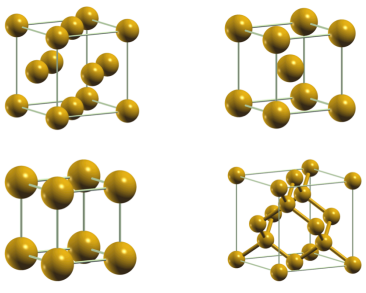
MSE 468 Lecture 8

Density-functional Practice Part 2

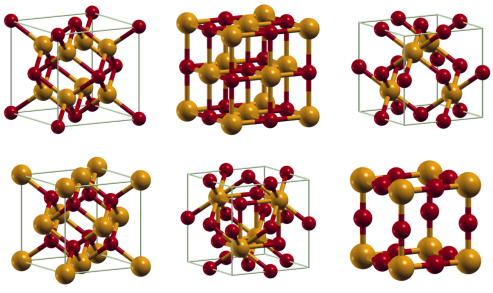
Verifying pseudopotentials

- There are more expensive codes that are able (in a different basis set) to consider all electrons explicitly: *no pseudopotential approximation*
- How do I know if a pseudopotential is good? Test against those results
- We need a very high-quality all-electron reference!
  - Bosoni (2024): PBE reference EOS, 10 crystals (unaries+oxides) for 96 elements (Z=1-96), cross-verified between the *FLEUR* and *Wien2K* codes

4 cubic unaries: FCC, BCC, SC, diamond



6 cubic oxides: X_2O, XO, X_2O_3, XO_2, X_2O_5, XO_3

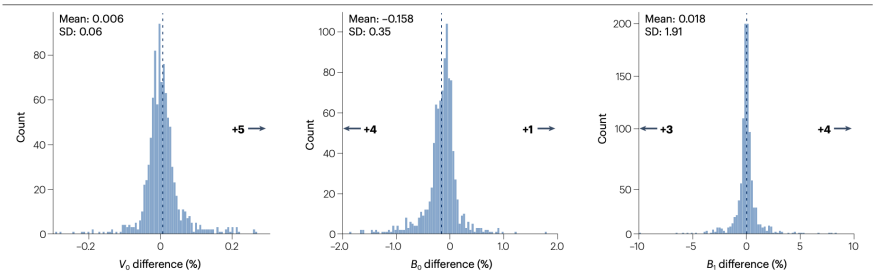


E. Bosoni et al., Nat. Rev. Phys. 6, 45 (2024). Earlier study: K. Lejaeghere et al., Science 351, aad3000 (2016)

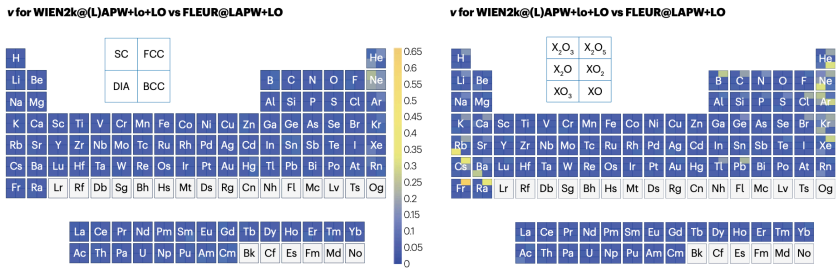
Verifying pseudopotentials

- High quality reference results on Birch-Murnaghan EOS parameters (V_0, B_0, B_1): e.g., ~0.1% volume discrepancy

Comparison of V_0, B_0, B_1 between FLEUR and Wien2K on the 960 systems



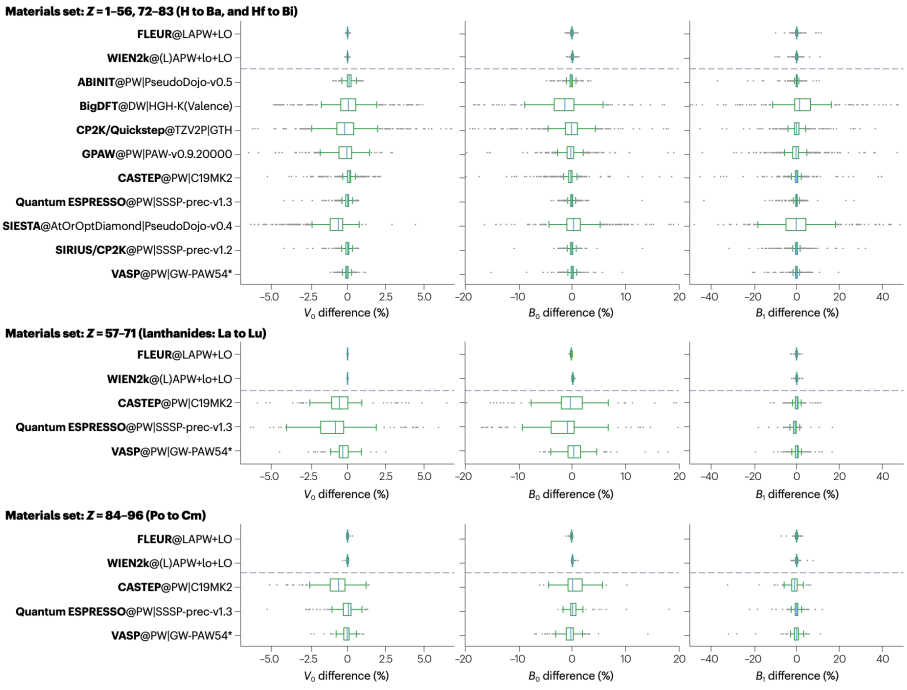
Discrepancy metric between EOS between the two codes



E. Bosoni et al., Nat. Rev. Phys. 6, 45 (2024)

Verifying pseudopotentials

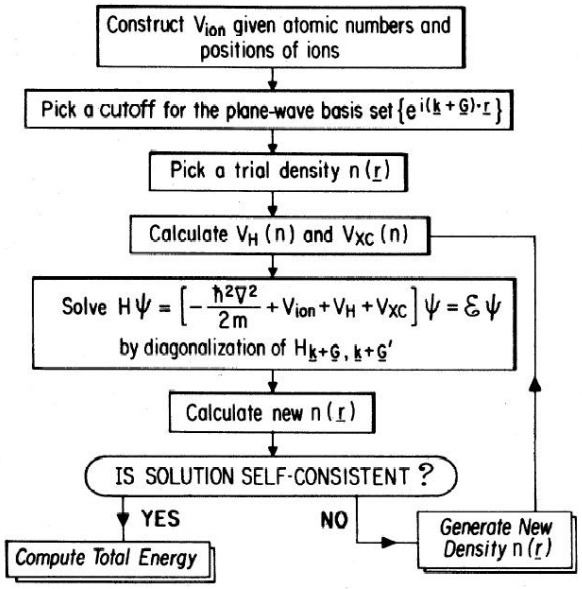
We can now verify pseudopotential codes (actually, code+basis set+pseudopotentials!)



