first-principles electronic structure calculations for the solid state

some remarks

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first-principles calculations

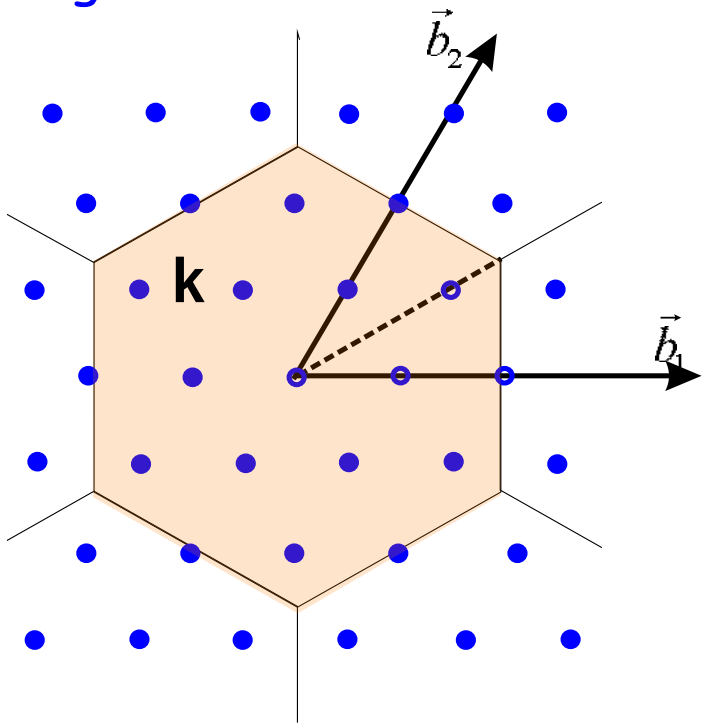
most of the techniques used for molecules can also be applied to the solid state: DFT, HF, MBPT, CC

e.g., DFT

$$E[n] = T[n] + \int \sum_I \frac{Z_I n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_I|} dr + \frac{1}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + E_{xc}[n]$$

charge density $n(\mathbf{r}) = \sum_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2$

needs a Brillouin zone integration



- metals need a dense **k**-point grid

self-consistency:

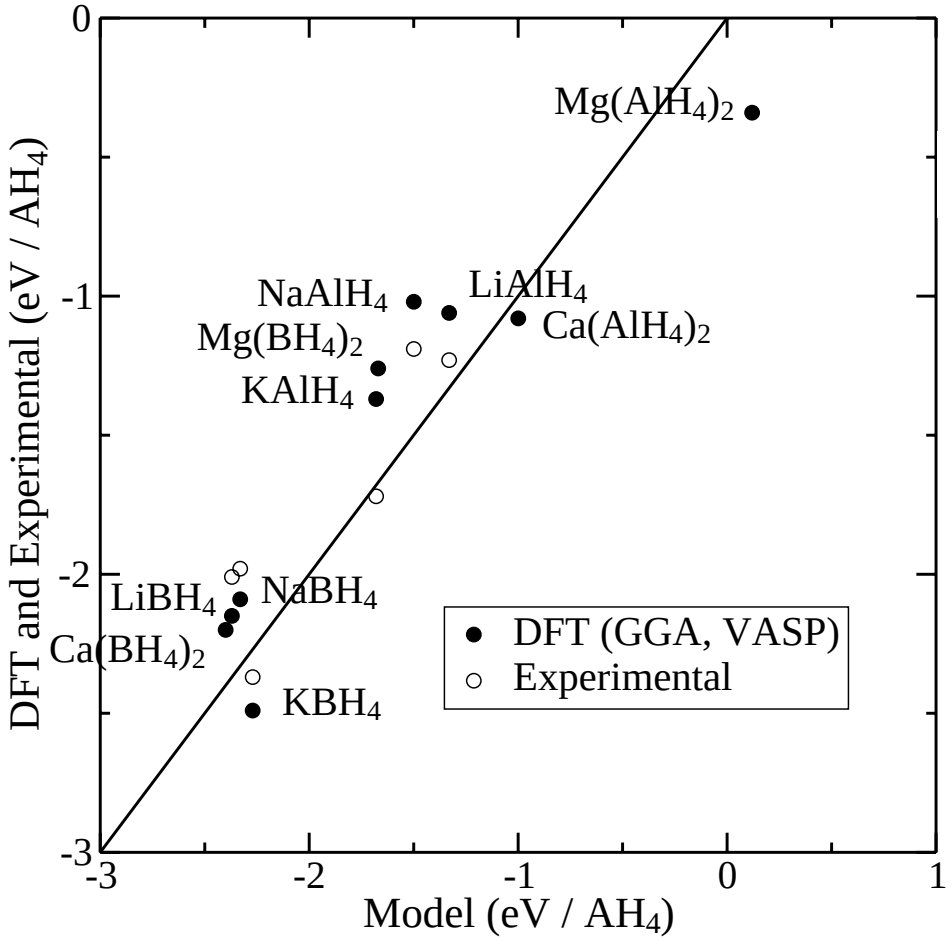
- metals converge slowly
- magnetic metals even more so

