$$v = \frac{n \cdot h}{2 L m}$$

$$E = \frac{1}{2} m \cdot v^2$$

$$E = \frac{m \cdot n^2 v^2}{2 m^2 4 L^2}$$

$$E = \frac{n^2 h^2}{8 m L^2}$$

Each point represents a state with 2 electrons
With real dimensions of L the parabola is “quasicontinuum” for electrons

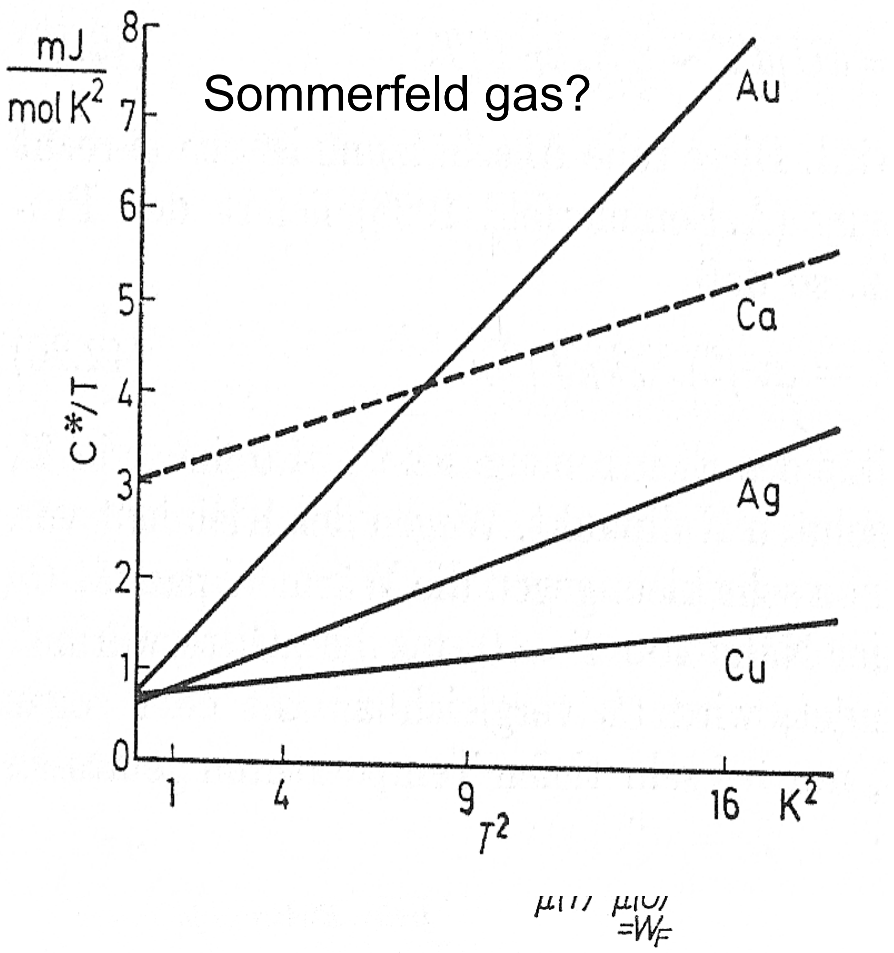


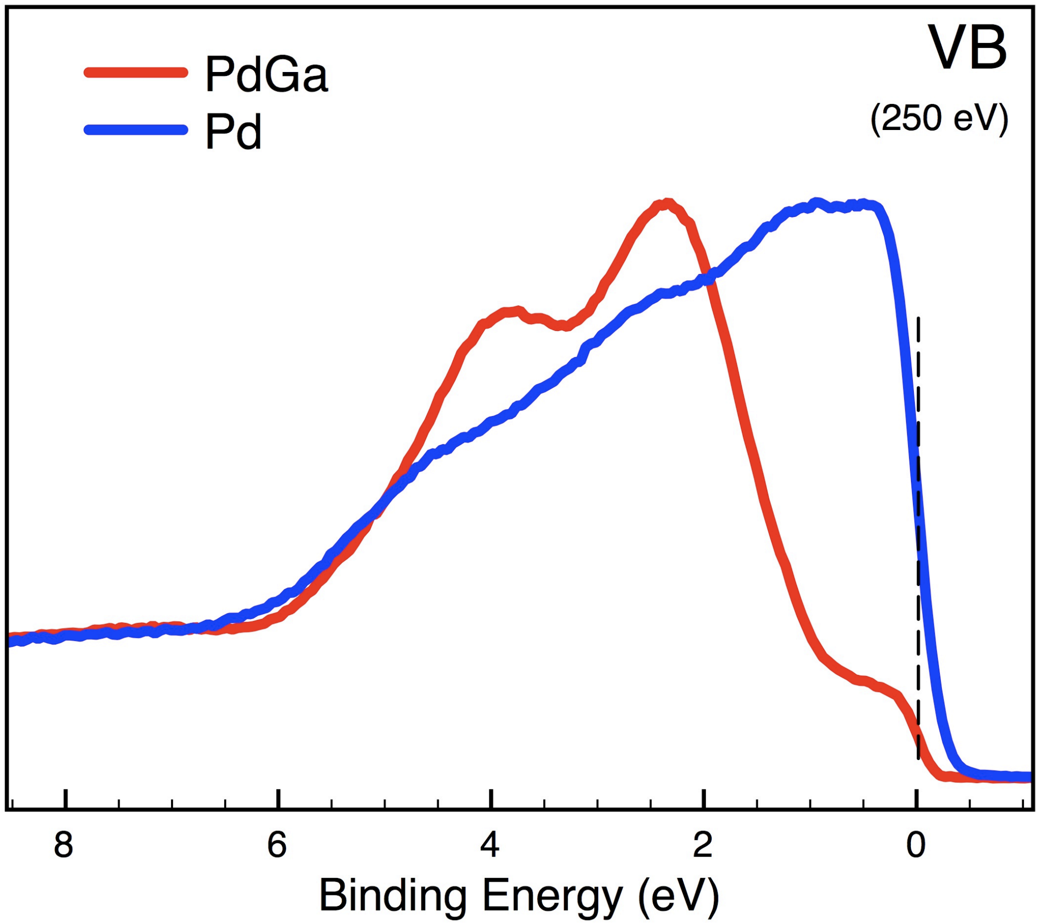
Electrons as waves in a potential box (the 1-D case)

Conditions for standing waves: “reflection” at box walls

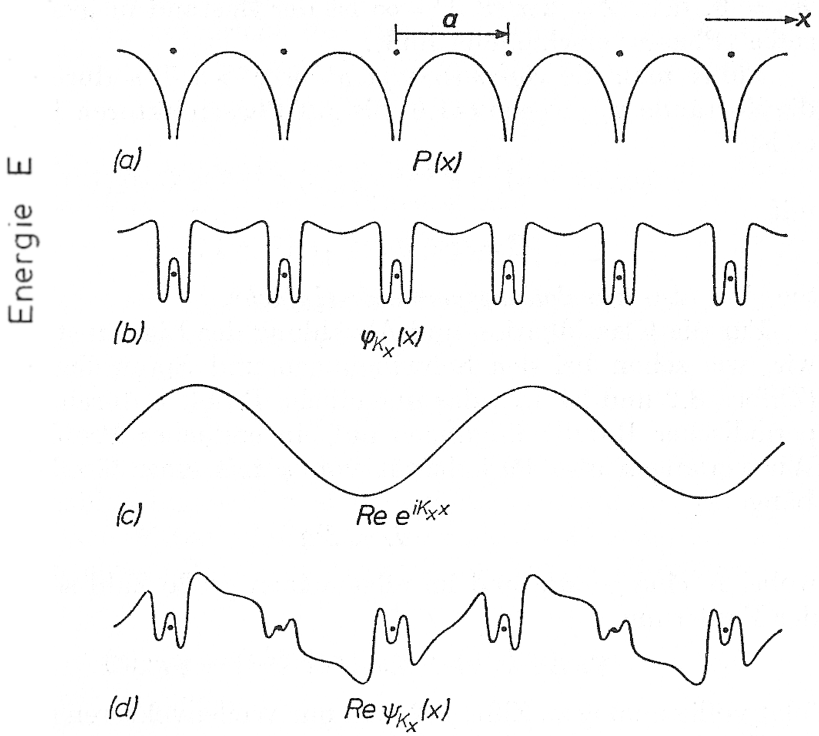
Selection criterion introduces quantum number