E. Bosoni et al., Nat. Rev. Phys. 6, 45 (2024)

Iterations to self-consistency

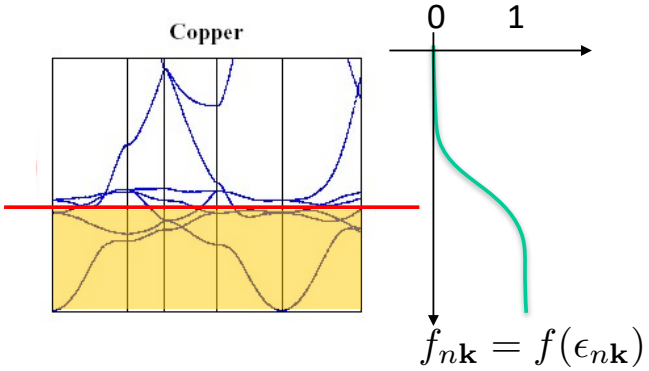
- Construct the external potential (array of non-local pseudopotentials)
- **Choose the plane-wave basis set cutoff, k-point sampling**
- Pick a trial electronic density
- Construct the Hamiltonian operator: Hartree and exchange-correlation
- Solve Kohn-Sham equations for the given Hamiltonian (e.g. by diagonalization)
- Calculate the new charge density
- Iterate

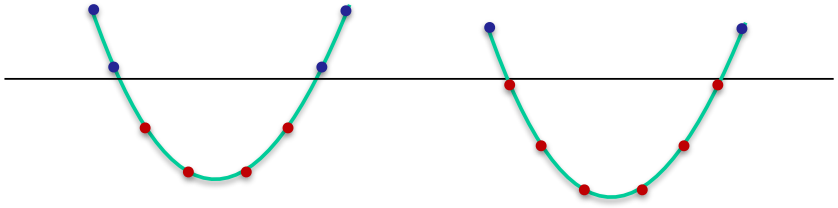


Smearing (for metals)

- In metals: occupation changes sharply at Fermi level
- Integration within a SCF loop difficult: requires *many* k-points, Fermi level oscillates around exact value

$$\rho(\vec{r}) = \sum_{n,\vec{k}} f_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}\left(\vec{r}\right) \right\|^2$$



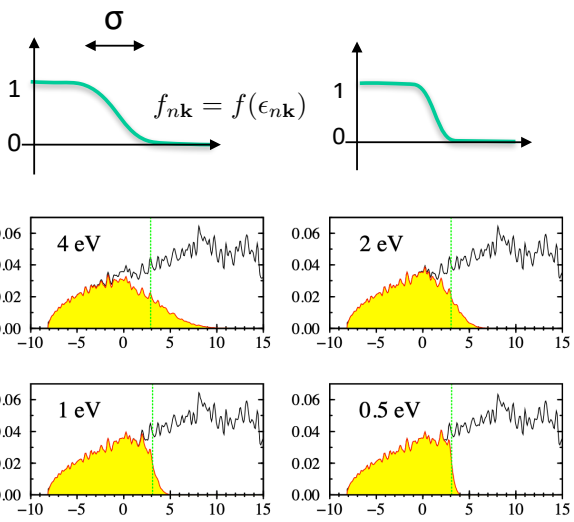


Smearing (for metals)

- Smearing σ acts as a (fictitious) temperature
- Typically of the order of ~0.1eV (it's ~1100 K!)
- What we compute is a free energy, not anymore the total energy

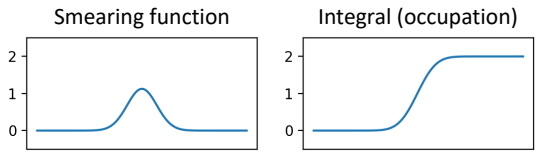
$$A = E - \sigma S$$

- Instabilities can still arise, a density mixing needs to be used ("mixing_beta"; smaller values: typically more robust, but slower convergence)

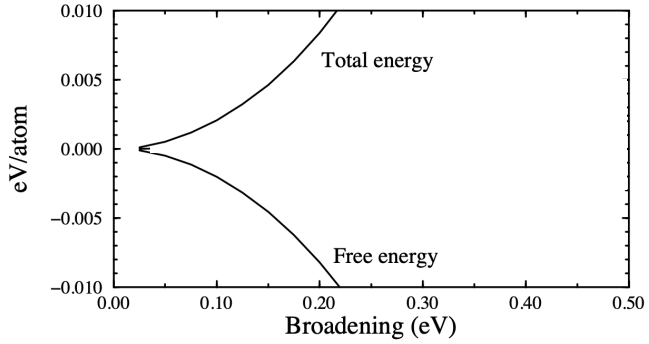


Smearing (for metals)

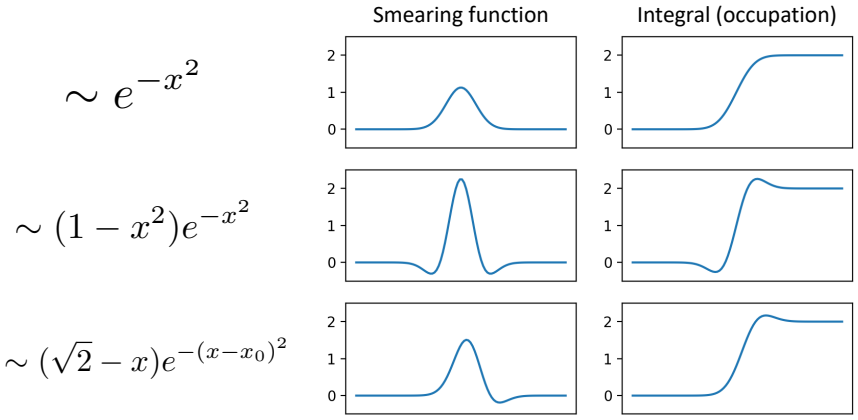
$\sim e^{-x^2}$

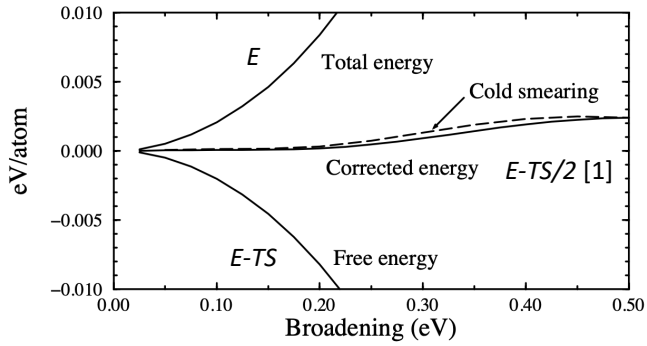


Gaussian



Smearing (for metals)

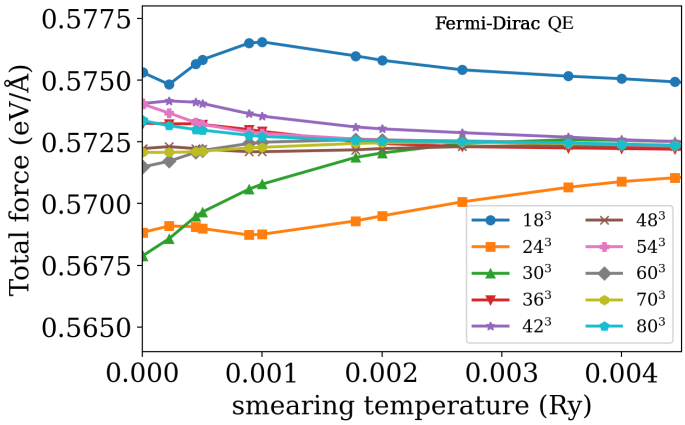




[1] M.J. Gillan, J. Phys. Cond. Matt. 1, 689 (1989)
(E-TS correction: valid only for Gaussian or Fermi-Dirac)

