

Advanced exchange and correlation functionals

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Most slides courtesy of Matteo Cococcioni
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Advanced exchange and correlation functionals

The accuracy of density functional theory depends crucially on the choice of the approximated functional for exchange and correlation

We are going to review the accuracy of some standard functionals

We are going to discuss more advanced functionals:

-) which principles were followed in their development?
-) how do they look like?
-) which physical phenomena do they describe?

Density-Functional Theory: LDA

First historical viable approximations to E_{xc} , turning DFT into a useful tool:

- **Local Density Approximation** (LDA, Kohn and Sham, 1965). Replace the *functional* with a *function* of the local density $n(\mathbf{r})$:

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{LDA}(n(\mathbf{r})) d\mathbf{r}, \quad V_{xc}(\mathbf{r}) = \epsilon_{LDA}(n(\mathbf{r})) + n(\mathbf{r}) \left. \frac{d\epsilon_{LDA}(n)}{dn} \right|_{n=n(\mathbf{r})}$$

where $\epsilon_{LDA}(n)$ is the exchange-correlation energy density for the homogeneous electron gas of density n . This can be calculated with various methods and parameterized. Various flavors exist¹: Perdew-Zunger (PZ), Vosko-Wilk-Nusair (VWN), Perdew-Wang (PW), ... all giving very similar results. Spin-polarized extension (LSDA):

$$E_{xc}[n_+(\mathbf{r}), n_-(\mathbf{r})] = \int \epsilon_{LSDA}(n_+(\mathbf{r}), n_-(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

(n_+ = spin-up, n_- = spin-down density, $n = n_+ + n_-$).

Density-Functional Theory: GGA

The first step beyond LDA is to account for density inhomogeneity:

- **Generalized Gradient Approximation** (GGA). The functional depends upon the local density and the *local gradient* $\nabla n(\mathbf{r})$ of the density:

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r}$$

Spin-polarized extension (sometimes referred to as σ -GGA):

$$E_{xc}[n_+(\mathbf{r}), n_-(\mathbf{r})] = \int \epsilon_{\sigma GGA}(n_+(\mathbf{r}), n_-(\mathbf{r}), \nabla n_+(\mathbf{r}), \nabla n_-(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

Various flavors exist: PBE, revPBE, RPBE, PW91, BLYP,... all giving similar results, with some differences. These are the "standard" functionals in most present-day calculations, with excellent price-to-performance ratio, but some noticeable shortcomings.

Small Molecules

Binding Energy

	exp (ev)	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 ₂ O	-10.078	-11.567	-10.165	
F ₂	-1.66	-3.32		1.37

Binding energy too high in LDA, GGA is closer but sometimes bound to weak. Pure Hartree Fock without corrections is terrible.

Lattice Parameters in Solids

	exp	LDA	Δ	GGA	Δ
Si	5.427	5.4	-0.50%	5.49	1.16%
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%

LDA tends to “overbind”, GGA “underbinds” GGA error more variable

Bulk Modulus 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%

LDA tends to be too stiff. GGA too soft

Oxides

	exp	LDA	Δ	GGA	Δ
MgO	4.21	4.17	-0.95%		
TiO ₂ (a)	4.59	4.548	-0.92%	4.623	0.72%
TiO ₂ (c)	2.958	2.944	-0.47%	2.987	0.98%
Al ₂ O ₃	5.128	5.091	-0.72%	5.185	1.11%
BaTiO ₃	4	3.94	-1.50%		
PbTiO ₃	3.9	3.833	-1.72%	3.891	-0.23%
SnO ₂	4.737	4.637	-2.11%		
β-MnO ₂ (a)	4.404	4.346	-1.32%	4.444	0.91%
β-MnO ₂ (c)	2.876	2.81	-2.29%	2.891	0.52%

Beyond the reach of LDA and GGA

The exact exchange-correlation (XC) energy and potential functionals are obviously unknown, but what is known about their properties suggests that they are highly nontrivial objects. In particular:

- the XC energy as a function of the number of electrons *has a cusp* when the number of electrons crosses an integer value number
- the XC potential should exactly *cancel the self-interaction* of an electron with itself that is present in the Hartree potential, exactly like in Hartree-Fock theory

Note that the XC potential is a *local* potential: $V_{xc} \equiv V_{xc}(\mathbf{r})$, thus a much simpler object than exchange in Hartree-Fock. However no simple, local function of the charge density (and of its gradient) can fullfil the above two requirements.

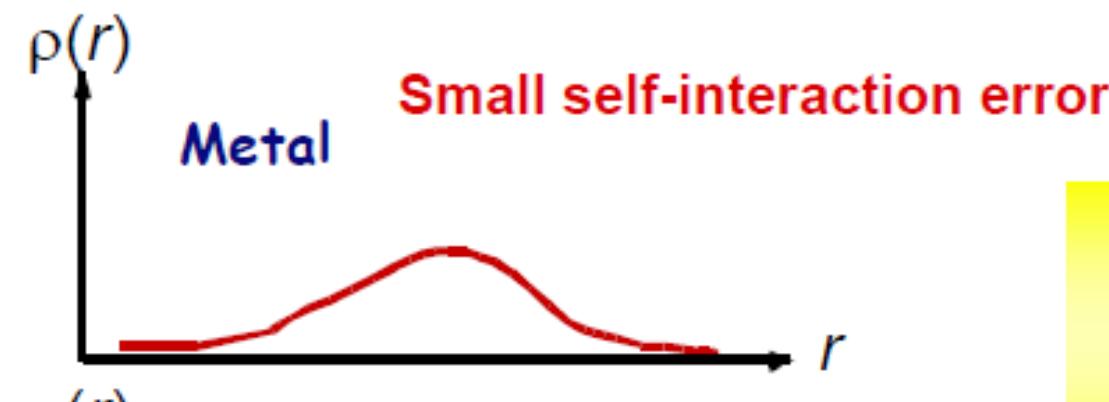
The lack of discontinuity and the presence of spurious self-interactions is at the heart of most problems with approximate DFT. The search for functionals that may solve such problems in an economical way is a very active research field.