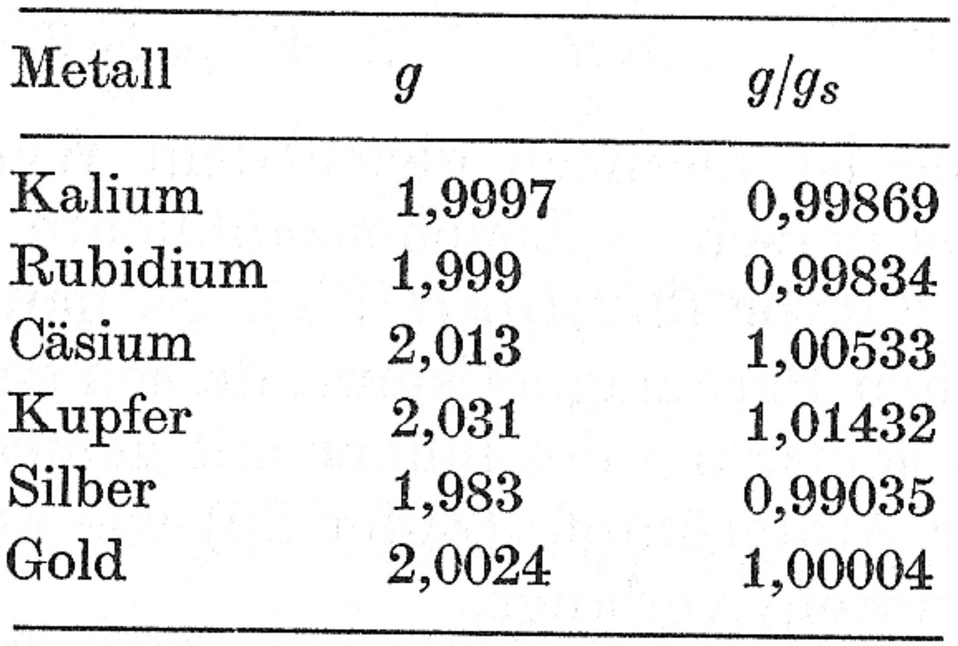
Density of states
how many electrons are free?


Sommerfeld gas?



Nature of electrons not free as lattice gas





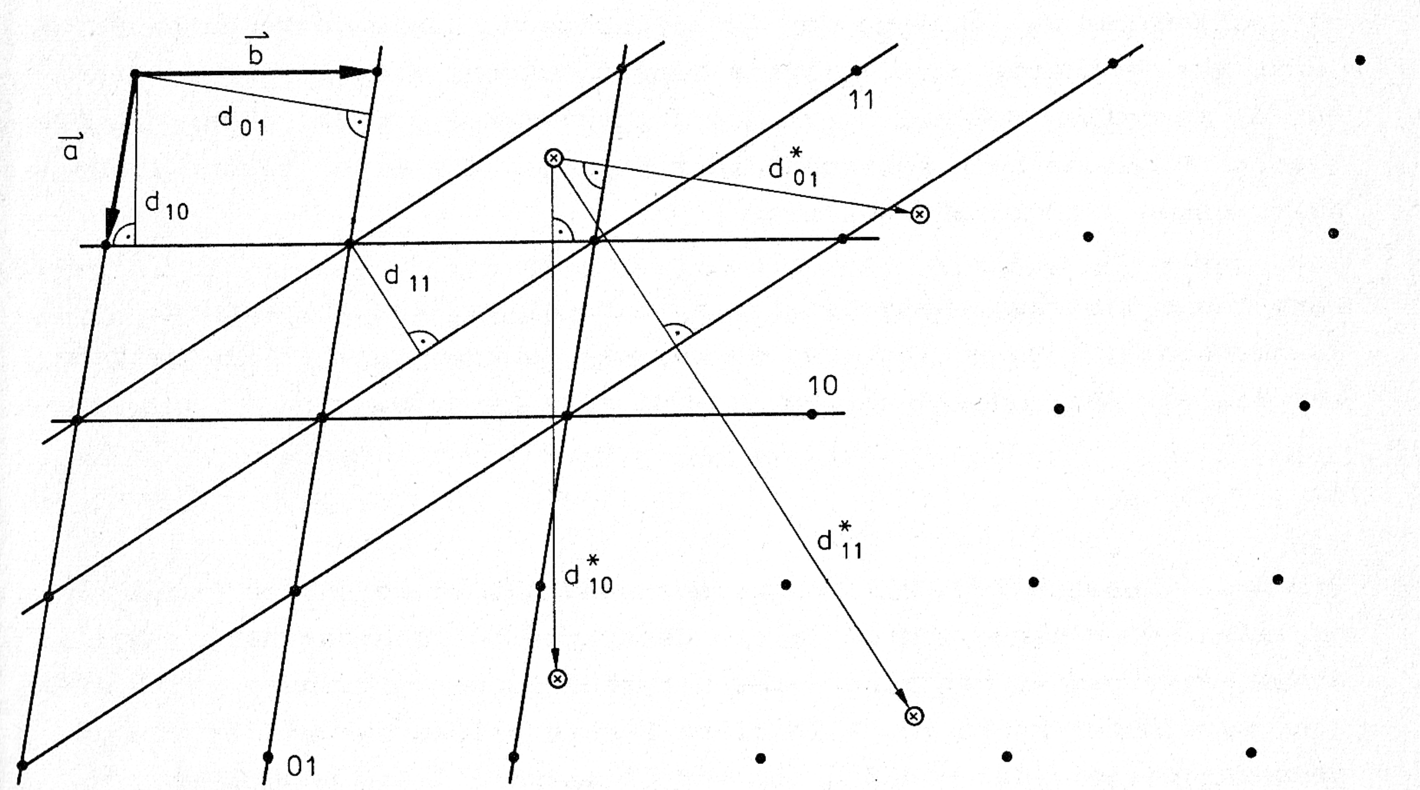
Metall	g	g/g_s
Kalium	1,9997	0,99869
Rubidium	1,999	0,99834
Cäsium	2,013	1,00533
Kupfer	2,031	1,01432
Silber	1,983	0,99035
Gold	2,0024	1,00004

The folding of electron waves with a periodic potential leads to wave states called “Bloch waves”

Contain the full structural information of system

Simplifications by approximating the potential through “muffin tins”