"Temperature" and smearing

Aluminum, one atom displaced
Showing forces on the atom as a function of smearing, for various k-mesh densities



You can check F. J. Dos Santos, N. Marzari, PRB 107, 195122 (2023)
and also an in-depth discussion here:
http://theossrv1.epfl.ch/Main/ElectronicTemperature

Local Spin Density Approximation (LSDA)

- In principle: E_{xc} treats spin exactly. In practice: poorly approximated, we only have the total charge density
- Solution: treat spin up and spin down densities separately (similar to unrestricted Hartree-Fock)
- Correlation energy fitted from Quantum Monte Carlo by e.g. Vosko, Wilk, Nusair (VWN)

  S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58,** 1200 (1980)

$$V_{\text{eff}}^{\uparrow} = V(r) + \int \frac{n(r')}{|r-r'|}dr' + \frac{\partial E_{xc}[n^{\uparrow}, n^{\downarrow}]}{\partial n^{\uparrow}}$$

$$V_{\text{eff}}^{\downarrow} = V(r) + \int \frac{n(r')}{|r-r'|}dr' + \frac{\partial E_{xc}[n^{\uparrow}, n^{\downarrow}]}{\partial n^{\downarrow}}$$

Up and down charge densities can be different

=

Magnetic systems in QE in practice

https://www.quantum-espresso.org/Doc/INPUT_PW.html

- **Collinear magnetism**: use **nspin = 2** (spin-polarized calculation, LSDA, magnetization along z axis)
  - k-points are doubled: you have pairs ($k^{\uparrow}$) and ($k^{\downarrow}$)
- **Non-collinear magnetism**: use **noncolin = .true.** (that implicitly sets *nspin = 4*): spin-polarized calculation, noncollinear (magnetization in generic direction)
  - k-points *not* doubled, but double number of bands and wave functions become two-component spinors

Initializing ferromagnetic and antiferromagnetic systems

- Important to initialize some non-zero starting magnetization, or the system by symmetry will never get magnetic!
- Ferromagnetic case:

```
ATOMIC_SPECIES
Fe       55.84     Fe.UPF
ATOMIC_POSITIONS crystal
Fe     0.000    0.000    0.000
starting_magnetization(1) = 0.1   ! for instance
```

NOTE: (1) indicates the species (Fe), not the specific atom!

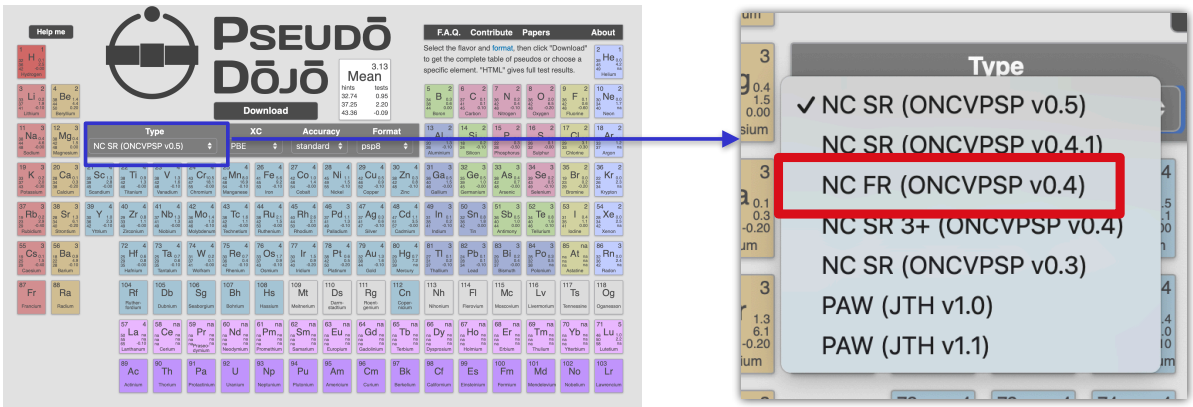
- And for the antiferromagnetic case?

```
ATOMIC_SPECIES
Fe1      55.84     Fe.UPF
Fe2      55.84     Fe.UPF
ATOMIC_POSITIONS crystal
...   ! <<< Put 2 atoms here in a larger supercell!
starting_magnetization(1) = 0.1   ! for instance
starting_magnetization(2) = 0.1   ! for instance
```

https://www.quantum-espresso.org/Doc/INPUT_PW.html

Spin-orbit (for heavy elements)

- Set **lspinorb = .true.** (AND **noncolin = .true.**).
  Note: It's more expensive!
- You need to use **fully-relativistic pseudopotentials!**
- SSSP does not have them (yet). A good library: PseudoDojo
  (note: recommended cutoffs in Hartree, not Rydberg: factor of 2!)



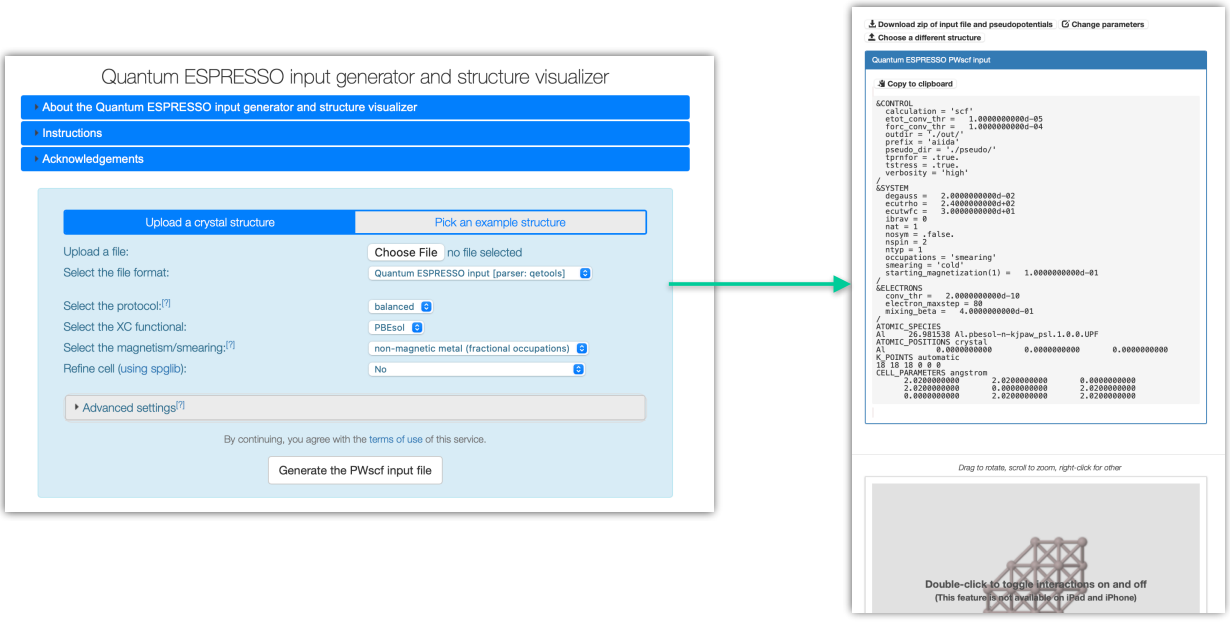
https://www.pseudo-dojo.org

Summary

- Bravais lattice
- Atoms in the basis
- Cutoff energy for the wavefunctions (and for the charge density: 4x-12x)
- k-point sampling
- Metal: fictitious temperature (smearing)
- Self-consistency recipe

Where can I start from?