Performances of LDA and GGA, summary

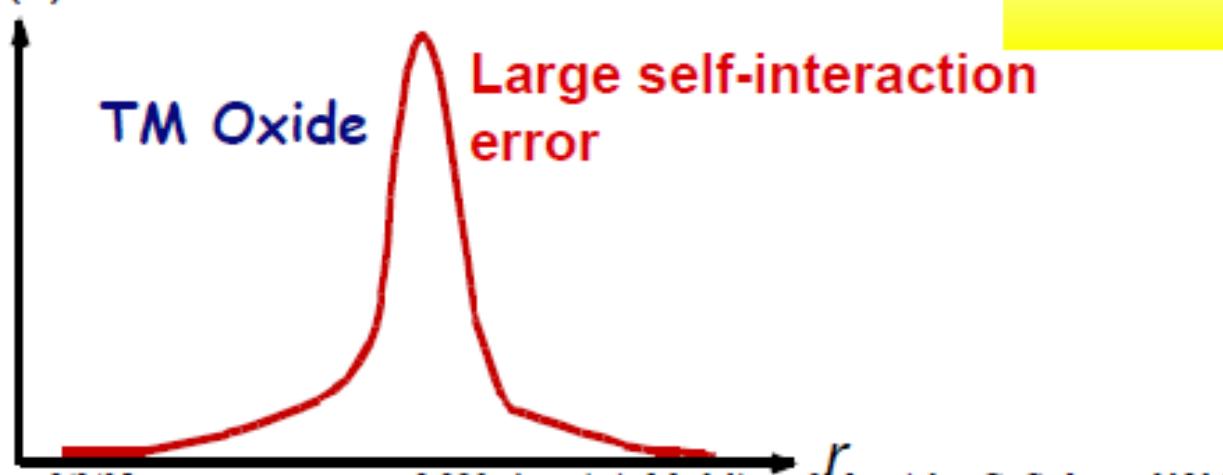
- + **Excellent structural results:** correct prediction of crystal structures, bond lengths, lattice parameters (within 1 ÷ 2%), binding and cohesive energies (GGA 5 to 10%; LDA much worse, strongly overestimates), vibrational properties. Especially good for *sp*-bonded materials but good also for more "difficult" materials, such as transition metal compounds.
- The infamous **band gap problem:** $\epsilon_c - \epsilon_v$ wildly underestimates the true band gap (mostly due to missing discontinuity in V_{xc} for integer number of electrons).
- Serious trouble in dealing with **strongly correlated materials**, such as e.g. transition metal oxides: sometimes the occupancy of atomic-like electronic states is badly wrong, sometimes the electronic structure is incorrect in more subtle ways. The origin of the trouble can be tracked to self-interaction.
- Incorrect treatment of **van der Waals** interactions: LDA works only apparently (due to overbinding), GGA doesn't bind. Deep reason: van der Waals is nonlocal, doesn't depend upon charge overlap. No functional based on local density and gradients can account for it: no charge overlap, no interactions.

In standard DFT an electron interacts with the effective potential generated by all the electrons (including itself)

$$H = \sum_i H_i = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{nuclear}(r_i) + \sum_{i=1}^{N_e} V_{\text{effective}}(r_i)$$



Self interaction in DFT
is key problem in transition
metal oxides



Functionals for strongly correlated materials

An incomplete list of more recent functionals, addressing (most or at least part of the) shortcomings of LDA and GGA in strongly correlated materials:

- **Self-Interaction Correction.** is Self-Interaction a problem? let's remove it! The first proposal of a Self-Interaction Correction (SIC) for extended systems, by Perdew and Zunger dates back to 1980. The functional becomes orbital-dependent, leading to some fundamental and numerical problems and unclear performances, so it never really took off. New ideas have since appeared and look more promising.

QUANTUM ESPRESSO implements in CP a simple form of SIC (D'Avezac et al.) working for systems with an unpaired spin.

- **Meta-GGA.** The functionals has a further dependence upon the *non-interacting kinetic energy density* $\tau(\mathbf{r})$:

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \psi_{i,\sigma}(\mathbf{r})|^2, \quad \sigma = +, -$$

The XC energy is written as

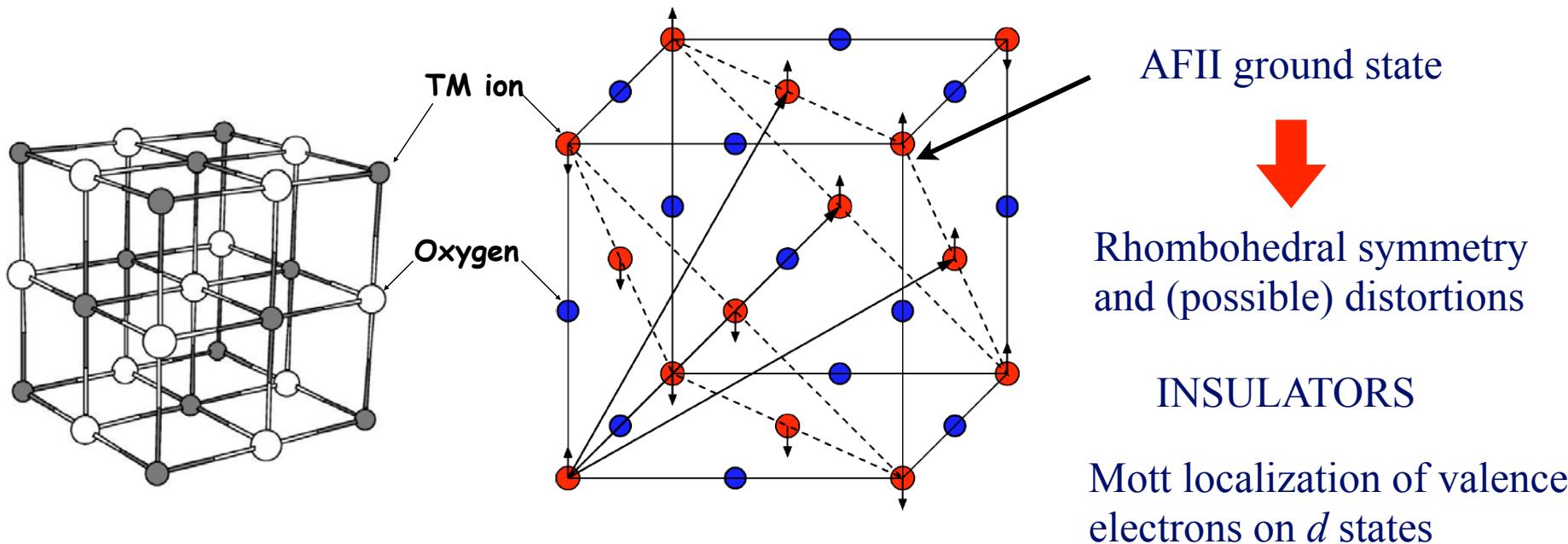
$$E_{xc}[n_+(\mathbf{r}), n_-(\mathbf{r})] = \int \epsilon_{mGGA}(n_+(\mathbf{r}), n_-(\mathbf{r}), \nabla n_+(\mathbf{r}), \nabla n_-(\mathbf{r}), \tau_+(\mathbf{r}), \tau_-(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

Meta-GGA functionals have the potential to treat in a different way correlations in electronically different materials. Formulation is significantly more complicated than GGA but mGGA is not much more expensive than GGA. QUANTUM ESPRESSO implements it, but it is numerically very unstable (i.e. the code easily starts to produce divergences) and thus very little used, in spite of its promises.

