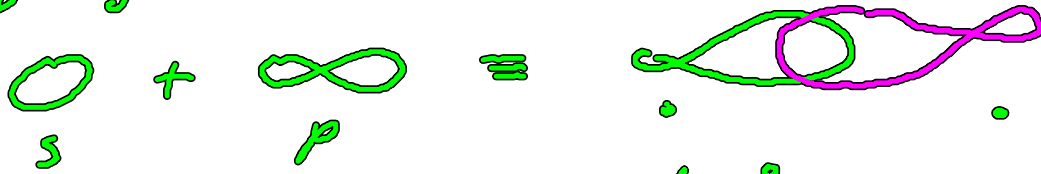


Covalent bonding cont.

sp^3 hybrids



4 sp^3 orbitals $\angle 109,47^\circ$

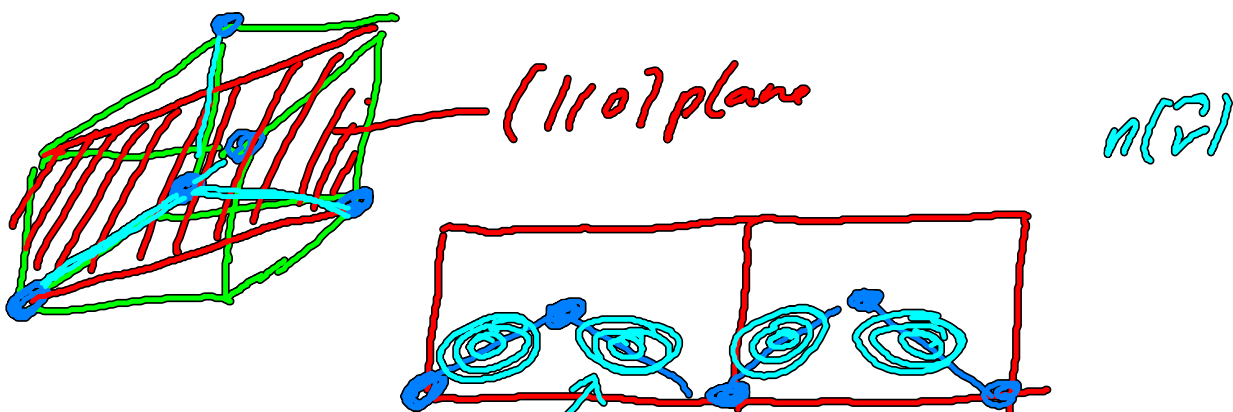
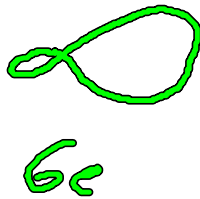
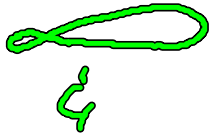
Best localization (narrowest lobes)

is found in carbon. Reason: 2p shell is the first

p-shell \Rightarrow there are no p-states in the core;