The real case: electrons in lattices

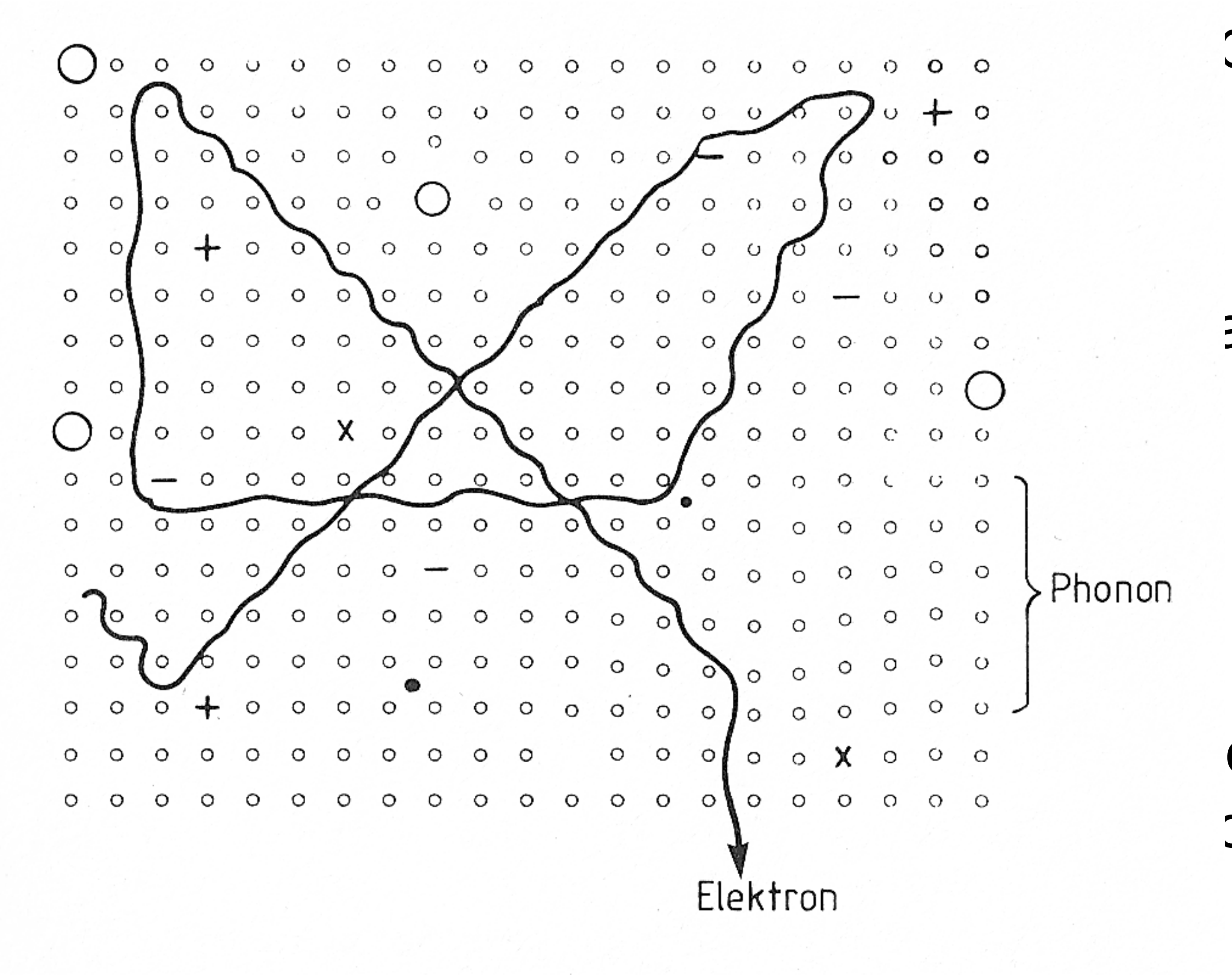


$$d^*_{hk} = a \cdot \frac{1}{d_{hk}} \qquad a = 2\pi \quad \Big| \quad d^*_{hkl} = \frac{2\pi}{d_{hkl}}$$

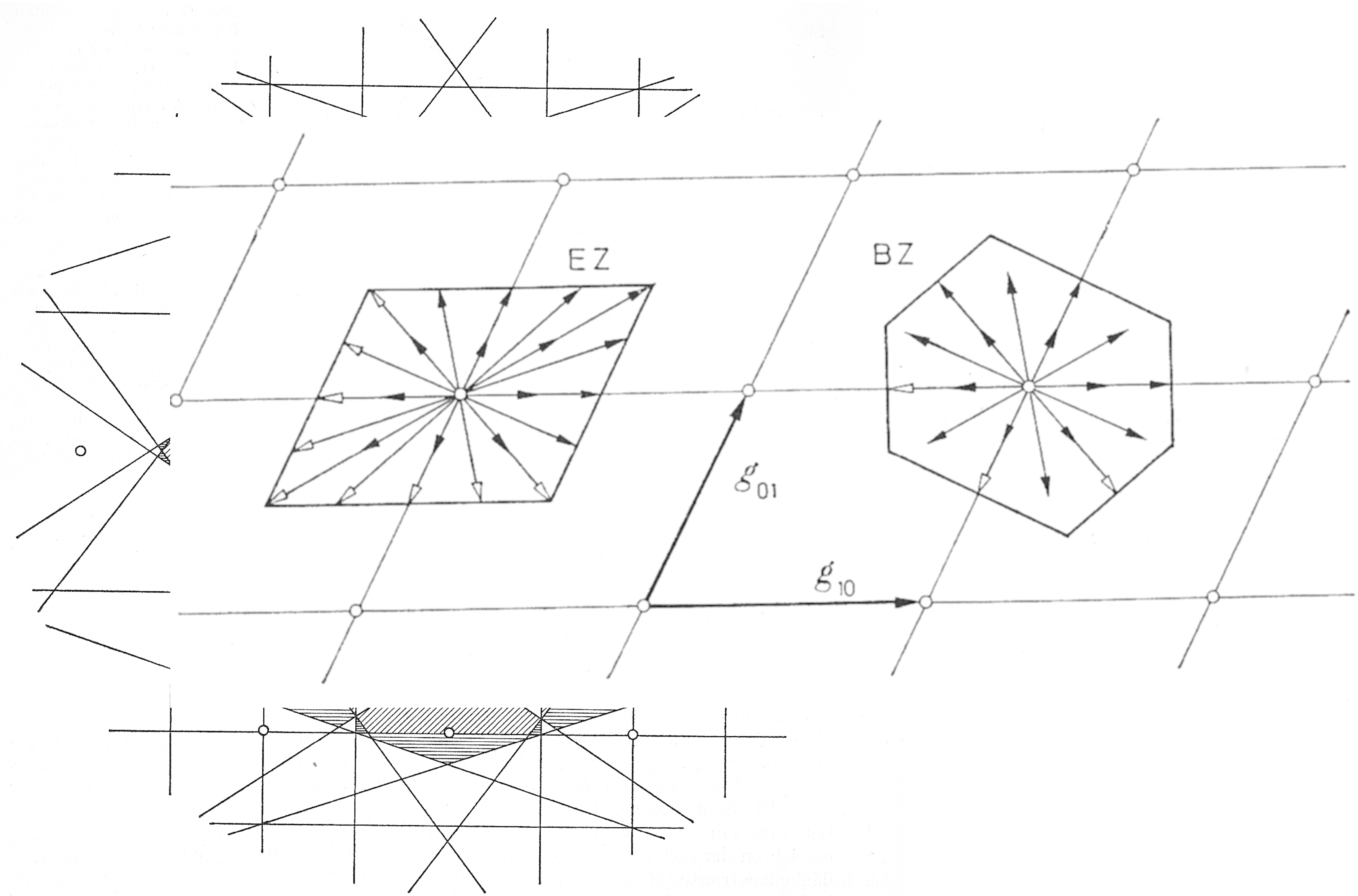
$$\vec{G}_{hkl} = h \cdot a^* + k \cdot b^* + l\, c^*$$