QUANTUM ESPRESSO implements a few meta-GGA functionals (TPSS, M06L, TB09) in ground-state calculations only and for Norm-Conserving PPs only.

DFT+U: Density functional theory with the Hubbard correction

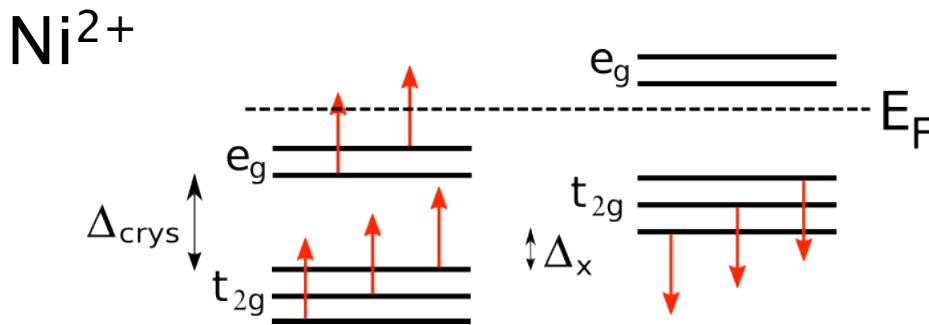
Problematic cases: Transition-Metal Oxides



Approximate DFT (e.g., LDA or GGA):

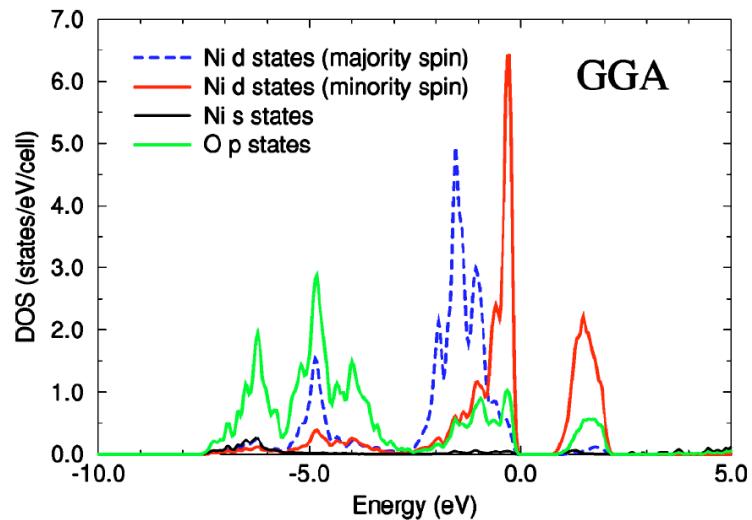
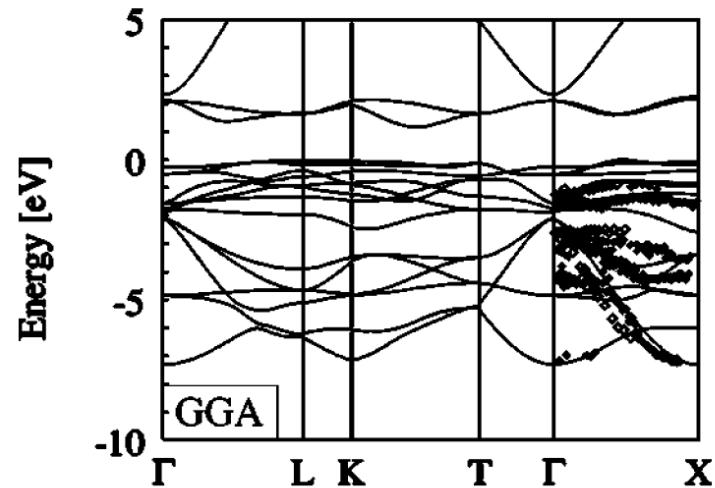
- Rhombohedral distortion overestimated
- Poor estimate of structural properties
- **FM ground state (FeO)**
- Too small or no gap at all
- Magnetization underestimated
- Wrong ordering of states

Example: GGA results for NiO



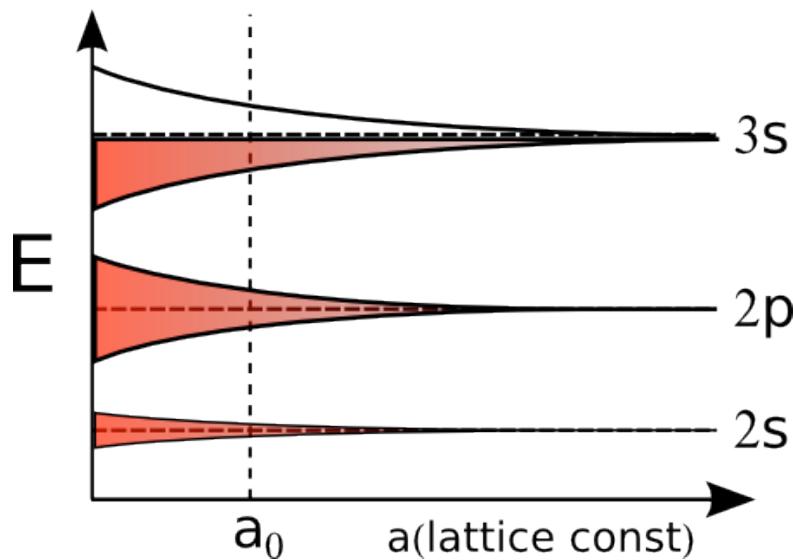
- Anti-ferromagnetic: OK
- Crystal structure cubic: OK
- Crystal field produces the band gap.