\Rightarrow no nodes in the core region

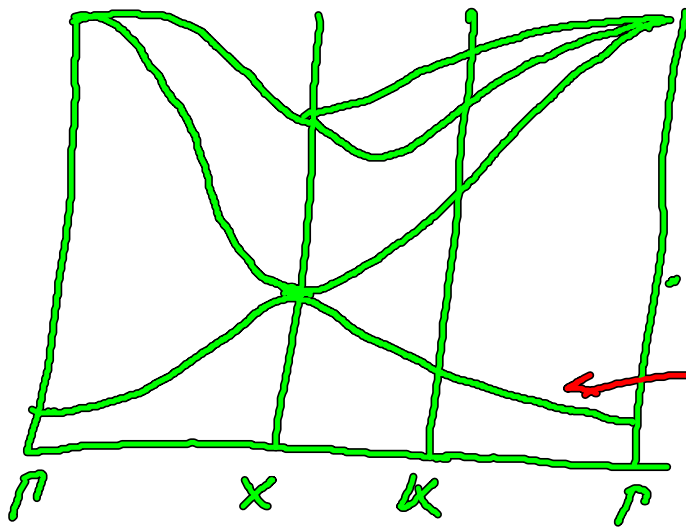
Si and Ge: wider lobes



C, Si, Ge
Si band structure

high overlap between the atoms

↑ CB



diamond structure
 = fcc structure
 with units
 of two atoms

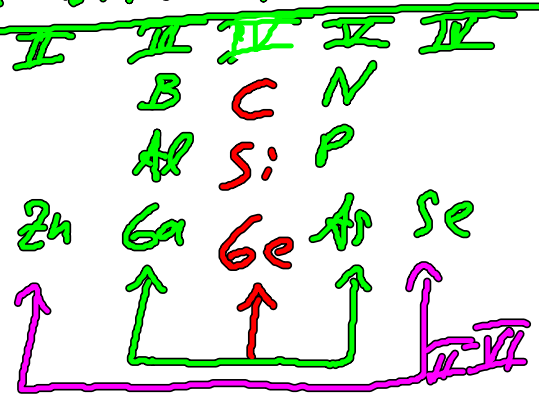
Density of States



Band structure

& DOS look similar for C, Si, Ge

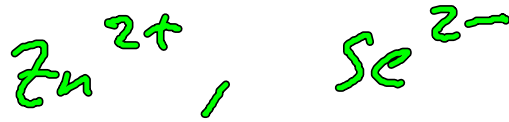
Comparison with other semiconductors



Ge: $n(v)$ signature between two Ge atoms

GeAs: qualitatively similar to Ge but $n(v)$ -peak shifted towards As

Zn Se: looks really very much ionic:



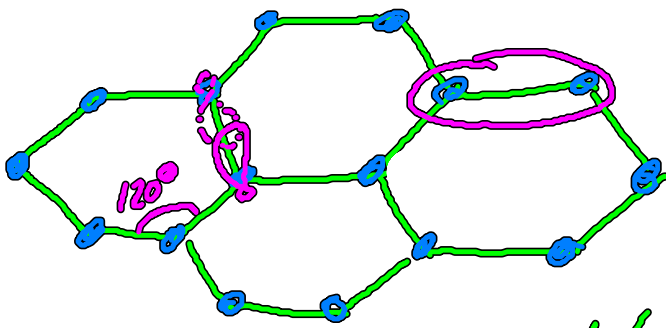
Carbon also can form sp^2 hybrids

$$\phi_1 = \frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}p_x$$

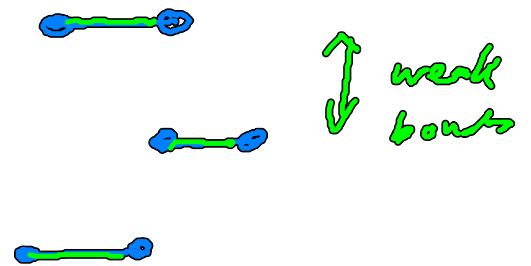
$$\phi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

$$\phi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y$$

$$\phi_4 = p_z$$



top view at graphite



side view

very short & strong bonds in the layer (intra layer);
 very weak inter layer bonds.

Figure theory vs exp.

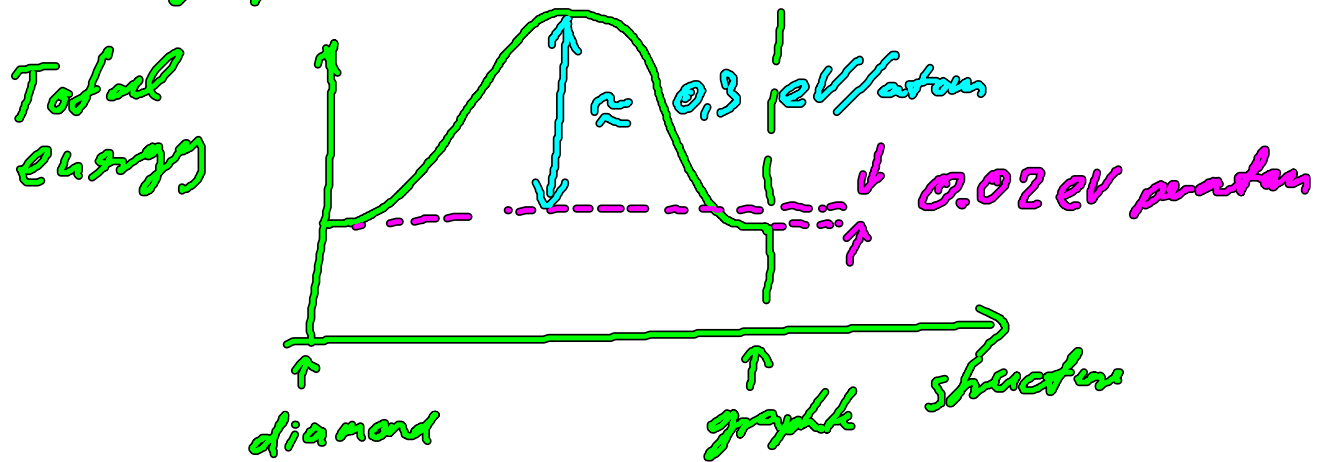
⇒ strong covalent, very directional bonds,
 electron density between layers is