The reciprocal lattice

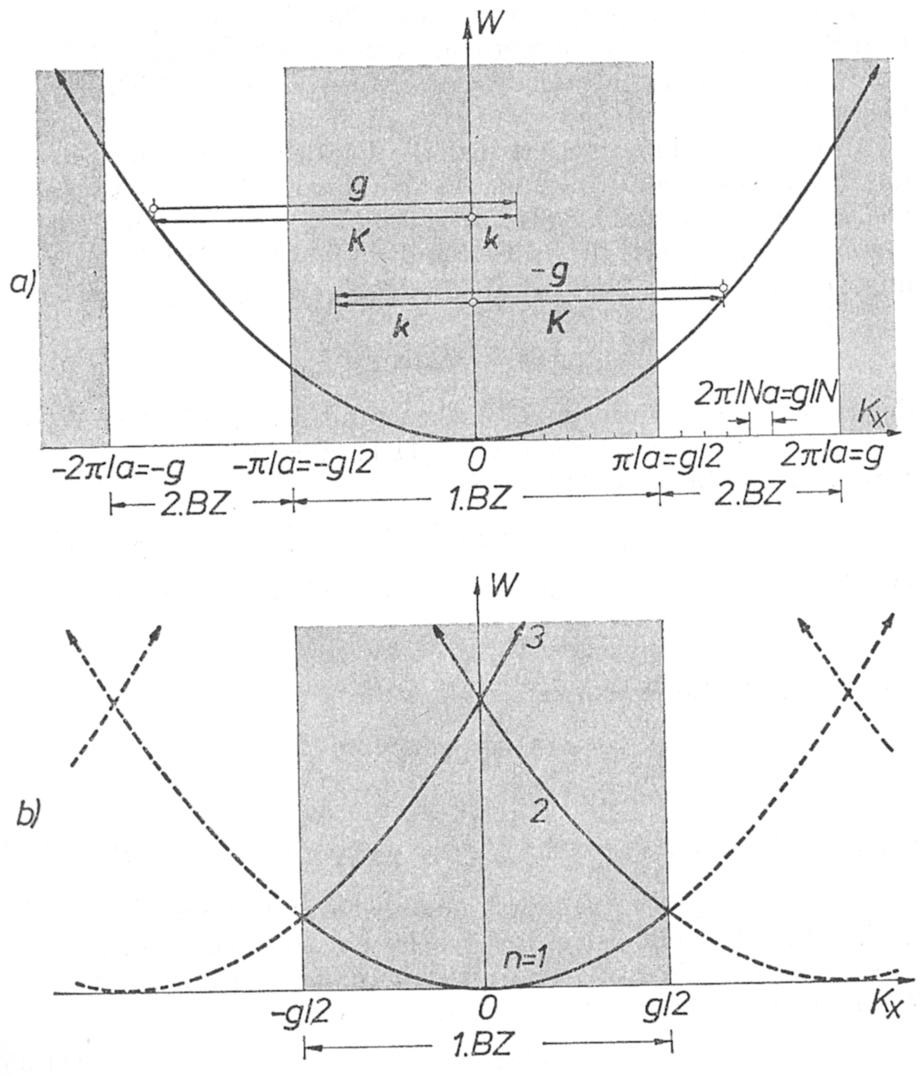
- Th pace.
- Is
  - –
  - – as vector
- Pr
  fo
  - – ce point:
    ction



Unit cells in RL: Brillouin zones



Energy bands in BZ



1 D case

Extended scheme (many BZ)

Reduced case: back transformation into 1 st BZ

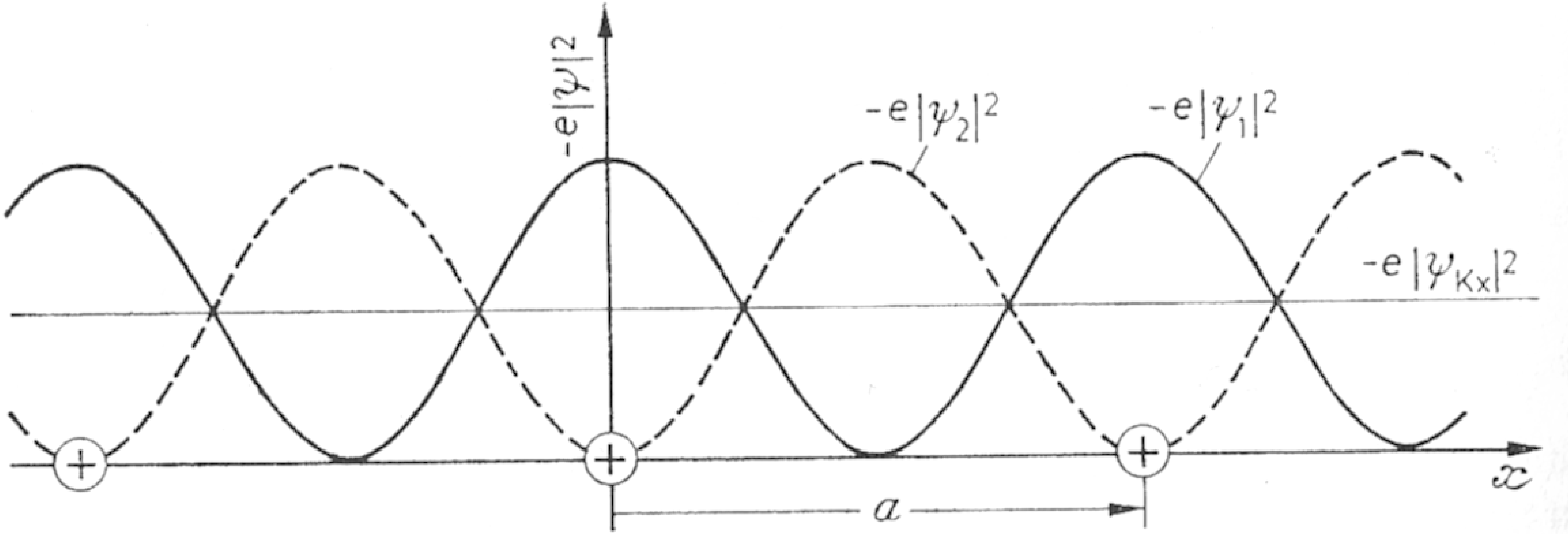
Note: only possible due to translational symmetry and definition of RL

The steeper the band the more strongly bound is the state

There is no potential within the 1 st BZ:
Free electrons

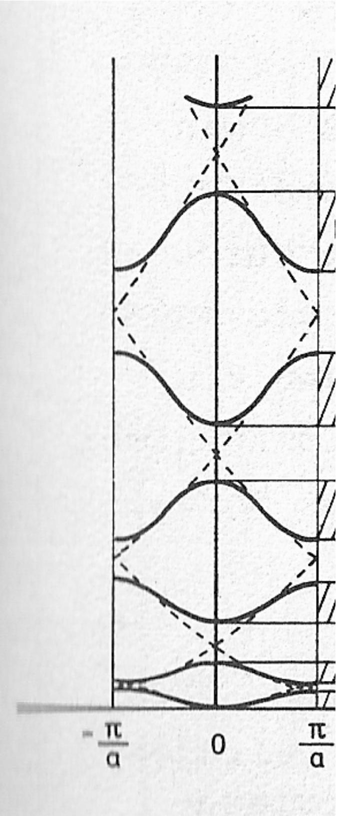
The effect of "binding"