- Materials Cloud's Quantum ESPRESSO input generator: https://qeinputgenerator.materialscloud.io/

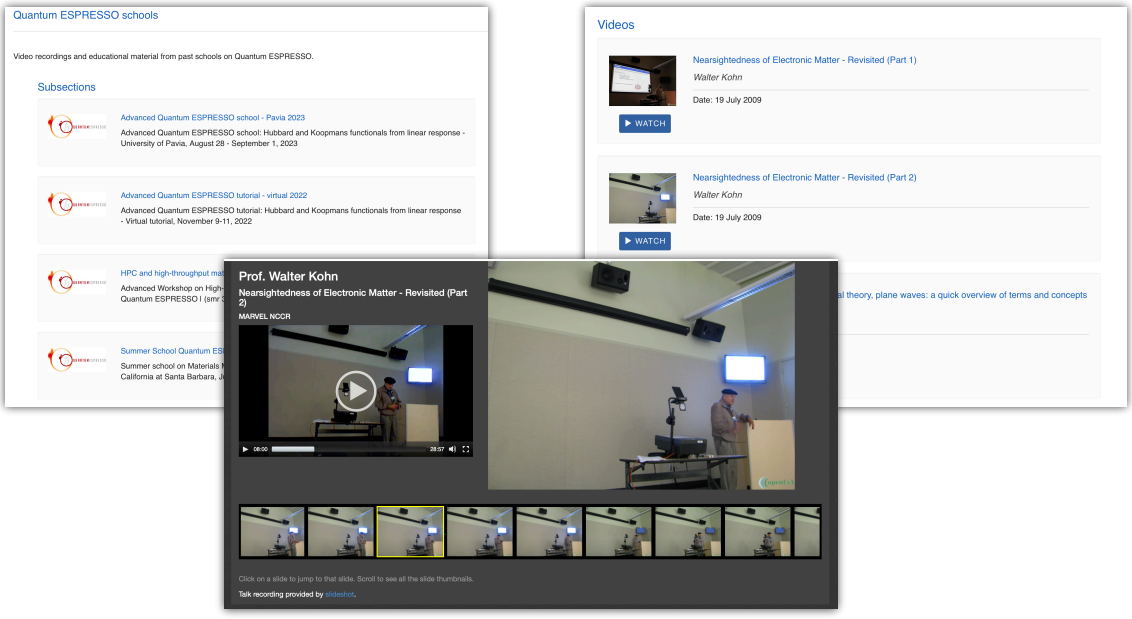


To learn more:

- Feliciano Giustino or Richard Martin's electronic-structure books
- Simon L. Altmann, "Band theory of solids: an introduction from the point of view of symmetry"
- T. Inui, Y. Tanabe, Y. Onodera, "Group Theory and its application in Physics"
- G. Grosso, G. Pastori Parravicini, "Solid State Physics"

To learn more:

- Quantum ESPRESSO schools: https://www.materialscloud.org/learn/sections/VLoB41/quantum-espresso-schools



Atomic Units

Table A11.2 Atomic units

Quantity	*Unit*	*Physical significance*	*Value*
Mass	m or m_e	Electron mass	9.10953×10^{-31} kg
Charge	e	Absolute value of electron charge	1.60219×10^{-19} C
Angular momentum	$\hbar$	Planck's constant divided by (2π)	1.05459×10^{-34} J s
Length	a_0	Bohr radius for atomic hydrogen (with infinite nuclear mass)	5.29177×10^{-11} m
Velocity	$v_0 = \alpha c$	Magnitude of electron velocity in first Bohr orbit	2.18769×10^{6} m s^{-1}
Momentum	$p_0 = mv_0$	Magnitude of electron momentum in first Bohr orbit	1.99288×10^{-24} kg m s^{-1}
Time	$\frac{a_0}{v_0}$	Time required for electron in first Bohr orbit to travel one Bohr radius	2.41889×10^{-17} s
Frequency	$\frac{v_0}{2\pi a_0}$	Angular frequency of electron in first Bohr orbit (v_0/a_0) divided by (2π)	6.57968×10^{15} s^{-1}
Energy	$\frac{e^2}{4\pi\varepsilon_0 a_0} = \alpha^2 mc^2$	Twice the ionisation potential of atomic hydrogen (with infinite nuclear mass)	4.35981×10^{-18} J $= 27.2116$ eV
Wave number	$\frac{\alpha}{2\pi a_0} = 2\bar{R}(\infty)$	Twice the Rydberg constant, i.e. twice the wave number corresponding to the ionisation potential of atomic hydrogen (with infinite nuclear mass)	2.19474×10^{7} m^{-1}

Conversion Factors

Appendix 11

Table A11.3 Conversion factors

1 Å (angström) = 0.1 nm = 10^{-10} m = 10^{-8} cm

1 fm (femtometer or Fermi) = 10^{-6} nm = 10^{-15} m

λ (in Å) × $\tilde{\nu}$ (in cm^{-1}) = 10^{8} (from $\lambda\tilde{\nu} = 1$)

$a_0 = 5.29177 \times 10^{-11}$ m = 0.529177 Å

$a_0^2 = 2.80028 \times 10^{-21}$ m^2

$\pi a_0^2 = 8.79735 \times 10^{-21}$ m^2

1 Hz = 1 s^{-1}

1 electron mass (m_e) = 0.511003 MeV/c^2

1 proton mass (M_p) = 938.280 MeV/c^2

1 a.m.u. = $\frac{1}{12}M_{12C}$ = 1.66057×10^{-27} kg = 931.502 MeV/c^2

1 J = 10^{7} erg = 0.239 cal = 6.24146×10^{18} eV

1 cal = 4.184 J = 2.611×10^{19} eV

1 eV = 1.60219×10^{-19} J = 1.60219×10^{-12} erg

1 MeV = 1.60219×10^{-13} J = 1.60219×10^{-6} erg

1 eV corresponds to:
a frequency of 2.41797×10^{14} Hz (from $E = h\nu$)
a wavelength of 1.23985×10^{-6} m = 12398.5 Å (from $E = hc/\lambda$)
a wave number of 8.06548×10^{5} m^{-1} = 8065.48 cm^{-1} (from $E = hc\tilde{\nu}$)
a temperature of 1.16045×10^{4} K (from $E = kT$)

1 cm^{-1} corresponds to
an energy of 1.23985×10^{-4} eV
a frequency of 2.99792×10^{10} Hz