very low.

graphite has higher volume than diamond (\approx Faktor 1.7)

crystal structure of carbon:

graphite has the lowest energy



barrier of 0.3 eV is not much.

However all atoms move simultaneously
the result is a huge barrier.

graphite exists for C but not for Si, Ge
large interlayer spacing \Rightarrow intercalation
e.g. Li-Batteries: cathode = graphite

it is possible to peel off a single of graphite.

truly 2 Dim. System.

a lot physics

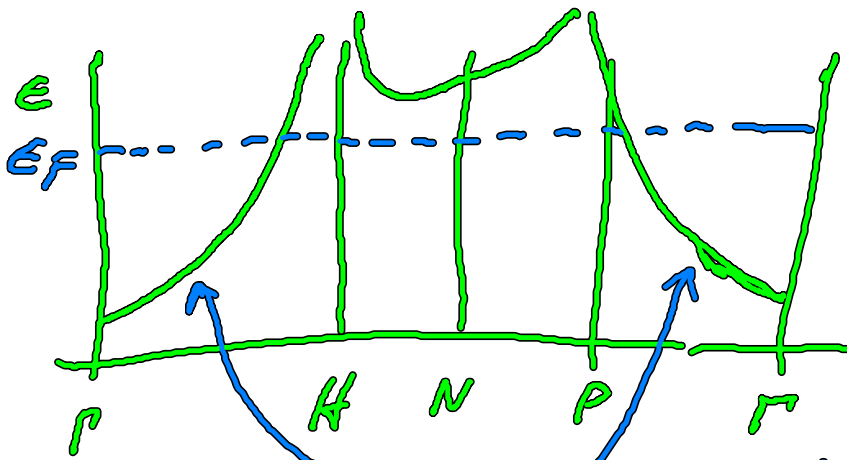
"graphene"

6.5 Metallic bonding

metals typically have a close packed structure
(fcc, hcp, bcc)

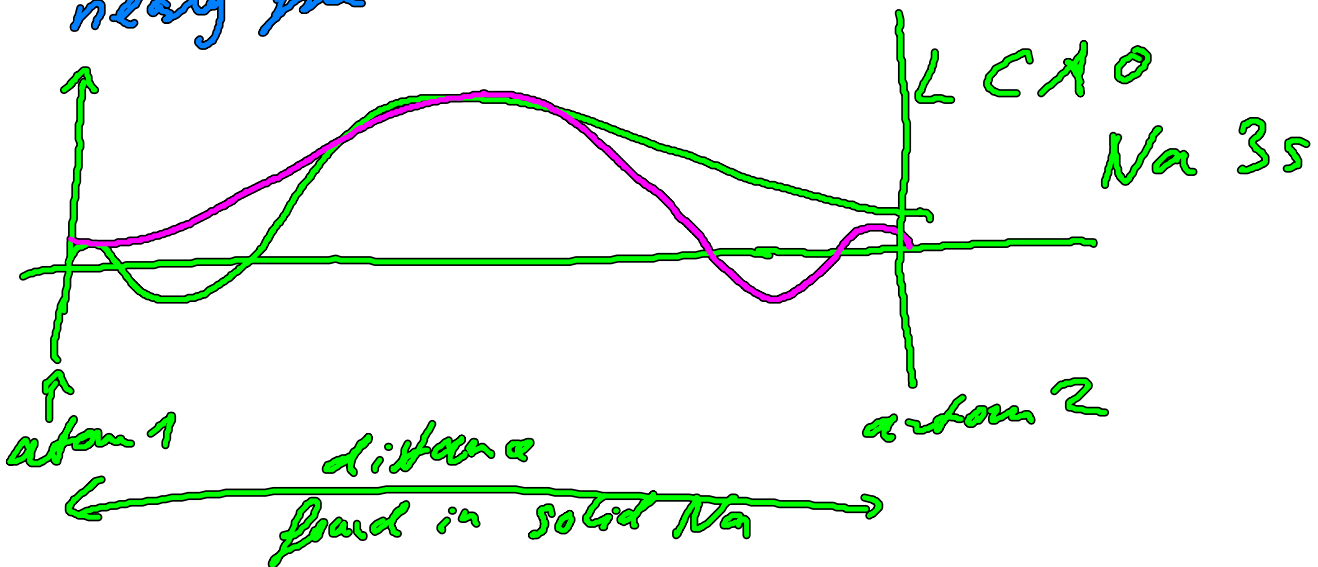
At first alkali metals: group I,
Li, Na, K, Rb, Cs (except hydrogen)