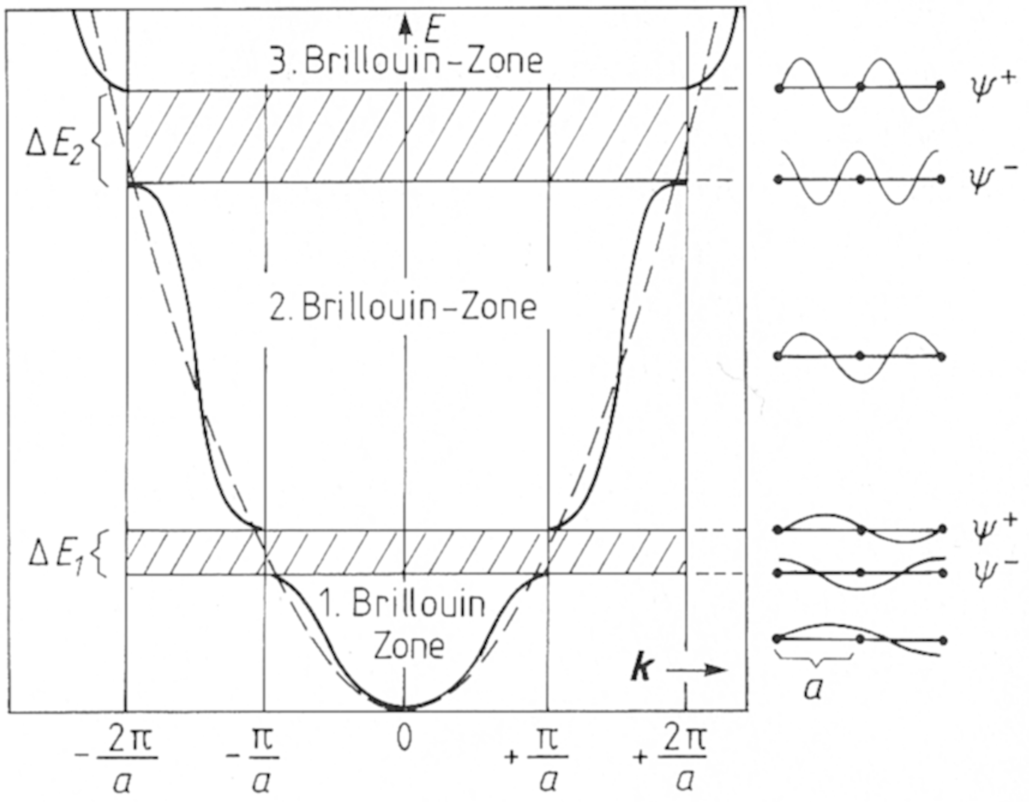
- When the electrons feel the periodic potential



- This causes two energy states with all energies in between forbidden (as destructive interference).

Energy bands in a lattice with potential



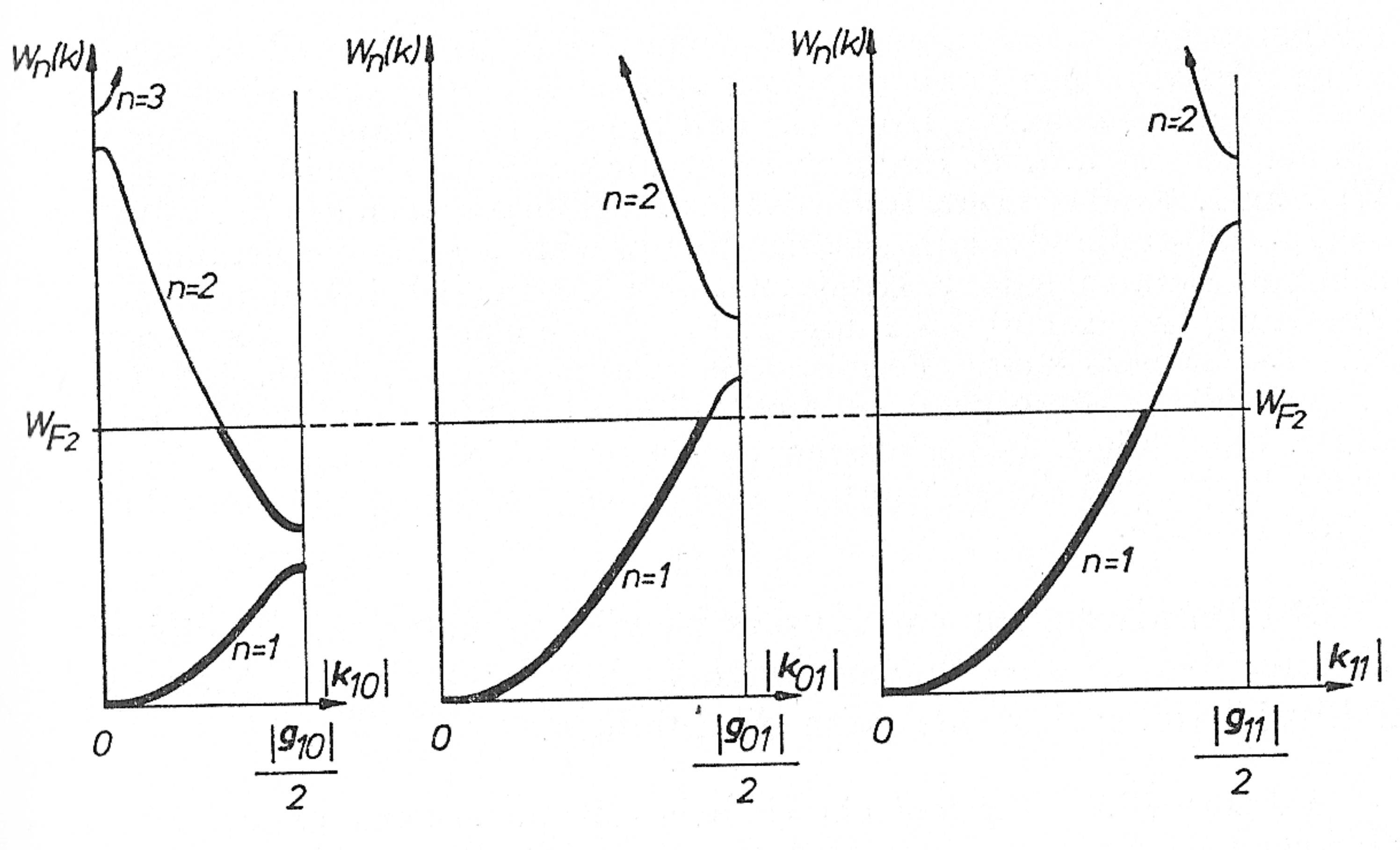


The Bloch waves produce discontinuities of electron bands at boundaries of BZ
This generates the band scheme with allowed and disallowed regions
Not the accumulation of electronic states!

Bands in real solids

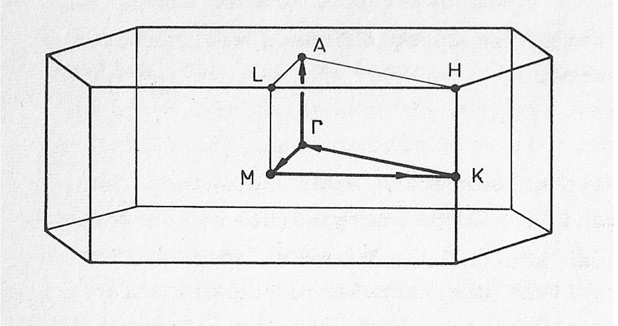
- The size of the bandgap depends on potential and thus on atom type.
- The bands are practically filled everywhere, as they are the geometric locations of wave vectors ending far out in the RL and being back-projected into the 1 st BZ.
- As the potential is translationally symmetric within the RL, all electrons feel the same energy difference when standing as waves.