1 atomic unit of energy = 27.2116 eV corresponds to
a frequency of 6.57968×10^{15} Hz
a wavelength of 4.55633×10^{-8} m = 455.633 Å
a wave number of 2.19475×10^{7} m^{-1} = 219475 cm^{-1}
a temperature of 3.15777×10^{5} K

1 a.m.u. corresponds to an energy of 931.502 MeV = 1.49244×10^{-10} J

$kT = 8.61735 \times 10^{-5}$ eV at $T = 1$ K

$hc = 1.23985 \times 10^{-6}$ eV × m = 12398.5 eV × Å

$\hbar c = 1.97329 \times 10^{-7}$ eV × m = 1973.29 eV × Å

ΔE (in eV) × Δt (in s) = 6.58218×10^{-16} eV × s (from $\Delta E \Delta t = \hbar$)

Accuracy of results and DFT limitations

Predicting Structure: The Energy Scales

Accuracy required to predict physical behavior is astonishing

Atomic energy:		-1894.074 Ry
FCC V	:	-1894.7325 Ry
BCC V	:	-1894.7125 Ry

Vanadium

Cohesive energy is 0.638 Ry (0.03% of total E)

FCC/BCC difference is 0.02 Ry (0.001% of total E)

How can we ever get physical behavior correct?

Large cancellation of errors + pseudopotentials!

LDA vs GGA: Lattice Parameters in Solids (in angstrom)

	exp	LDA	Δ	GGA	Δ
Si	5.43	5.4	-0.55%	5.49	1.10%
Ge	5.65	5.62	-0.53%	5.74	1.59%
GaAs	5.65	5.62	-0.53%	5.73	1.42%
Al	4.03	3.98	-1.31%	4.09	1.57%
Cu	3.60	3.52	-2.35%	3.62	0.44%
Ag	4.07	4.00	-1.69%	4.17	2.47%
Ta	3.30	3.26	-1.12%	3.32	0.80%
W	3.16	3.14	-0.67%	3.18	0.67%
Pt	3.91	3.90	-0.41%	3.97	1.49%
Au	4.06	4.05	-0.13%	4.16	2.48%

Data from Filippi et al., PRB 50, 14947 (1994), Khein et al., PRB 51, 4105 (1995)

LDA tends to “overbind”, GGA “underbinds”.

LDA vs GGA: Bulk Moduli in Solids (in GPa)

	exp	LDA	Δ	GGA	Δ
Si	99	96	-3.03%	83	-16.16%
Ge	77	78	1.30%	61	-20.78%
GaAs	76	74	-2.63%	65	-14.47%
Al	77	84	9.09%	73	-5.19%
Cu	138	192	39.13%	151	9.42%
Ag	102	139	36.27%	85	-16.67%
Ta	193	224	16.06%	197	2.07%
W	310	337	8.71%	307	-0.97%
Pt	283	307	8.48%	246	-13.07%
Au	172	198	15.12%	142	-17.44%

Data from Filippi et al., PRB 50, 14947 (1994), Khein et al., PRB 51, 4105 (1995)

LDA tends to be too stiff. GGA too soft.

Small Molecules: binding energy (eV)

	expt	LDA	GGA	HF
H_2	-4.753	-4.913	-4.540	-3.64
LiH	-2.509	-2.648	-2.322	
O_2	-5.230	-7.595	-6.237	-1.28
H_2O	-10.078	-11.567	-10.165	
F_2	-1.66	-3.32	-2.320	1.37

From Kurth et al., Int. J. Quantum Chem. 75, 889 (1999)

Binding energy (atomisation energy) too high in LDA,
GGA is closer but sometimes bonding is too weak.
Pure Hartree Fock without corrections is very bad.

Hydrogen bonding

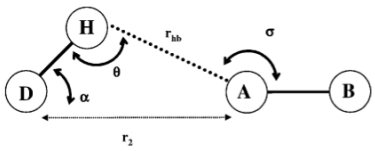


TABLE 1: Association Energies (in kcal/mol) for Medium-weak Hydrogen-Bonded Dimers[a]

dimer	hbs	best value	PBE	PBE error per hb
$H_2O\cdots NH_3$	1	−6.36[b]	−7.15	−0.79
$H_2O\cdots H_2O$	1	−4.96[c]	−5.37	−0.41
$HF\cdots HF$	1	−4.53[c]	−5.08	−0.55
$NH_3\cdots NH_3$	2	−2.94[b]	−2.74	0.10
$HCl\cdots HCl$	1	−1.95[c]	−2.08	−0.13
$CO\cdots HF$	1	−1.67[d]	−1.37	0.30
$CH_4\cdots NH_3$	1	−0.66[e]	−0.69	−0.03

From Ireta et al., J. Phys. Chem. A 108, 5692 (2004)

DFT-PBE can predict the strength of hydrogen bonds
with an accuracy of ~1 kcal/mol

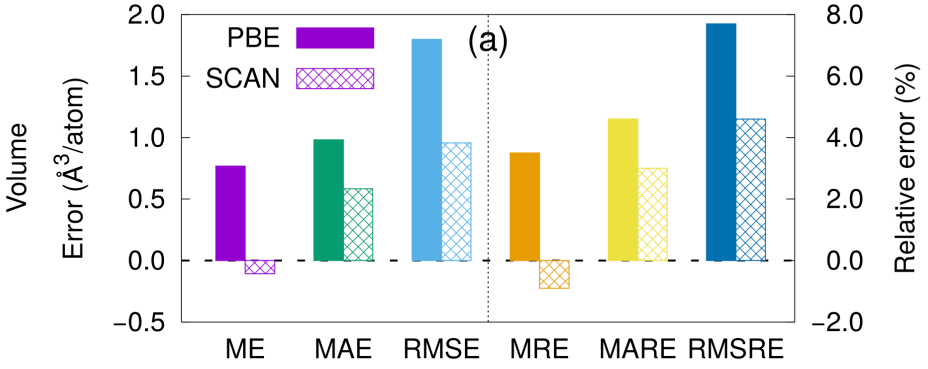
Exceptions when bonds are highly bent (θ<130°):
error can be up to 1.5 kcal/mol

PBE (GGA) vs SCAN (meta-GGA)
Easy: equilibrium volume

Reminder: GGA (Generalised Gradient Approximation): functional depends not only on local value of density, but also depend on its first derivative (gradient).