one valence electron: Li: 2s
Na: 3s
etc.



alkali metals
assume the bcc
structure

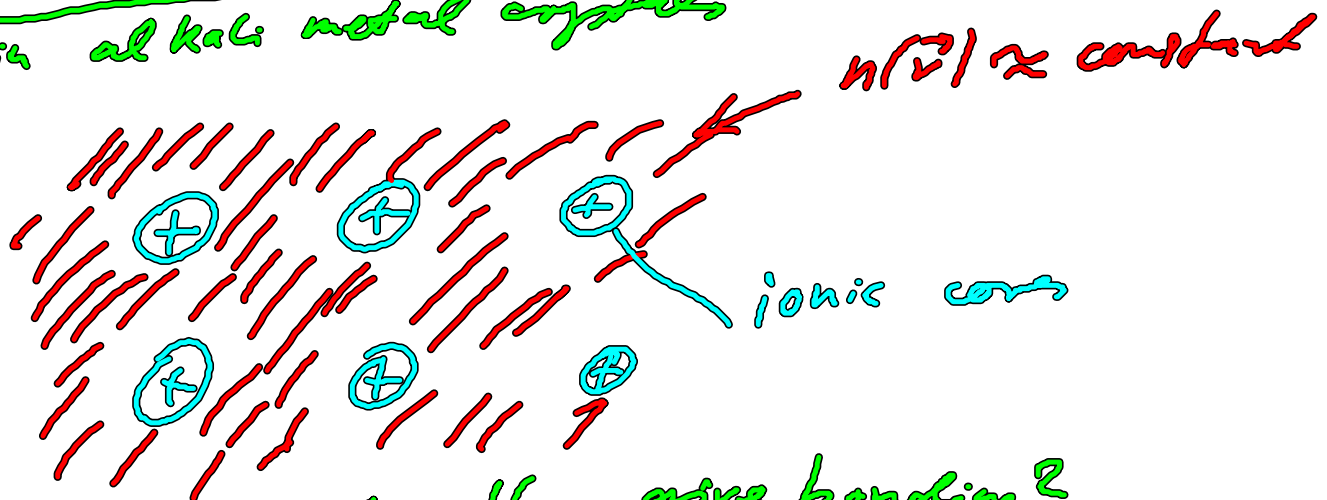
free electron par
nearly free electron bandstructure



very large overlaps between s-orbitals,
at center of neighboring.

⇒ broad bands

Schematic picture of electrons & nuclei
in alkali metal crystals



free? how does this give bonding?

for sure this is not directional.

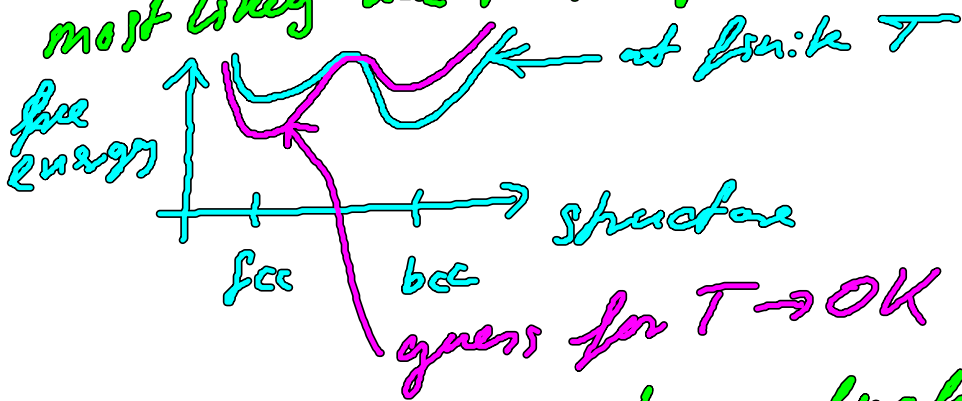
⇒ easy displacement of individual atoms
⇒ elastic and ductile

unoccupied states exist immediately
above the the highest occupied state

⇒ electric field can induce a current flow

⇒ metals are electron conductors.