- **Band gap is too small**
- **O-p states should be at the top of the valence band.**



Band theory

Consider solid Na($2s^2 2p^6 3s^1$):

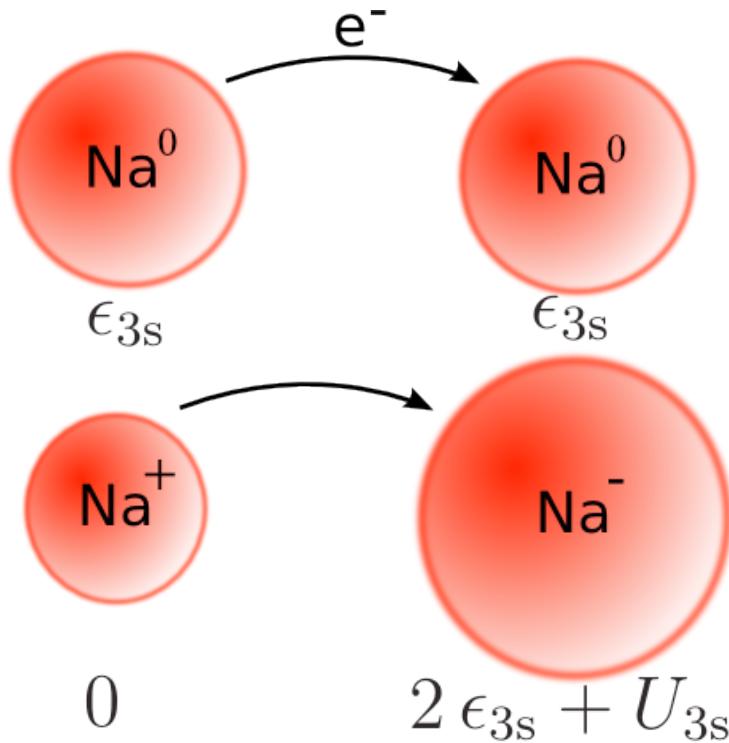


At the equilibrium lattice constant a_0 :
Independent electrons: band theory
Half filled band \rightarrow metal

Consider very large a :
• Half-filled 3s orbital becomes narrower, but it is still half-filled.
• **Band theory still predicts a metal!**

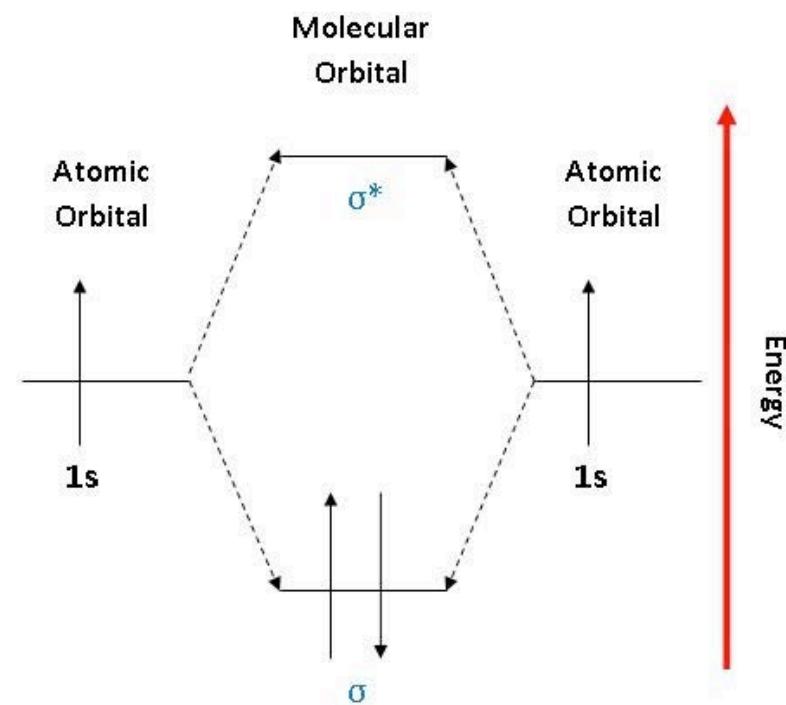
Isolated Na atoms still described as a metal; what is going wrong?

Single- vs many-electrons perspectives: Mott localization

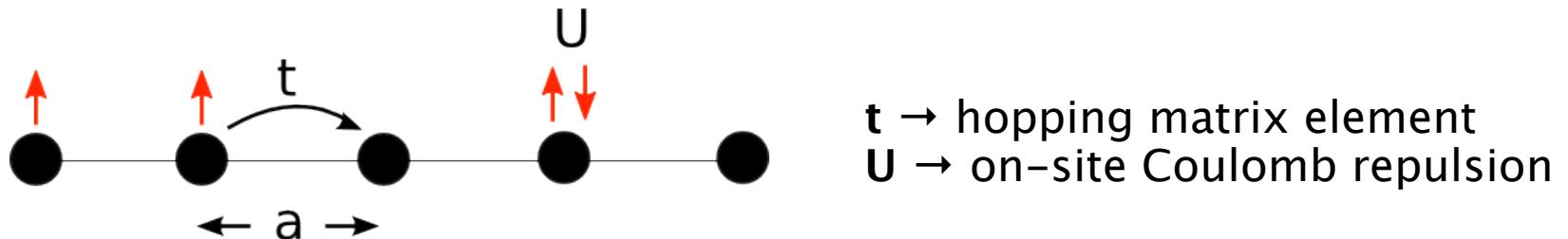


$$U_{3s} = \int d^3r \int d^3r' |\phi_{3s}(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\phi_{3s}(\mathbf{r}')|^2$$

$$H = \begin{pmatrix} h_{aa} & v_{ab} \\ v_{ab} & h_{aa} \end{pmatrix}$$



Introduction to the Hubbard model



$$\hat{H} = \underbrace{\epsilon \sum_{i,\sigma} \hat{n}_{i,\sigma}}_{\mathcal{H}_{\text{band}}} - t \underbrace{\sum_{\langle i,j \rangle, \sigma} \left(\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + \text{h.c.} \right)}_{\mathcal{H}_{\text{band}}} + \underbrace{U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}_{\mathcal{H}_{\text{Coulomb}}}$$

J.Hubbard, Proc. Roy. Soc. Lond. (1963–1967)

$$\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \quad \hat{c}_{i\sigma}^\dagger, \hat{c}_{i\sigma} \text{ creation/annihilation operators}$$