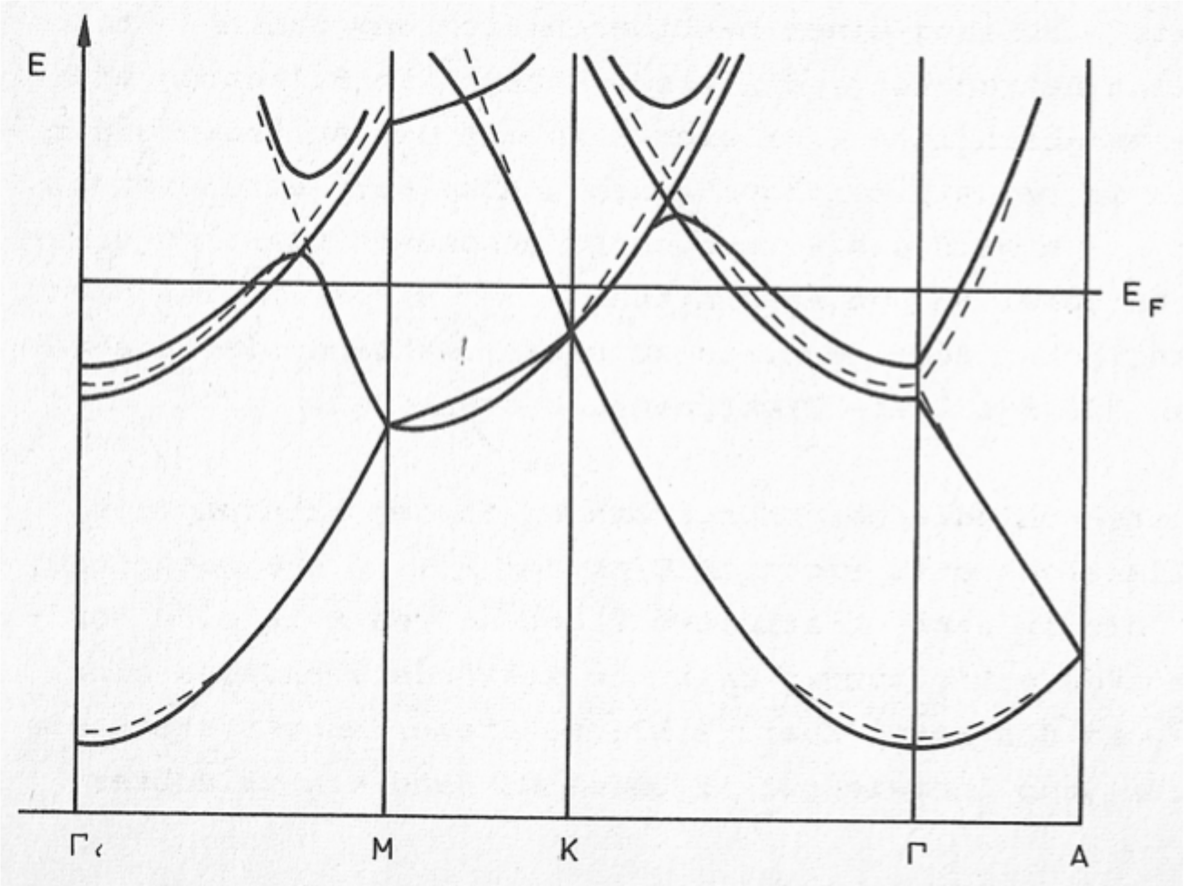
Anisotropy: the shape of the RL matters



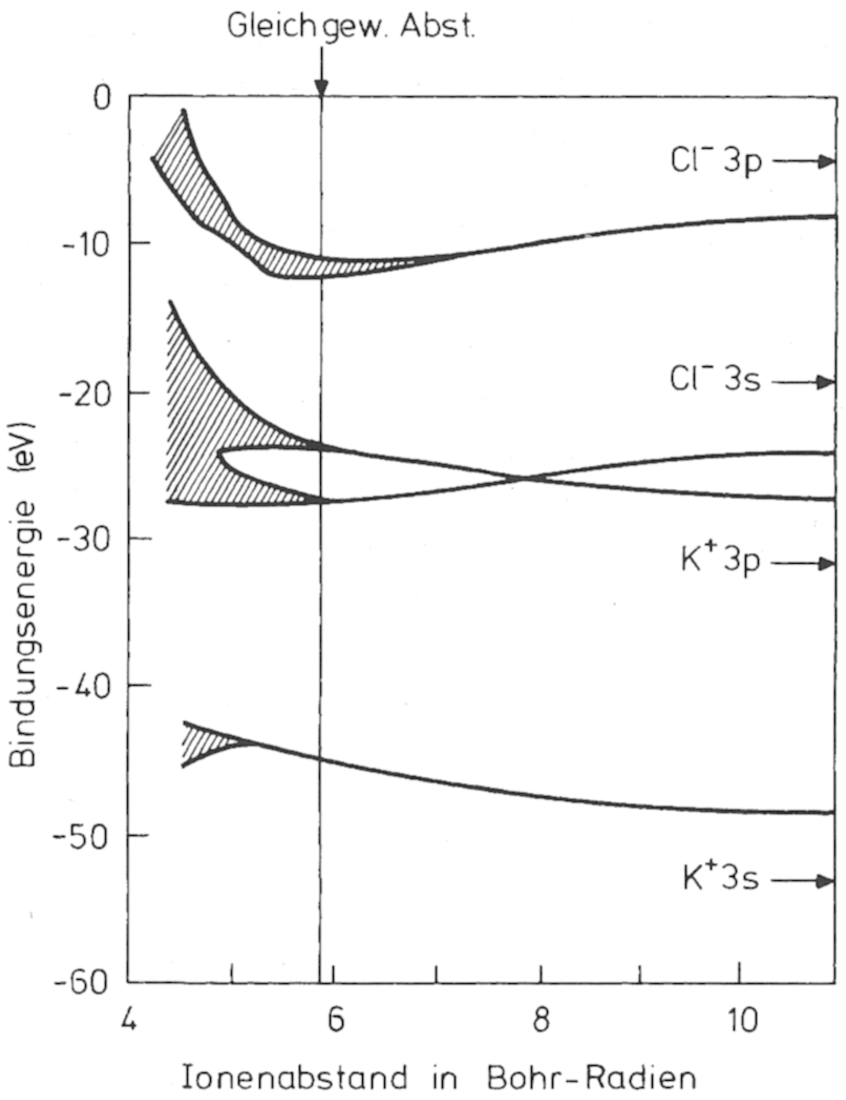
Bandgaps produce spectra and discontinuities: different in different lattice orientations

Mg: example for a “free electron” metal





The strongly “non-free” case



An ionic crystal

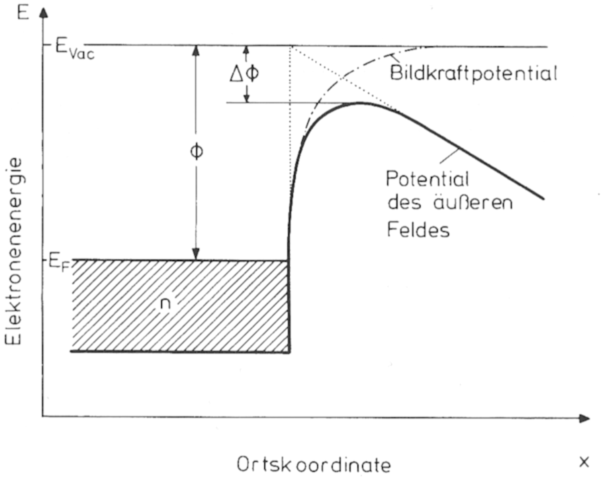
At equilibrium distance no width in bands: no binding by dispersion

The anion crosses potential line of free metal

The valence state shows a slight dispersion: the crystal is not completely ionic

Ions touch each other (min of Cl3s)

Can electrons leave the solid?