delocalized bonds are expected to result in the closest packing: fcc, hcp
 alkali metals are bcc — why?
 most likely due to temperature



How can $n(\vec{r}) \approx \text{const.}$ approximate bonding?

$$E = T_S [n] + \underbrace{\int n(\vec{r}) n(\vec{r}') d^3r d^3r'}_{E_{xc}[n]} + \underbrace{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'}_{E^{\text{ion-ion}}}$$

$$E_{xc}[n] + \underbrace{\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{I, J \\ I \neq J}} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}_{E^{\text{ion-ion}}}$$

$$n(\vec{r}) = \text{const} = \frac{N}{V_0}$$

alkali: one valence electron per atom: $N = M$

evaluate $\frac{E^{\text{Coulomb}}}{N}$

for bcc structure

$$= -24.35 \left(\frac{a_B}{r_s} \right) \text{ eV}$$

$a_B = \text{bohr radius}$

$r_s = \text{density parameter} : \frac{4}{3} \pi r_s^3 = \frac{1}{n}$

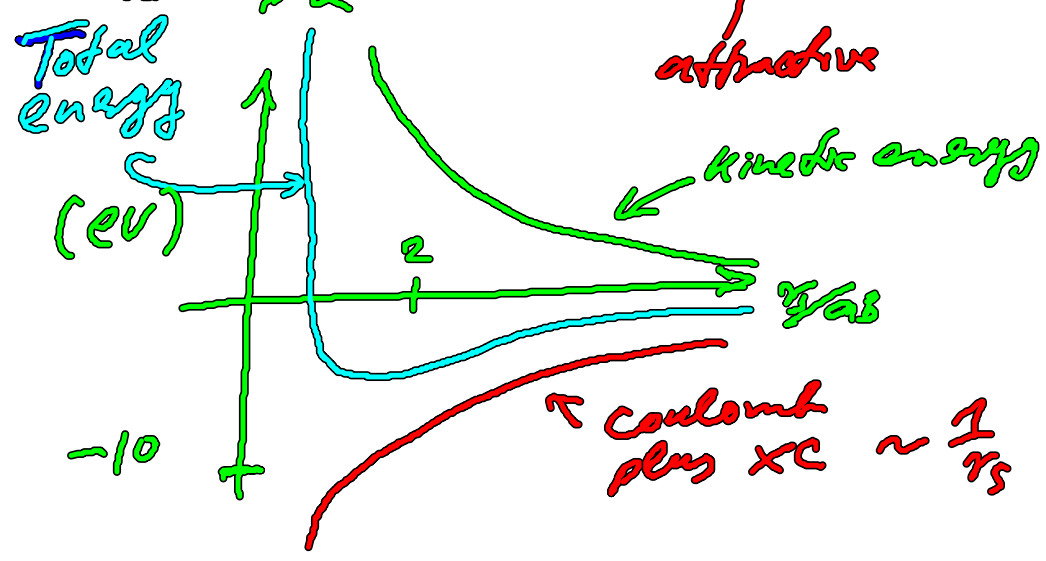
attractive

$$\frac{1}{n} T_3 [n] = \frac{\hbar^2}{2m} \uparrow \text{spin} \quad \frac{1}{n} \quad \frac{\sqrt{3}}{(2\pi)^3} \quad \left. \vphantom{\frac{1}{n}} \right\} k_F \quad k^2 d^3k$$

$$= + 30.1 \left(\frac{a_0}{r_s} \right)^2 \text{ eV}$$

$$E_{xc} [n] \sim n^{2/3} \quad \rightarrow \quad - 8.33 \left(\frac{a_0}{r_s} \right) \text{ eV}$$

wing χ_2 with $\alpha = 2/3$



we did slightly better than jellium

$v(r)$ was not constant
but $n(r)$ was constant

\Rightarrow already the crudest model of delocalized electrons leads to bonding.