Meta-GGA: includes also dependence on orbital kinetic-energy density:

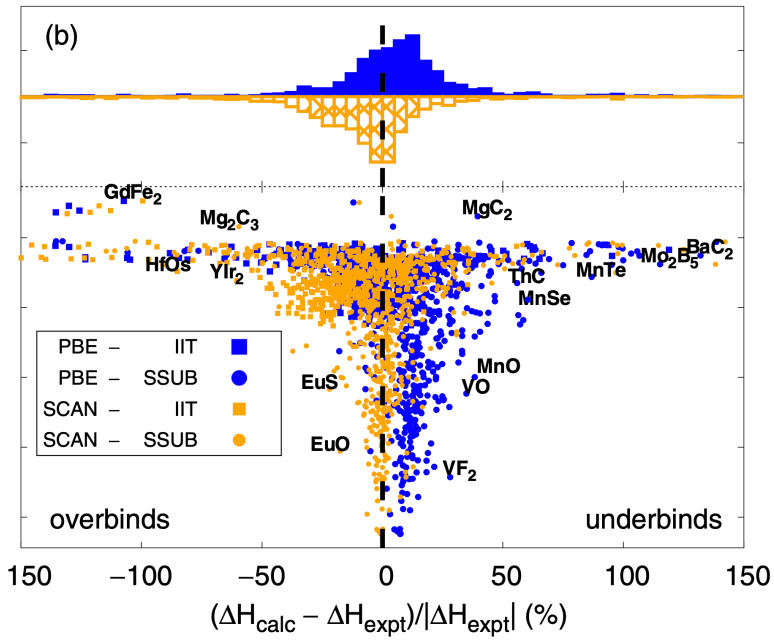
$$\tau = \sum_i \frac{1}{2}|\nabla\psi_i|^2$$



SCAN functional: J. Sun et al., PRL 115, 036402 (2015)

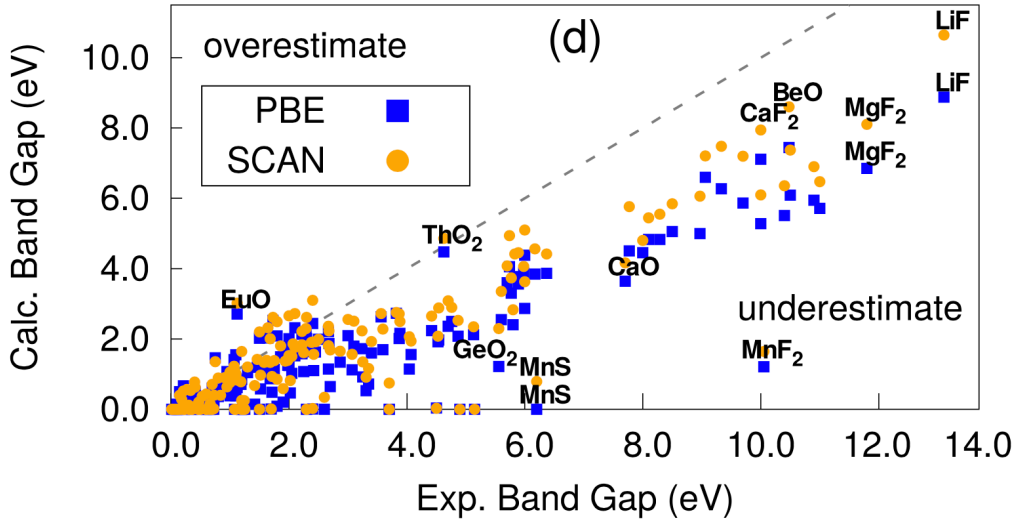
Benchmarks: Eric B. Isaacs and Chris Wolverton, Phys. Rev. Materials 2, 06380 (2018)

Difficult: formation energies



Eric B. Isaacs and Chris Wolverton, Phys. Rev. Materials 2, 06380 (2018)

Out-of-bounds: (transport) band gaps



Eric B. Isaacs and Chris Wolverton, Phys. Rev. Materials 2, 06380 (2018)

Newer popular meta-GGAs

- **SCAN**: J. Sun et al., *Strongly Constrained and Appropriately Normed Semilocal Density Functional*, PRL 115, 036402 (2015)
- **rSCAN**: A. P. Bartók, J. R. Yates, *Regularized SCAN functional*, J. Chem. Phys. 150, 161101 (2019)
  - rSCAN is a modification to the functional form of the SCAN functional to eliminate numerical instabilities, matching the original form very closely and with comparable performance.
- **r2SCAN**: J. W. Furness et al., *Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation*, J. Phys. Chem. Lett. 11, 8208–8215 (2020)
  - rSCAN is regularized form of the SCAN functional: it improves SCAN's numerical performance but breaks constraints from the exact XC functional.
    r2SCAN restores exact constraint adherence to rSCAN: it maintains rSCAN's numerical performance while it restores the transferable accuracy of SCAN.
- *And many more meta-GGAs... (check LibXC)*

Minor (used to be major) problem with standard DFT: Van der Waals

- Van der Waals interaction important for many areas: biology, soft solids, layered materials, adsorption events, …
- Van der Waals interaction is a result of time-correlations in the fluctuations of the charge densities of two systems. It's also long ranged. So, it is not included straightforwardly in mean field approximations to DFT, like LDA or GGA
- LDA tends to give some binding in the VdW regime but for the wrong reasons…

Important for layered materials with weak VdW bonds between the layers

Graphite

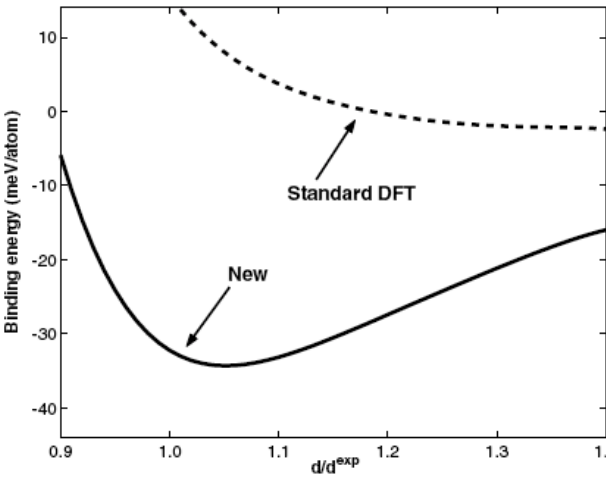


Table 1
Calculated properties of graphite, compared to experimental data

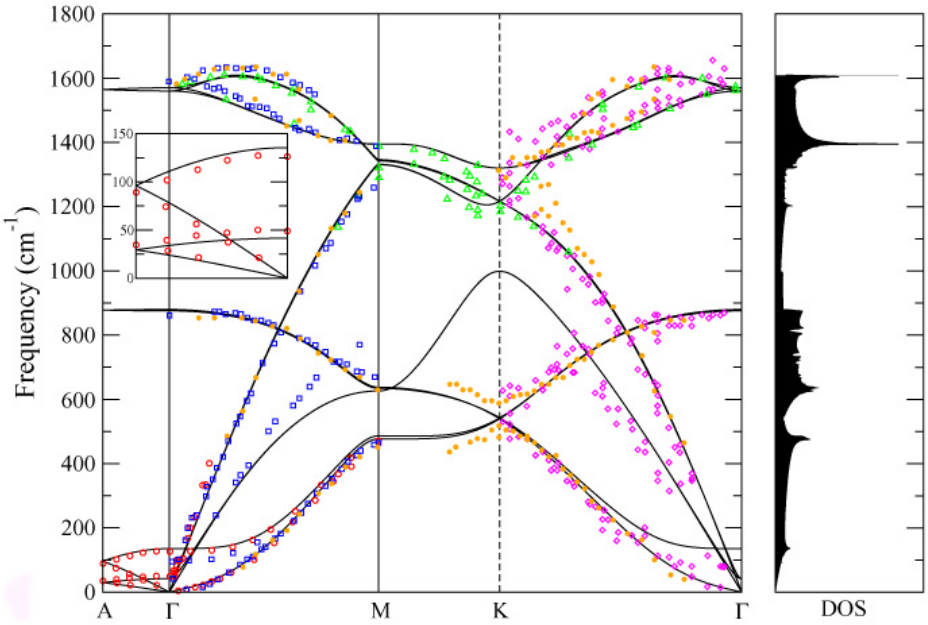
Method	a [Å]	c [Å]	E_0 [meV/atom]	B_0 [GPa]
Early DFT (LDA)	2.45	6.6	20[a]	51
Standard DFT (GGA)	2.47	$\gg$7.5	~5	~7
Revised DFT [1]	2.47	7.0	34	33
Exp.	2.46	6.7	35 ± 10[b]	33[c]

The table shows the geometry (a, c), binding energy (E_0) and bulk modulus (B_0) obtained with the early-standard DFT, the current-standard DFT, and our revised DFT.
[a] Ref. [26].