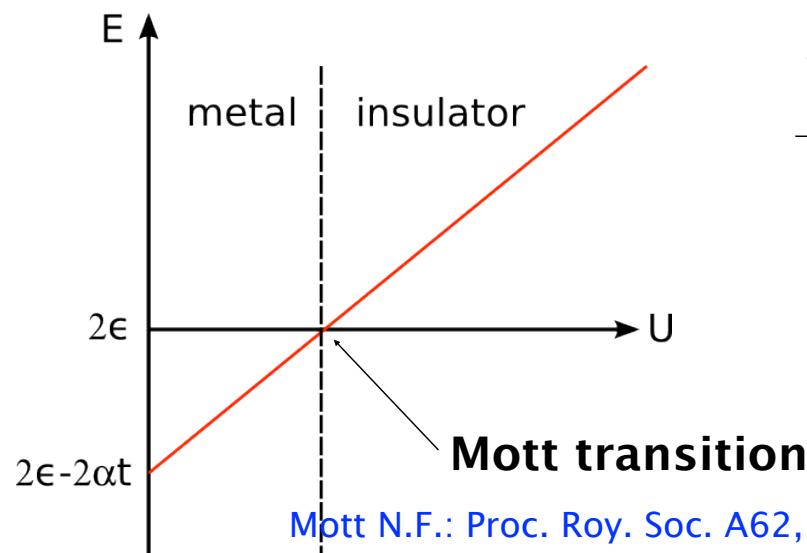
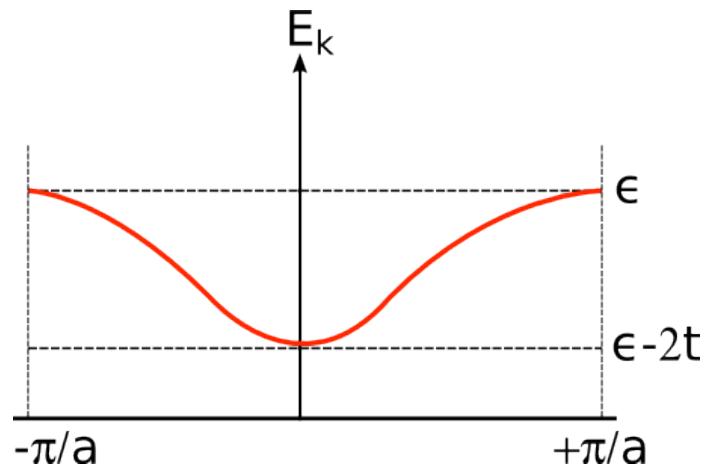
Band term is easy to solve; introduce $\rightarrow \hat{c}_{j\sigma} = \frac{1}{\sqrt{N}} \sum_k e^{i \frac{2\pi k}{N} j} \hat{b}_{k\sigma}$
N: number of atoms

More on the Hubbard model

$$\mathcal{H}_{\text{band}} = \sum_{k,\sigma} \left[\epsilon - 2t \cos\left(\frac{2\pi k}{N}\right) \right] \hat{b}_{k\sigma}^\dagger \hat{b}_{k\sigma}$$

$$\langle \mathcal{H}_{\text{band}} \rangle \simeq 2N(\epsilon - \alpha t)$$

$$\langle \mathcal{H}_{\text{Coulomb}} \rangle \simeq N U$$



$$E = \langle \mathcal{H}_{\text{band}} \rangle + \langle \mathcal{H}_{\text{Coulomb}} \rangle$$

$$E = N(2\epsilon + U - \alpha t)$$

band-shape dependent constant

- Metallic when $t \gg U$
- Insulating when $t \ll U$

DFT+U

A very simple idea: let's describe localized d or f electrons as located on isolated (atomic) states in a “crystal bath”. Let's use the Hubbard model to describe their behavior.
We need to “embed” the Hubbard Hamiltonian in the DFT energy functional

V. I. Anisimov *et al.*, PRB 48, 16929 (1993)

A. Liechtenstein *et al.* PRB 52, R 5467 (1995)

We add the Hubbard functional, subtract its MF value (to avoid double-counting)

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + E_{Hub} [\{n_i\}] - E_{dc} [\{n_i\}]$$

Original formulation:

$$E_{Hub} = \frac{U}{2} \sum_{i \neq j} n_i n_j \quad E_{dc} = \frac{U}{2} N(N - 1)$$

The Hubbard correction acts selectively on localized states:

$$E_U = E_{Hub} - E_{dc} = E_U [\{n_i\}] \quad n_i = \sum_{kv} f_{kv} \langle \phi_i | \psi_{kv} \rangle \langle \psi_{kv} | \phi_i \rangle$$

DFT+U: rotationally invariant formulation

The expression of the corrective “+U” functional should be independent from the specific choice of localized states

$$E_{Hub}[\{n_{mm'}^I\}] = \frac{1}{2} \sum_{\{m\}, \sigma, I} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{mm'}^{I\sigma} n_{m''m'''}^{I-\sigma} \\ + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{mm'}^{I\sigma} n_{m''m'''}^{I\sigma} \}$$

$$E_{dc}[\{n_{mm'}^I\}] = \sum_I \left\{ \frac{U^I}{2} n^I (n^I - 1) - \frac{J^I}{2} [n^{I\uparrow} (n^{I\uparrow} - 1) + n^{I\downarrow} (n^{I\downarrow} - 1)] \right\}$$

A. Liechtenstein *et al.* PRB 52, R 5467 (1995)

where:

$$n_{mm'}^{I\sigma} = \sum_i f_i \langle \psi_i^\sigma | \phi_{m'}^I \rangle \langle \phi_m^I | \psi_i^\sigma \rangle \quad n^{I\sigma} = \sum_m n_{mm}^{I\sigma} \quad n^I = \sum_\sigma n^{I\sigma}$$

ψ_i^σ are Kohn-Sham states

ϕ_m^I are *localized* atomic orbitals (*d* or *f*)

A simpler formulation

Effective interactions:

$$\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a_k(m, m', m'', m''') F^k$$

$$F^k = \int d\mathbf{r} \int d\mathbf{r}' \phi_{lm}^*(\mathbf{r}) \phi_{lm'}(\mathbf{r}) \frac{r_<^k}{r_>} \phi_{lm''}^*(\mathbf{r}') \phi_{lm'''}(\mathbf{r}') \quad a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle$$

Let's neglect interaction anisotropy:

$$U = F^0 \neq 0 \quad J = \frac{F^2 + F^4}{14} = 0$$

After some algebra....