Qualitative picture is o.k.
quantitatively not acceptable

"theory" $\Rightarrow \frac{r_s}{a_0} \approx 1.9$

Li, Na, K ... real metal
 $\frac{r_s}{a_0}$ 3,27 (Li) ... 5,25 (K)

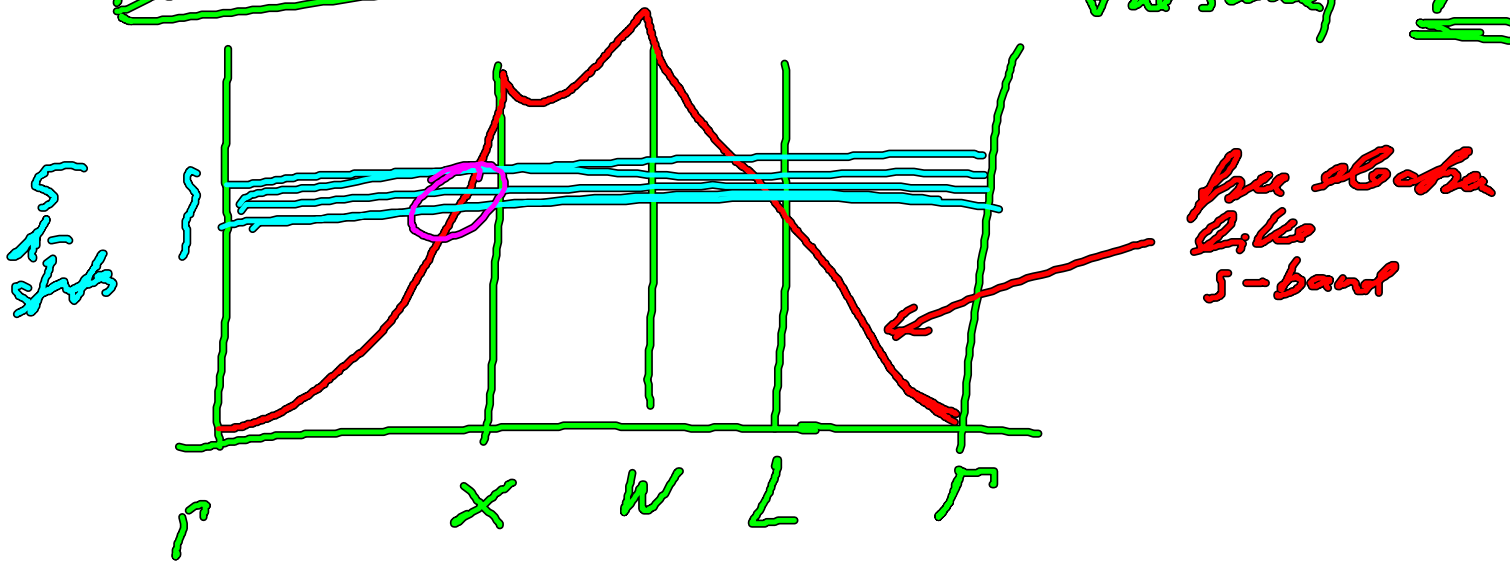
\Rightarrow we need a good calculation of $v(\vec{r})$ and $n(\vec{r})$ to get things right.

Transition metals (TM)