the work horse: Density Functional Theory (DFT)

formation energies / heats of formation covalent/ionic bonding

calculated with DFT/*GGA* (PBE) are typically accurate

on a scale of 0.1 eV (10 kJ/mol)



... but the error can be larger ...

formation energy MgH_2

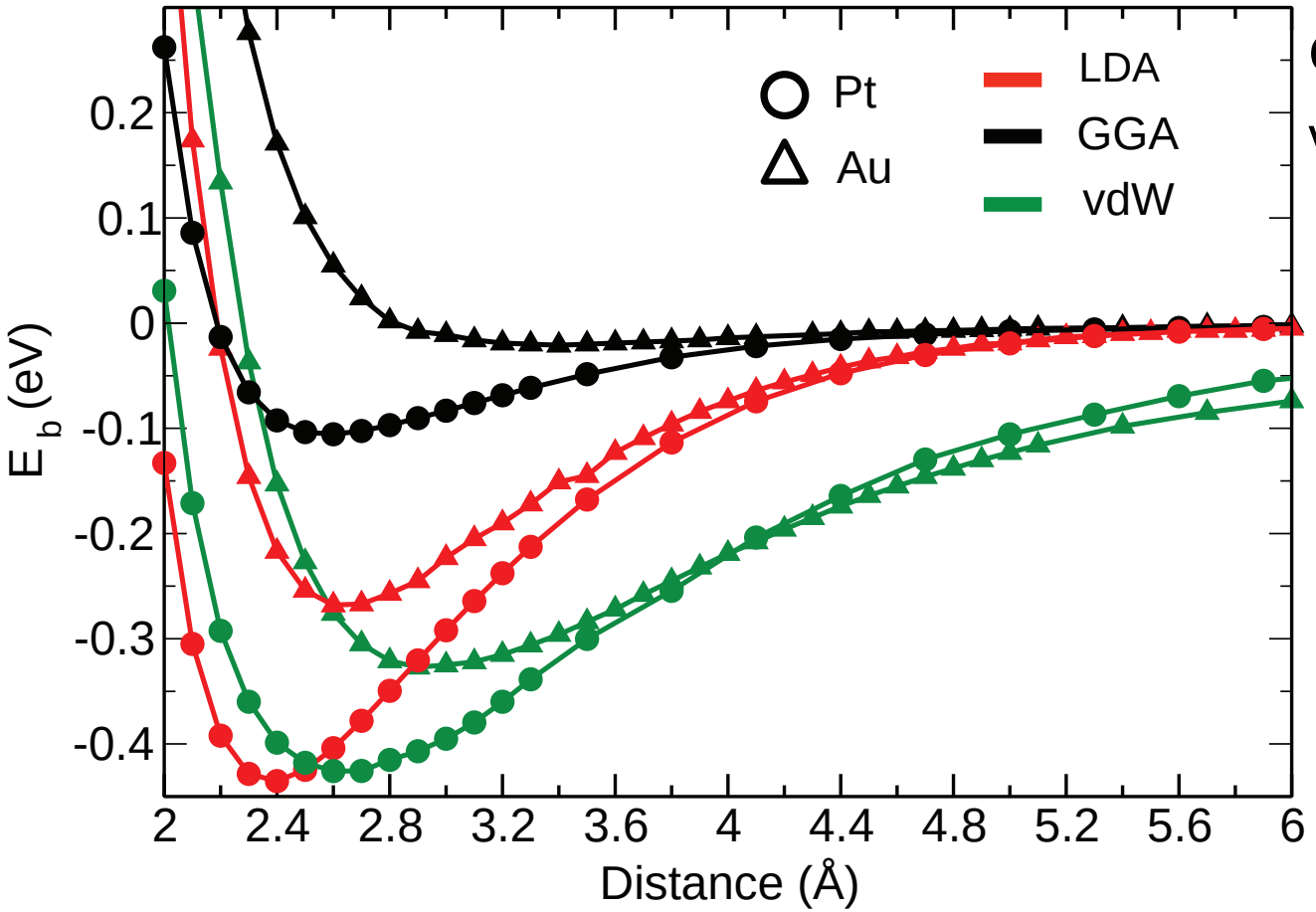
0.57 eV/H_2 (*GGA*/PBE/ZPE)