Rydberg, H. et al. Hard numbers on soft matter. Surface Science 532, 606-610 (2003).

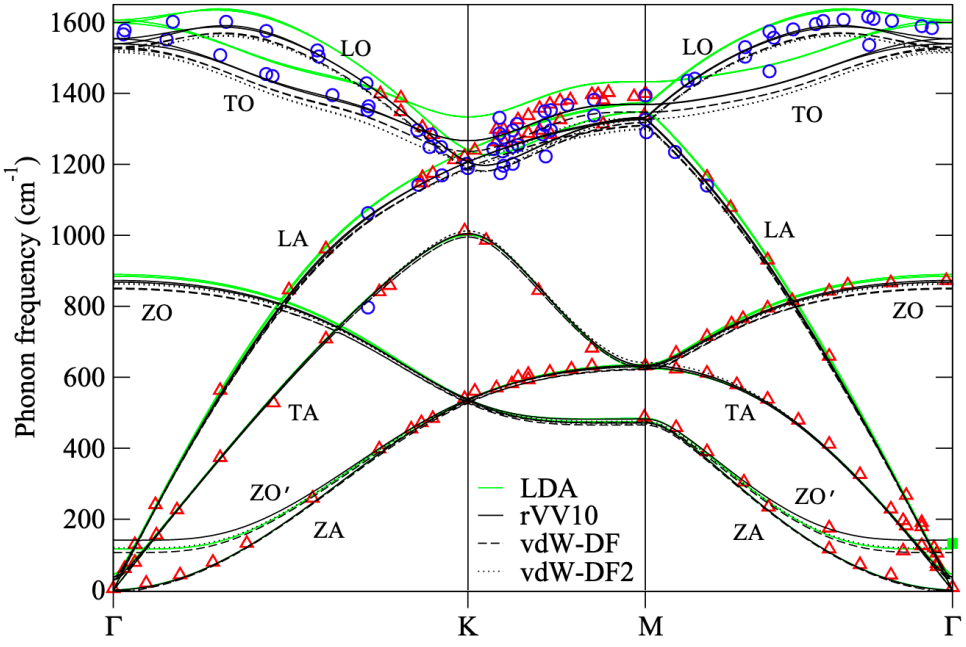
It determines structure and binding, but does not matter much for everything else

Graphite phonon dispersions (USING EXPERIMENTAL c/a)



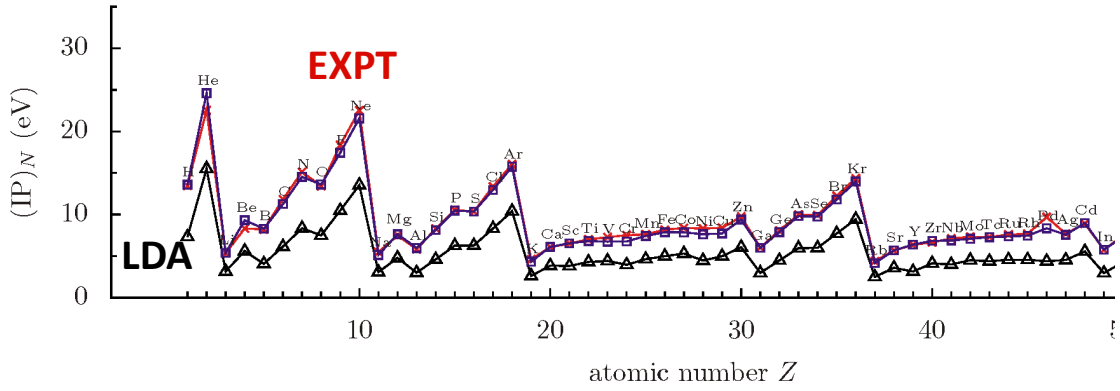
Mounet and Marzari, Phys. Rev. B (2005)

LDA vs. VdW-DFT in graphite



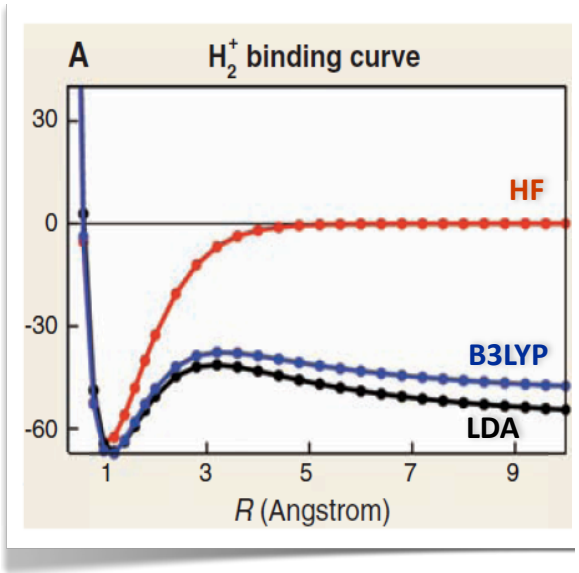
R. Sabatini et al., PRB 93, 235120 (2016)

Notable failure: Photoemission spectra (ionization potential from HOMO)



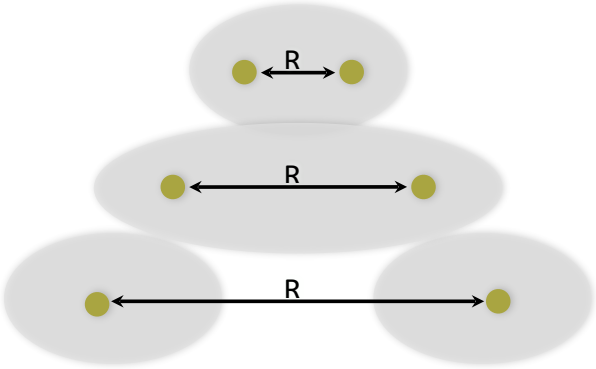
I. Dabo *et al.* Phys. Rev. B 82 115121 (2010)

Major problem: Self-interaction



A.J. Cohen, P. Mori-Sanchez, W. Yang, Science (2008)

H_2^+ dissociation limit: 1 single electron



- Correct solution when very far away: two degenerate solutions: fully on the left or fully on the right - remember notebook on 2 quantum wells
- Actually, any linear combination is still a valid eigenstate, with the same energy!
- However, while the Schrödinger equation (and Hartree-Fock) do not have any self-interaction, some self-interaction is (incorrectly) present in Kohn-Sham DFT!
- (Note: in exact DFT there would not be any self-interaction)