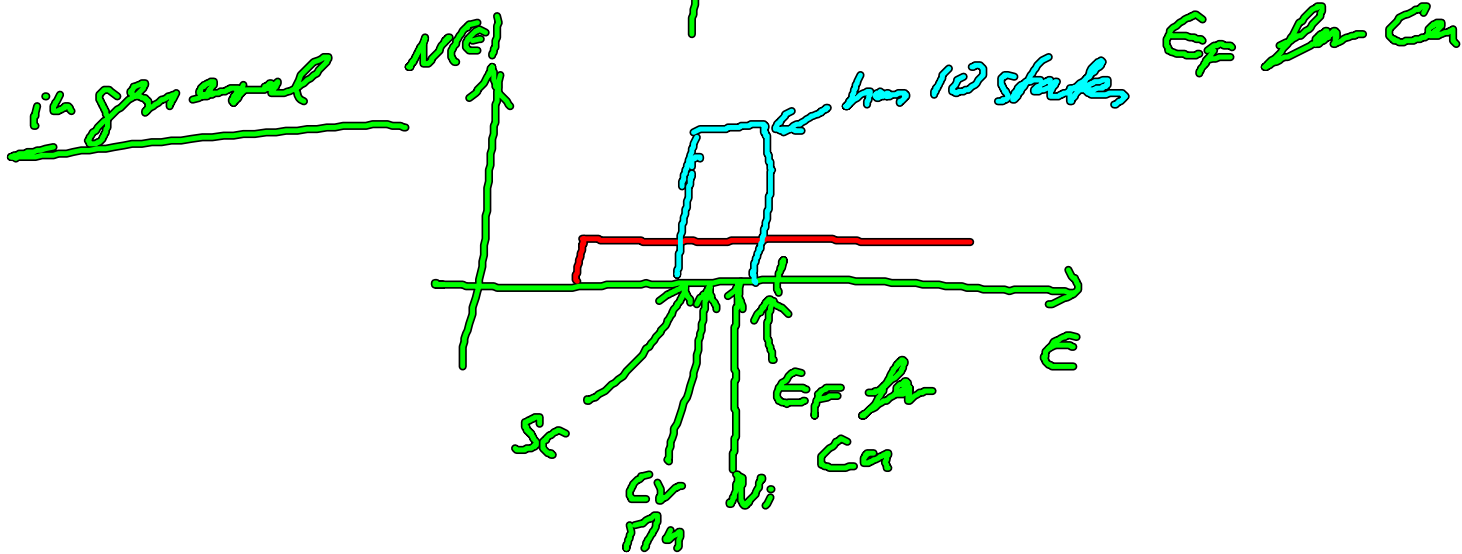
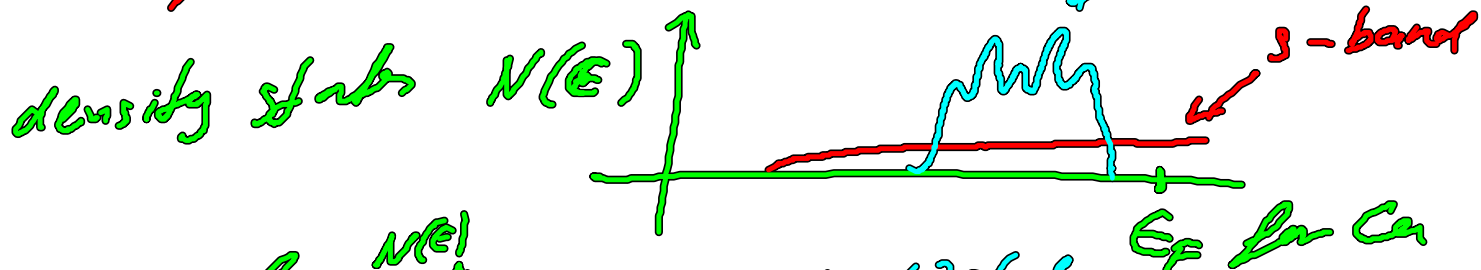
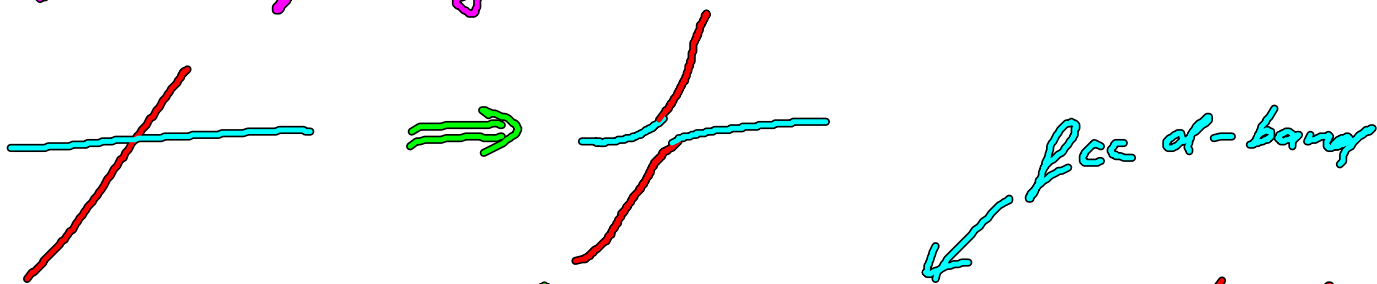
much stronger bond than alkalis
 alkalis $E_{\text{coh}} \approx 7\text{eV}$
 TM ... 8.9eV for W.