0.76 eV/H_2 (Exp)

van Setten et al., JPCC **111**, 9592 (2007); PRB **72**, 073107 (2005)

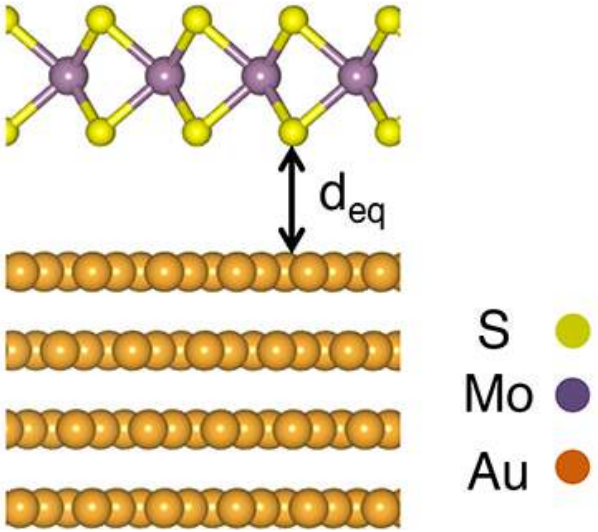
Density Functional Theory (DFT)

weak interactions need a van der Waals functional



GGA: PBE

vdW: opt88-vdW-DF

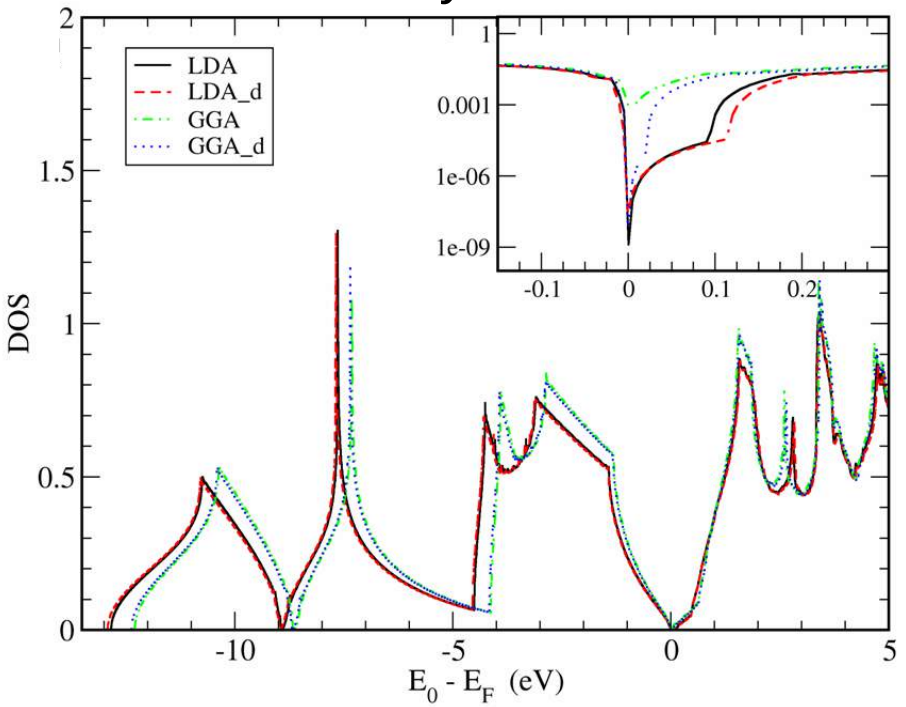


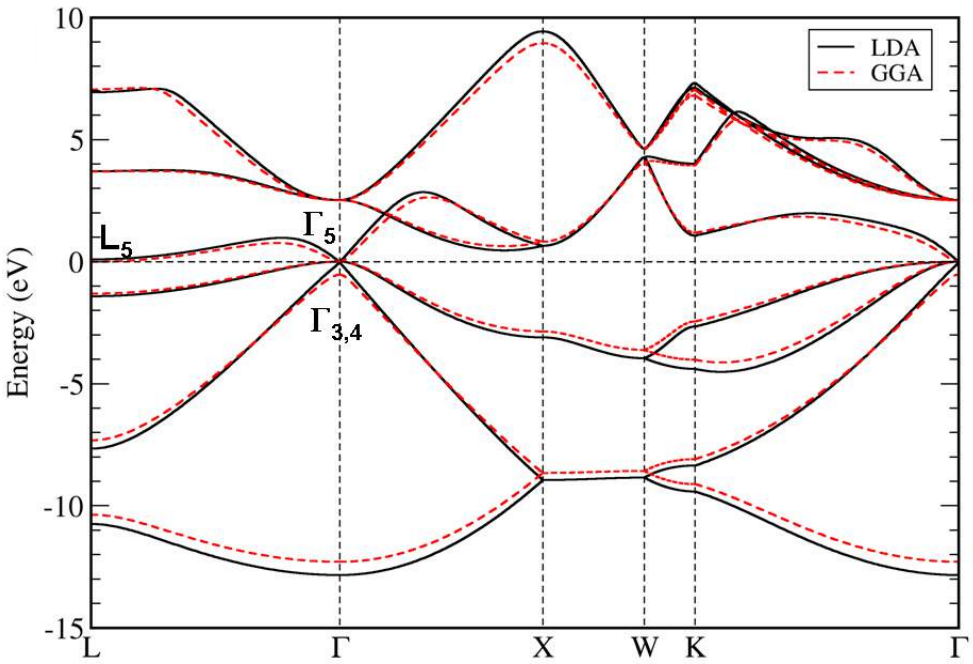
Farmanbar & GB, submitted, arXiv:1510.04337

Density Functional Theory (DFT)