Dudarev *et al.*, PRB 57, 1505 (1998)

$$E_{DFT+U}[\rho(\mathbf{r})] = E_{DFT}[\rho(\mathbf{r})] + \sum_{I,\sigma} \frac{U^I}{2} Tr \left[\mathbf{n}^{I\sigma} (1 - \mathbf{n}^{I\sigma}) \right]$$

How does it work?

Because of the rotational invariance we can use a diagonal representation:

$$E_U = E_{Hub} - E_{dc} = \sum_I \frac{U^I}{2} \sum_{m,\sigma} [\lambda_m^{I\sigma} (1 - \lambda_m^{I\sigma})]$$

where:

$$\mathbf{n}^{I\sigma} \mathbf{v}_m = \lambda_m^{I\sigma} \mathbf{v}_m \quad \lambda_m^{I\sigma} = \sum_{k,v} f_{kv} \langle \psi_{kv}^\sigma | \phi_m^I \rangle \langle \phi_m^I | \psi_{kv}^\sigma \rangle$$

Potential:

$$V_U |\psi_{kv}^\sigma\rangle = \frac{\delta E_U}{\delta (\psi_{kv}^\sigma)^*} = \sum_I \frac{U^I}{2} \sum_{m,\sigma} (1 - 2\lambda_m^{I\sigma}) |\phi_m^I\rangle \langle \phi_m^I | \psi_{kv}^\sigma \rangle$$

$$\left. \begin{array}{l} \lambda_m^{I\sigma} > \frac{1}{2} \Rightarrow V_U < 0 \\ \lambda_m^{I\sigma} < \frac{1}{2} \Rightarrow V_U > 0 \end{array} \right\}$$

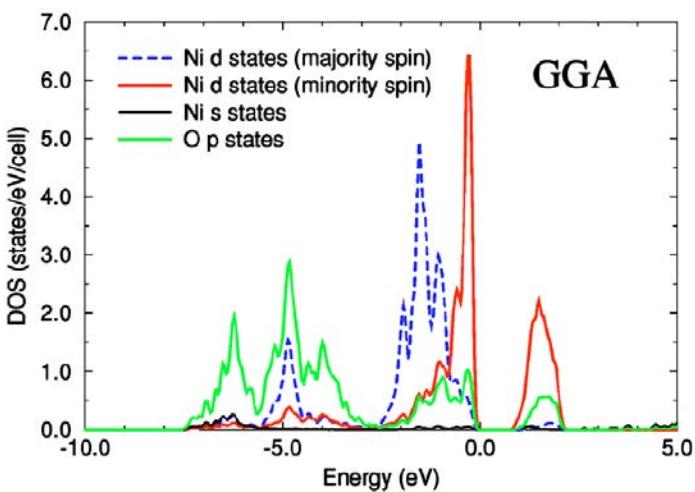
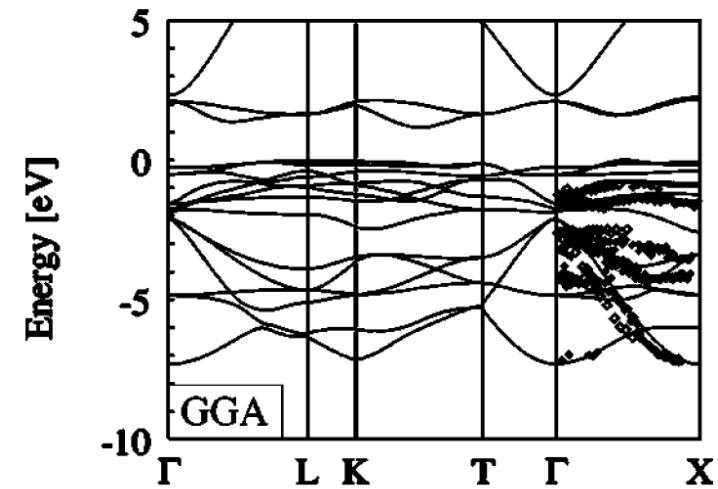


Partial occupations of atomic states
are discouraged

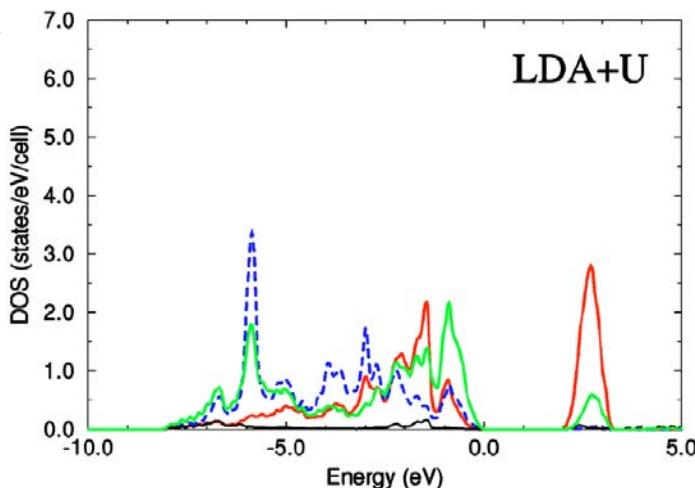
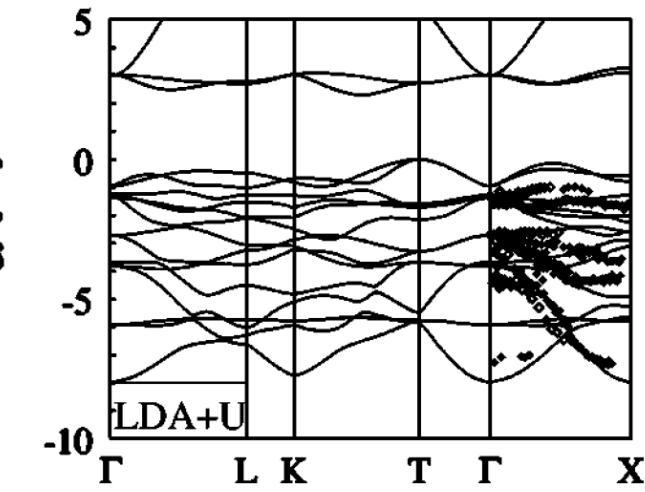
 Potential discontinuity re-established (and
inserted in the spectrum)