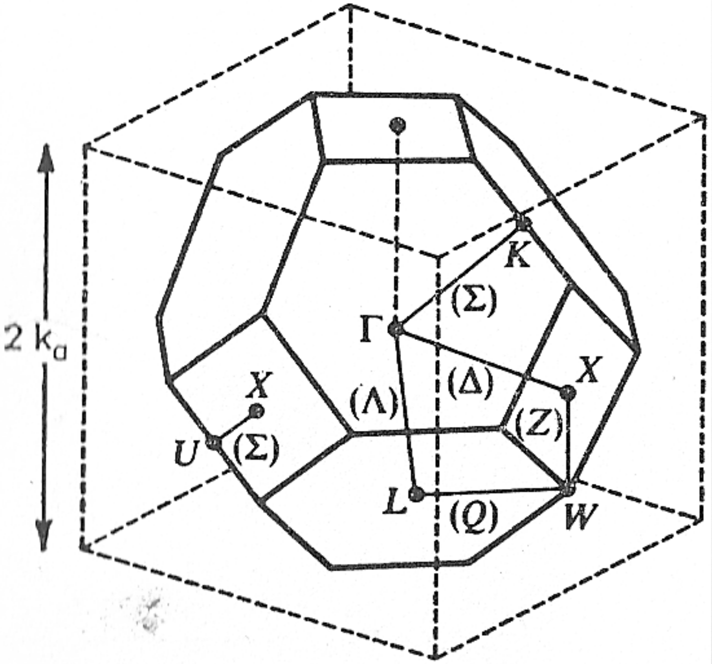
Li	Be											B	C		
2,9	4,98											4,45	5,0		
Na	Mg											Al	Si	P	S
2,75	3,66											4,28	4,85	–	–
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
2,30	2,87	3,5	4,33	4,3	4,5	4,1	4,5	5,0	5,15	4,65	4,33	4,2	5,0	3,75	5,9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
2,16	2,59	3,1	4,05	4,3	4,6	–	4,71	4,98	5,12	4,26	4,22	4,12	4,42	4,55	4,95
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
2,14	2,7	3,5	3,9	4,25	4,55	4,96	4,83	5,27	5,65	5,1	4,49	3,84	4,25	4,22	–

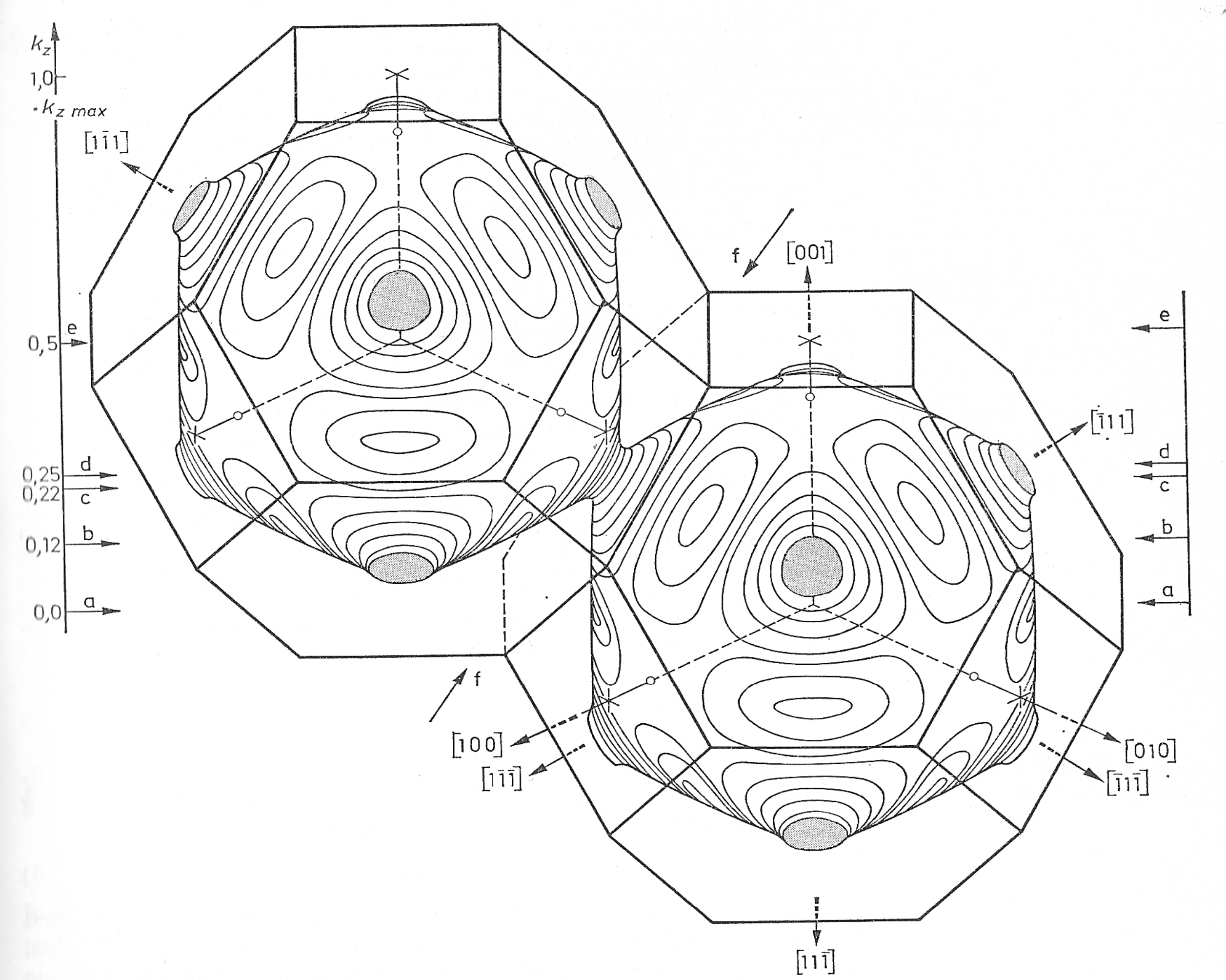
The potential of the “box” sold goes over the Fermi level due to “image force” External fields (strong (1 10 7 /V/cm per eV) for measurable effects) are required for emission (electron sources in EM).

In the particle model an” energy kick” from an incoming electron or photon can lift electrons across potential well: some binding energy is “missing”.

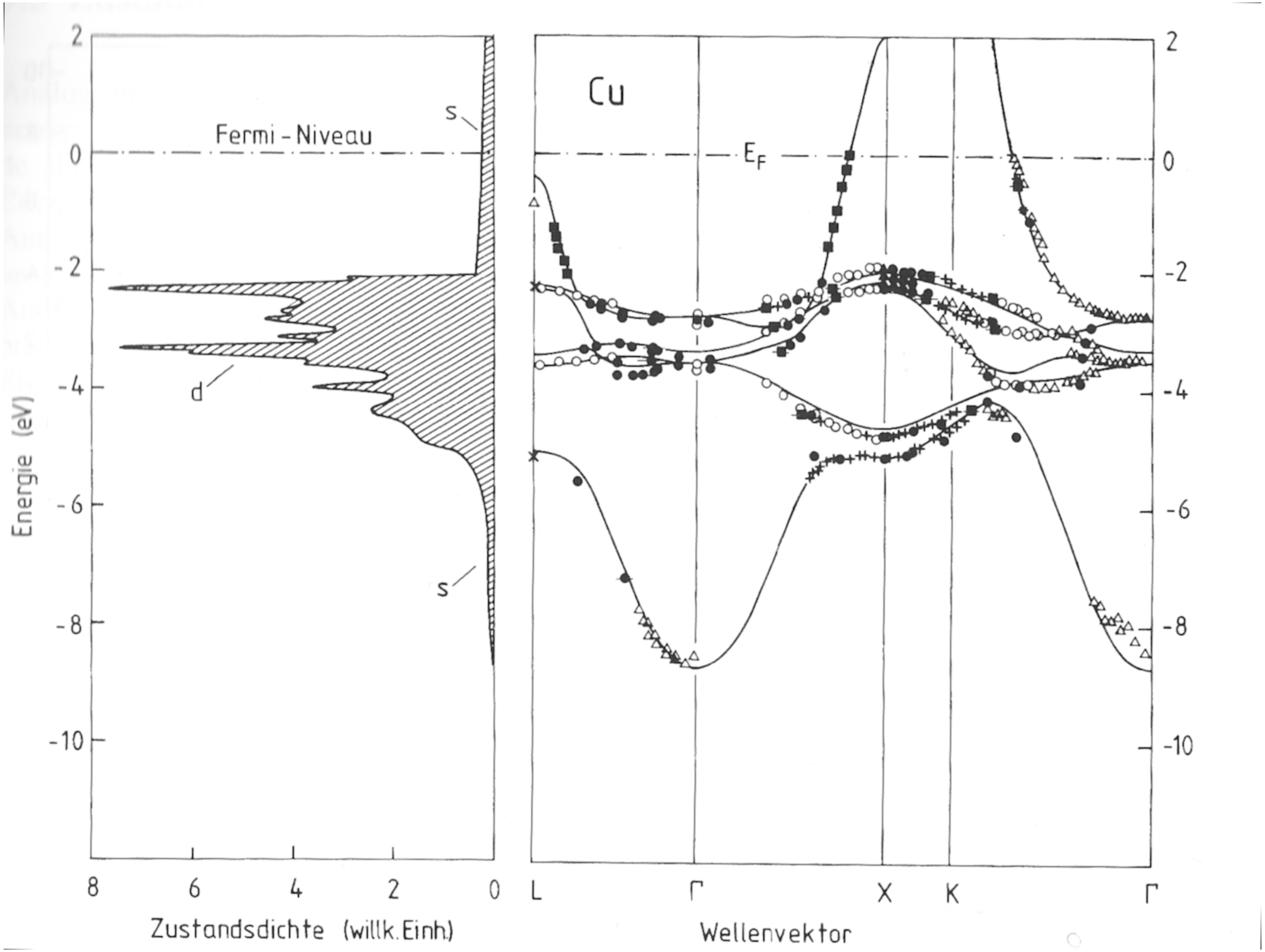
Work function are strong as chemical bonds are and depend critically upon surface states as these modify the image forces.