Reason:
partially
covalent

Band structure of Cu (Ag, Au nearly the same) fcc



s-band and d-bands "cross"
 if same symmetry "avoided crossing"



atomic behavior

3d atoms

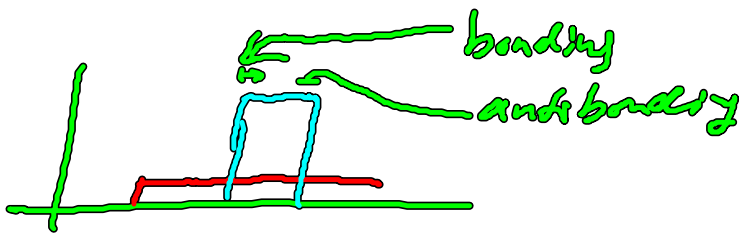
Sc	$3d^1$	$4s^2$
Ti	$3d^2$	$4s^2$
..	$3d^3$	$4s^2$

all TMs
 have V_{xy}

V	$3d^5 4s^1$
Cr	$3d^5 4s^1$
Mn	$3d^5 4s^2$
Fe	$3d^6 4s^2$
Co	$3d^7 4s^2$
Ni	$3d^8 4s^2$
Cu	$3d^{10} 4s^1$

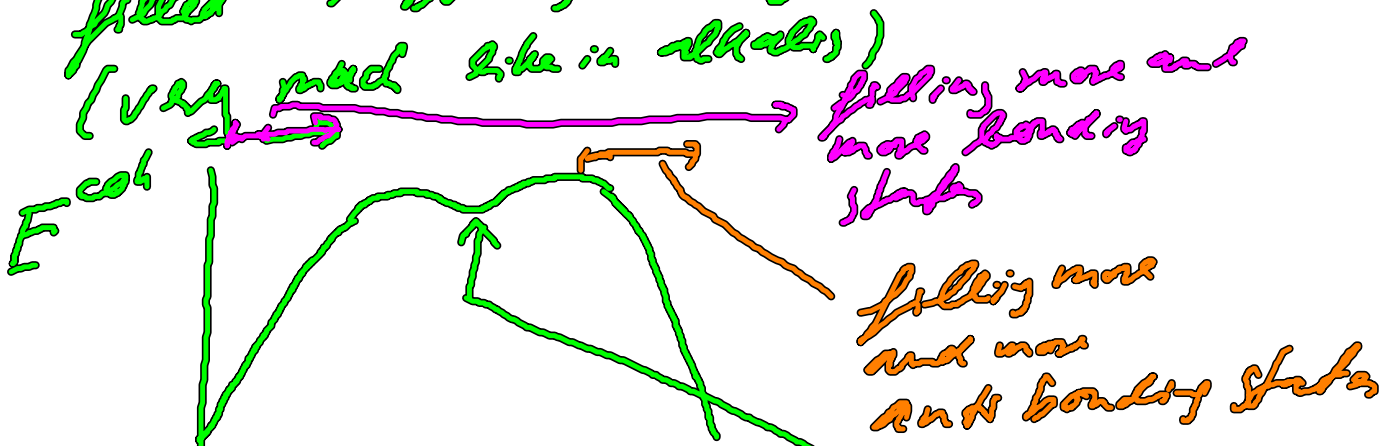
Similar DOS
- just the Fermi level is at a different energy.

3d TM are very localized = first d shell, i.e. no d-core; \Rightarrow no nodes in the radial wavefunctions.
d-band width $\approx 3\text{eV}$



The energetically low bands are bonding.
The energetically high bands are antibonding.

for Cu, Ag, Au all d-states are filled \Rightarrow bonding is only due to s-states
(very much like in alkalis)



3d	Sc	...	Mn	Cu	dip due to contraction in atoms, e.g. stability of d5, magne
4d	Y		Pd	Ag	

Figure: Moruzi = 1978

6.6 hydrogen bonding ⇒ Tuesday

d