 A gap opens: $E_g \approx U$

LDA+U NiO



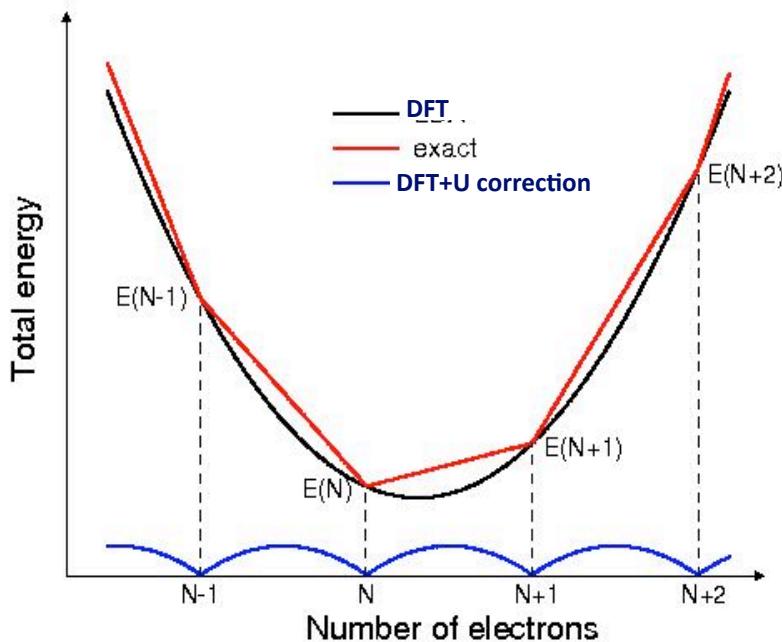
- ✓ Gap improves
- ✓ O *p* states on top of the valence band



M. Cococcioni and S. de Gironcoli, PRB 71, 035105 (2005)

The meaning of U in DFT+U

$$E_{exact} \approx E_{DFT} + \sum_I \frac{U^I}{2} \sum_{mm'\sigma} [n_{mm'}^{I\sigma}(\delta_{mm'} - n_{mm'}^{I\sigma})] = E_{DFT+U}$$



The (approximate) DFT energy has an *unphysical curvature*

The exact solution is *piecewise linear*
+U correction reproduces the exact solution

U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995); Dudarev, and coworkers PRB (1995)

LRT U: M. Cococcioni PhD (2002), and M. Cococcioni and S. de Gironcoli. PRB (2005)

$$U = \frac{d^2 E_{DFT}}{dn^2}$$

- **DFT+U.** In DFT+U a Hubbard-like term, accounting for strong Coulomb correlations in systems with highly localized, atomic-like states, is added to the XC functional:

$$E_{DFT+U}[n(\mathbf{r})] = E_{DFT}[n(\mathbf{r})] + E_U[n(\mathbf{r})].$$

In the simplified rotationally invariant method (S. L. Dudarev *et al.*, Phys.Rev. B, 57, 1505 (1998)), the Hubbard term has the form:

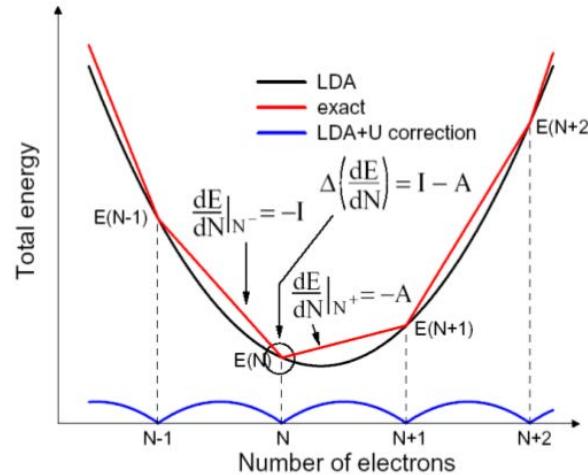
$$E_U[n(\mathbf{r})] = \frac{U}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma}(1 - \mathbf{n}^{\sigma})],$$

U being a (system-dependent) Coulomb repulsion (typically a few eV) and \mathbf{n}^{σ} is the matrix of orbital occupancies for a set of atomic-like states ϕ_m :

$$n_{mm'}^{\sigma} = \sum_{\sigma} \sum_i f_i^{\sigma} \langle \psi_i^{\sigma} | P_{mm'} | \psi_i^{\sigma} \rangle, \quad P_{mm'} = |\phi_m\rangle \langle \phi_{m'}|$$

There are several variants of DFT+U, with more parameters, and several possible choices of atomic-like states (simpler choice: atomic states, not orthogonalized)

DFT+U is a quick-and-dirty but economical solution for a deep problem of DFT: the lack of discontinuity in approximated functionals, due to incomplete self-interactions cancellation, favors fractionary occupancy. In the picture, the behavior of a system connected to a reservoir of electrons, as a function of the occupancy N .



U can be taken as an adjustable parameter, but the above picture suggests that U can be computed from first principles extracting it from the fictitious curvature of the XC functional:

$$U \equiv \frac{\partial^2 E_{DFT}}{\partial n^2}, \quad n = \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma}]$$

The procedure is described in detail in M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

DFT+U can dramatically improve our description of strongly correlated materials, with a modest computational overhead. It also improves band gaps and the level alignment in heterostructures.

- **Hybrid functionals**, such as B3LYP or PBE0, containing some amount of exact exchange, as in Hartree-Fock theory (spin-restricted case for simplicity):

$$E = T_s + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_H - \underbrace{\frac{e^2}{2} \sum_{i,j,\parallel} \int \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{E_x^{HF}}$$

In Hybrid DFT:

$$E = T_s + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} + E_H + \overbrace{\alpha_x E_x^{HF} + (1 - \alpha_x) E_x^{DFT} + E_c^{DFT}}^{E_{xc}^{hyb}},$$

with $\alpha_x = 20 \div 30\%$. This is the method of choice in Quantum Chemistry, yielding very accurate results and correcting most GGA errors, at the price of an additional parameter (the amount of exact exchange).

QUANTUM ESPRESSO implements most popular hybrid functionals: B3LYP, PBE0, HSE, gau-PBE, for NC-PPs and (with some restrictions) US-PPs. In a plane-wave basis set, however, hybrid functionals are computationally very heavy.