The real case: Cu as "simple" metal

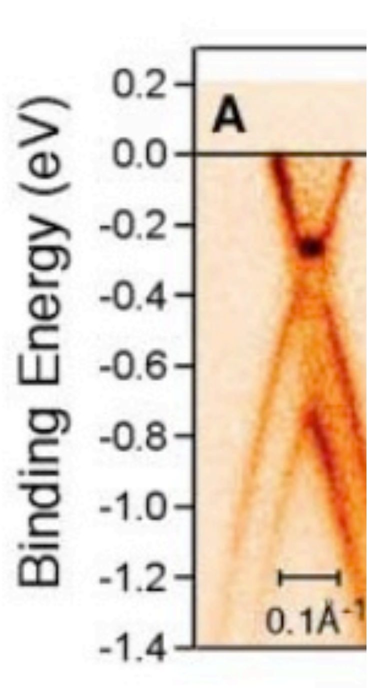


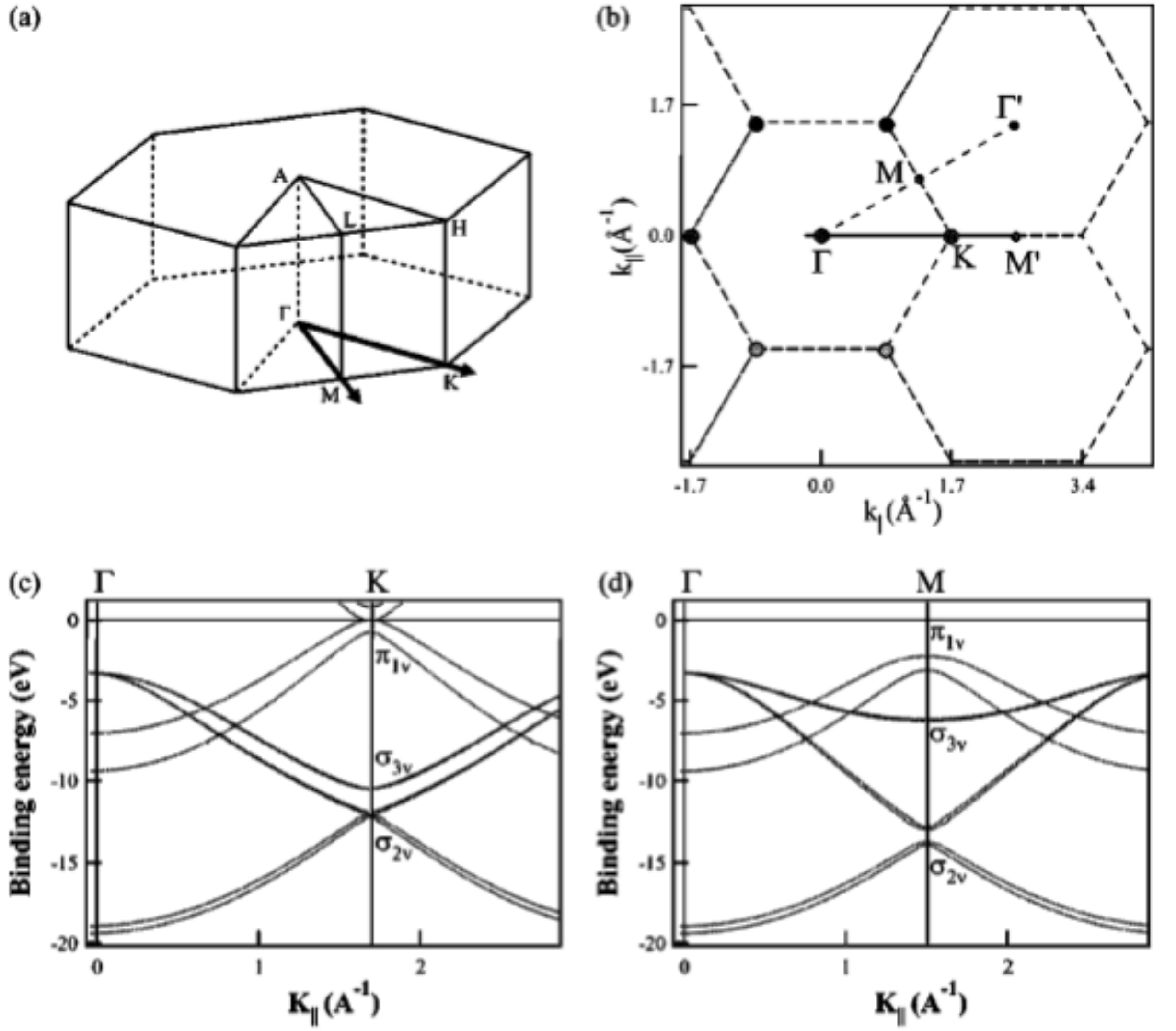


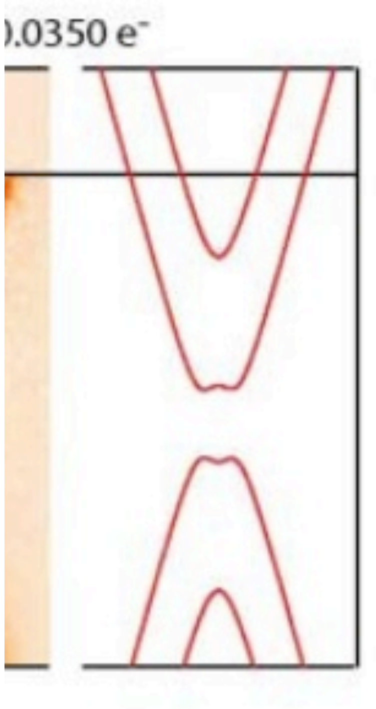
Energy bands in a lattice with potential



A famous finale: graphene (graphite)







V. Pantin et al.
2006