spectrum obtained from DFT/GGA (LDA) is not so impressive

density of states bulk Germanium band structure





exp.: Ge is a semiconductor with band gap 0.7 eV

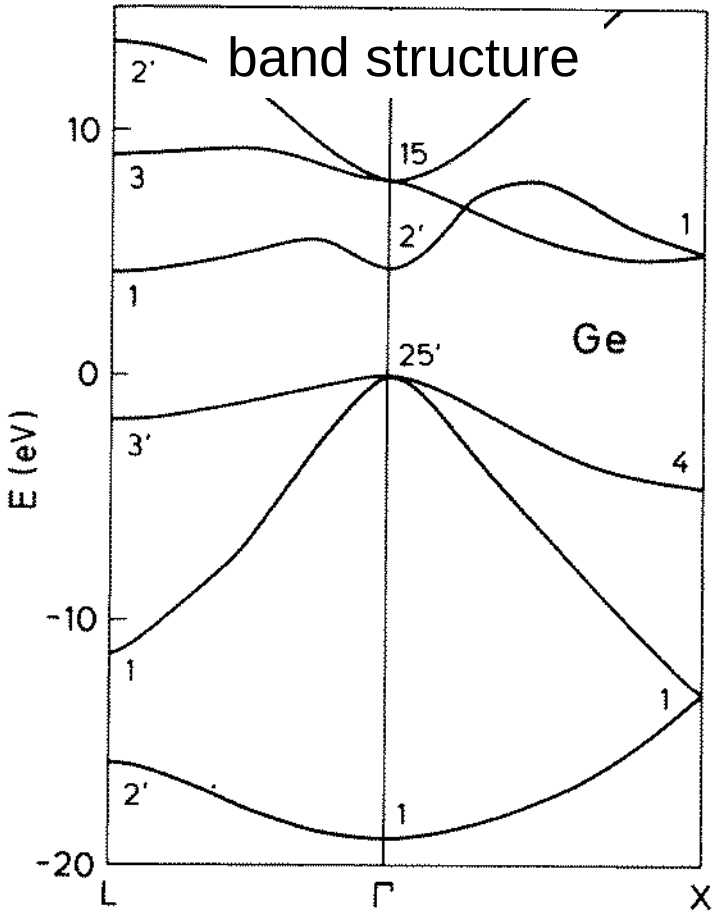
GGA/LDA: Ge is a metal

band dispersions are quite reasonable ~ 1-10%

Vanpoucke, Thesis, UTwente (2008)

Hartree-Fock (HF)

HF computationally more expensive than DFT: 1-2 orders of magnitude



HF total energies are worse than DFT

the spectrum obtained from HF

is even less impressive

exp:. Ge semiconductor with band gap 0.7 eV

HF: Ge insulator with band gap 4.2 eV

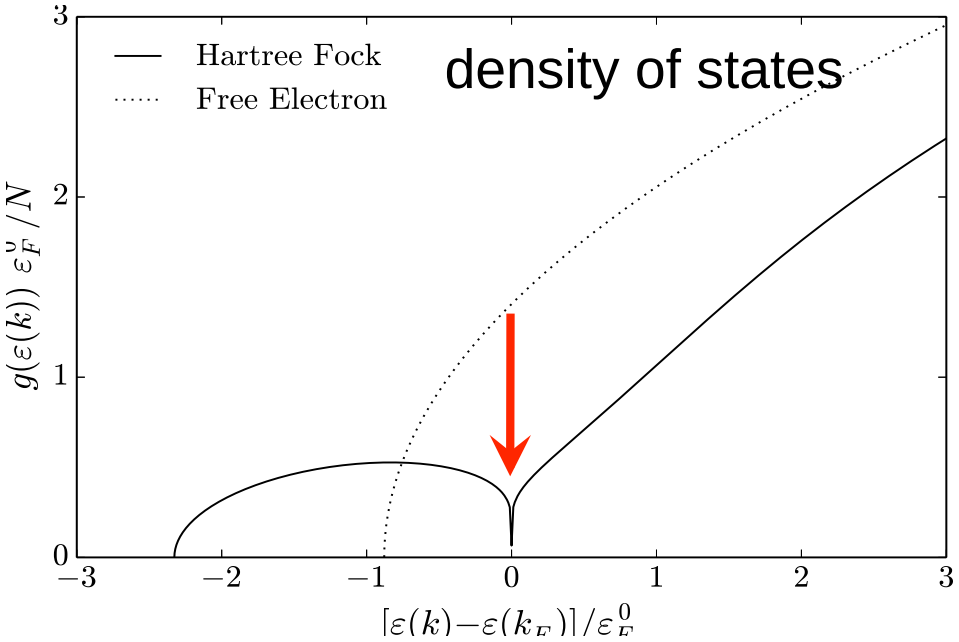
band dispersions unreasonable ~50% too wide

Svane, PRB 35, 5496 (1987)