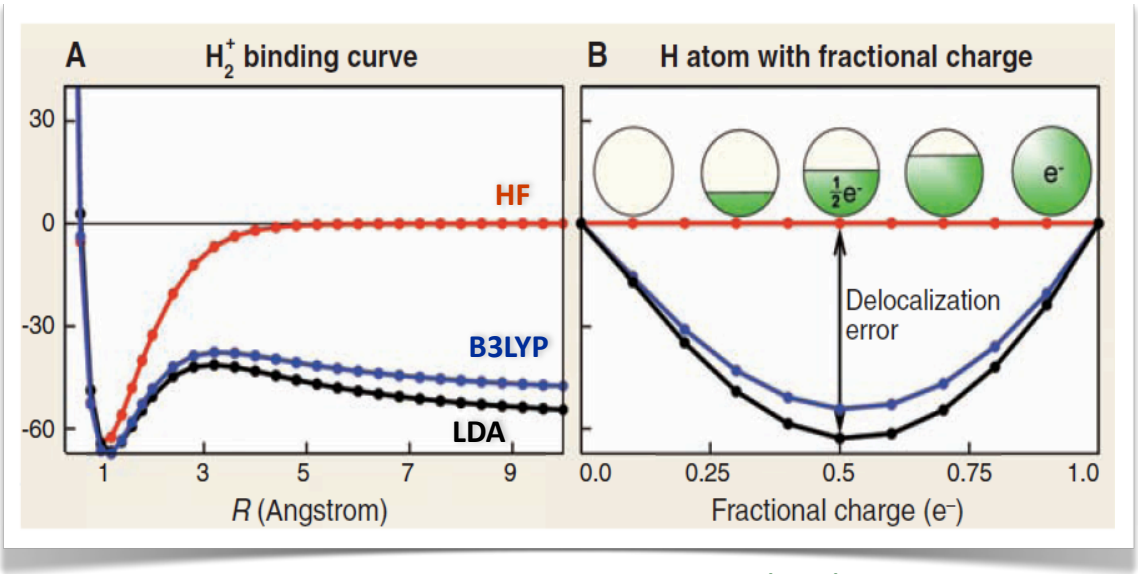
$$\hat{H} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r})$$ **Schrödinger**

For 1 electron, these two terms should cancel out exactly

$$\hat{H}_{KS} = -\frac{1}{2}\vec{\nabla}^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$$ **Kohn-Sham**

Linearity with respect to fractional occupations

- In approximate DFT, V_H typically larger than V_{xc}
- Minimise energy => minimise V_H: artificial splitting the electron in two halves to minimise electrostatic interaction

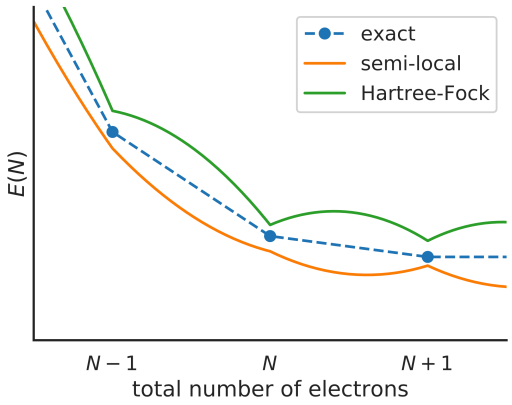


A.J. Cohen, P. Mori-Sanchez, W. Yang, Science (2008)

Linearity with respect to fractional occupations

- One possible solution:
  ensure that the energy cost of removing a fraction of electron from the left is compensated exactly by adding the same fraction to the right

- This is equivalent to saying that the energy (as a function of fractional occupation) is piecewise-linear

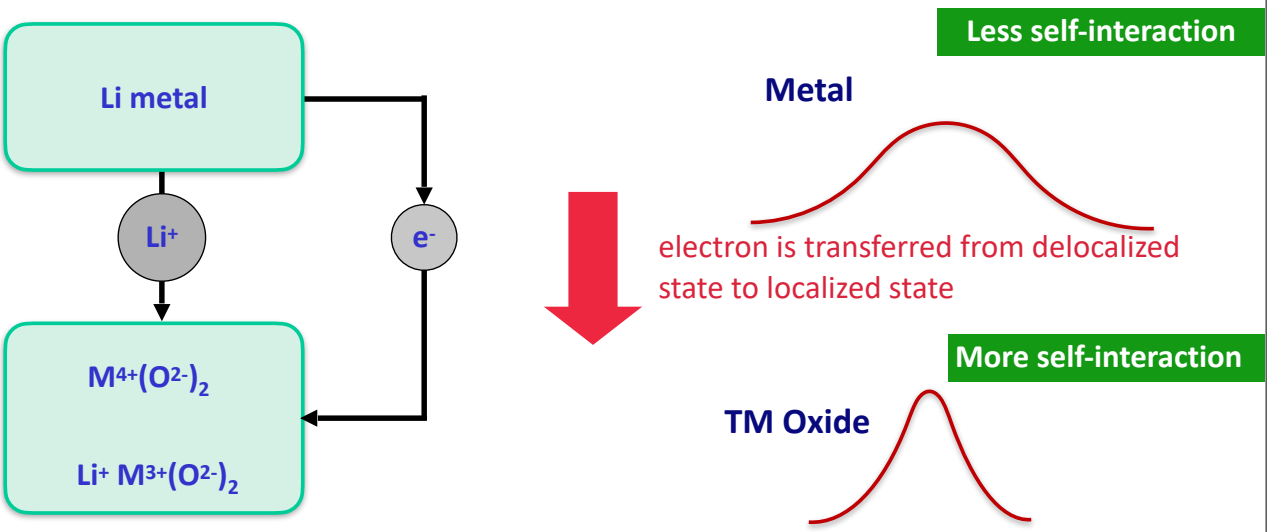


From https://koopmans-functionals.org/en/latest/theory/piecewise_linearity.html

See also, for instance:
Mori-Sánchez et al., J. Chem. Phys. 125, 201102 (2006)
I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
Kronik, Kümmel, Phys. Chem. Chem. Phys., 16467 (2020)
I. Timrov et al., Phys. Rev. B 103, 045141 (2021)
E. Linscott et al., arXvi 2302.07759 (2023)

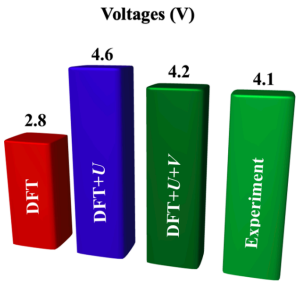
Self-interaction effects in practical applications

Important not only for dissociations, but also for practical applications!
E.g. Li batteries: Li insertion into cathode transfers electron from a delocalized to a localized state



Self-interaction effects in practical applications

One approach to cure it:
(Self-consistent) DFT+U+V
Project on localised orbitals (e.g. *d* or *f*) from KS wavefunctions and treat with local Hubbard model



I. Timrov et al., Phys. Rev. B 103, 045141 (2021)

Other approach: self-interaction correction (SIC): PZ, KIPZ; Koopmans' functionals; ...; see e.g. *E. Linscott et al., JCTC 19, 7097 (2023)* and all references therein

Hybrid functionals: simplest but most expensive solution