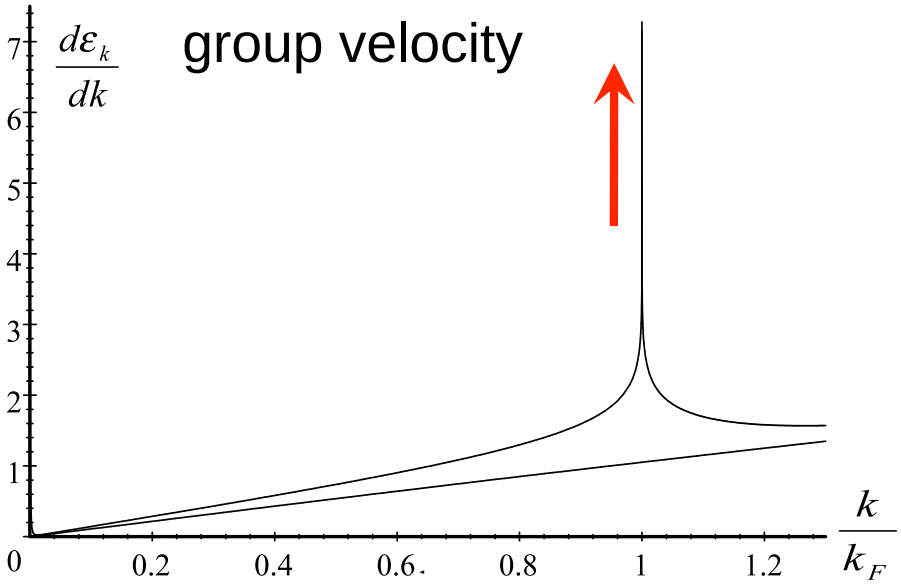
Hartree-Fock (HF): from bad to worse

For metals the spectrum obtained from HF is a disaster

e.g. homogeneous electron gas (jellium) free electron spectrum ≈ MBPT



density of states
at E_F is zero



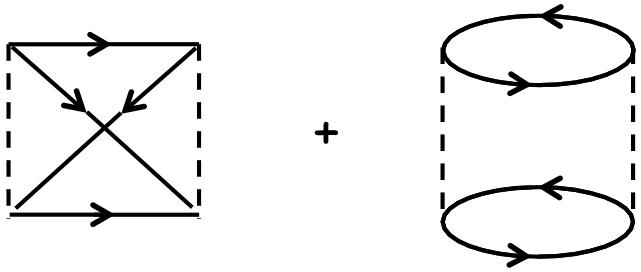
electron velocity
at E_F is infinity

metals: electrons with energy E ≈ E_F are doing the conduction

Brocks, AQM lecture notes (2004)

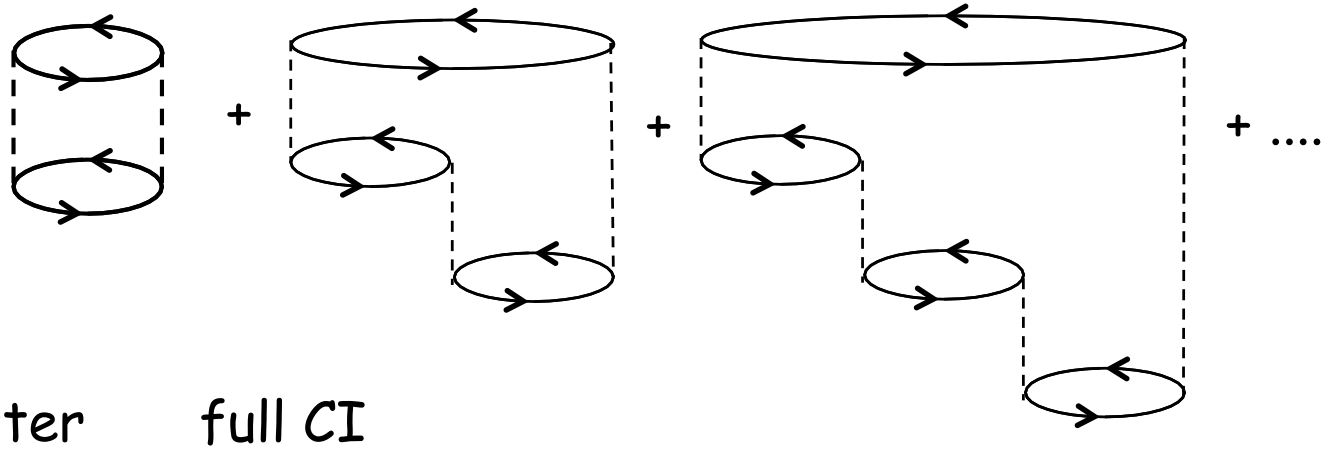
Electron correlations

truncated correlated methods don't work well for extended systems

MP2 =  for metals ➔ ∞

CI SDT.... ➔ 0

infinite summation methods work

RPA = 

coupled cluster full CI

all these methods are computationally very expensive