Exact Exchange Potential with Plane Waves

The calculation of $\hat{V}_x \psi_{\mathbf{k},v}$ proceeds as follows:

- bring bands to real space with FFT:

$$\psi_{\mathbf{k},v}(\mathbf{G}) \xrightarrow{\text{FFT}} \psi_{\mathbf{k},v}(\mathbf{r})$$

- for each wave-vector \mathbf{q} and each occupied band v' , build “charge densities” $\rho_{\mathbf{q}}(\mathbf{r})$:
$$\rho_{\mathbf{q}}(\mathbf{r}) = \psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}) \psi_{\mathbf{k},v}(\mathbf{r})$$

- bring “charge” to reciprocal space with FFT, solve Poisson equation:

$$\rho_{\mathbf{q}}(\mathbf{r}) \xrightarrow{\text{FFT}} \rho_{\mathbf{q}}(\mathbf{G}), \quad V_{\mathbf{q}}(\mathbf{G}) = \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} \rho_{\mathbf{q}}(\mathbf{G})$$

- FFT back to real space, multiply by occupied band at $\mathbf{k} - \mathbf{q}$ s, add to the result:
$$V_{\mathbf{q}}(\mathbf{G}) \xrightarrow{\text{FFT}} V_{\mathbf{q}}(\mathbf{r}), \quad (\hat{V}_x \psi_{\mathbf{k},v})(\mathbf{r}) = (\hat{V}_x \psi_{\mathbf{k},v})(\mathbf{r}) + V_{\mathbf{q}}(\mathbf{r}) \psi_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})$$

Practical algorithm

- For any given grid of N_k \mathbf{k} -points, you need to define a subgrid of $N_q \leq N_k$ \mathbf{q} -vectors. In principle it should span all \mathbf{k} -points, in practice it may be smaller.
- Self-consistency is first achieved with closest LDA/GGA functional; then V_x is turned on and a double self-consistency loop is started (self-consistency is reached at fixed V_x , V_x is updated with new wavefunctions, and so on)
- Scaling: rather catastrophic. $V_x\psi$ requires at least $\mathcal{O}(4N_k N_q M^2 N \log N)$ floating-point operations for M bands and N points in the FFT grid, vs $\mathcal{O}(2N_k MN \log N)$ for $V_{xc}\psi$ in plain DFT. Tricks for speeding up the calculation:
 - Use a reduced \mathbf{q} -vector grid (when applicable): variables `nqx1`,`nqx2`,`nqx3`
 - Use a reduced cutoff for FFT's done in V_x : variable `ecutfock`
 - Use many processors, with the “band” parallelization

Even with these tricks, hybrid functional calculations are soooo slow.

Simple Molecules

	HF			PBE			PBE0			EXP
	PW	G	PW	PAW	G	PW	PAW	G		
N_2	114	115	239	244	244	221	225	226	227	
O_2	36	33	139	143	144	121	124	125	118	
CO	173	175	265	269	269	252	255	256	261	

PAW : Paier,Hirschl,Marsman and Kresse, J. Chem. Phys. 122, 234102 (2005)

Energies in kcal/mol = 43.3 meV

van der Waals

van der Waals interaction is relatively weak but widespread in nature.

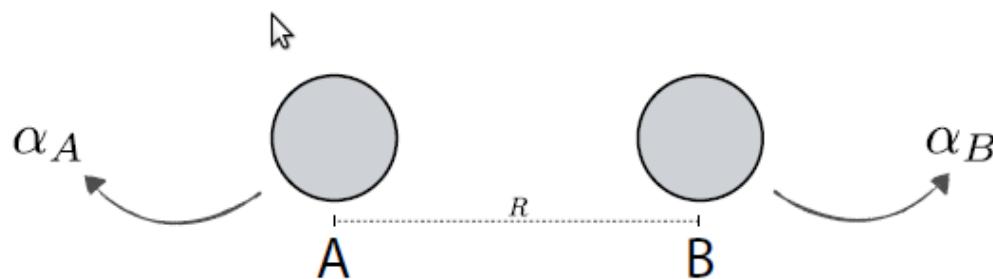
An important source of stability for molecular solids and physisorption of molecules on surfaces.



It is due to **truly non-local correlation** effects.

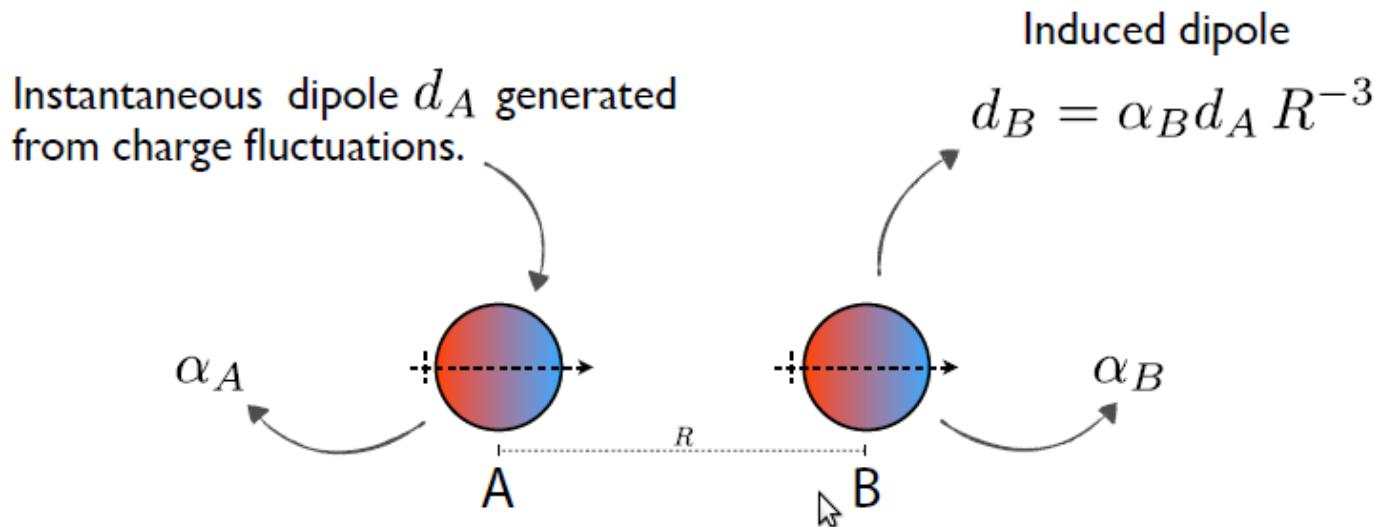
It is contained in the true XC functional but LDA/GGA/MetaGGA and Hybrids do not describe it properly.

vdW : non local correlation



Two neutral atoms separated by R much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

vdW : non local correlation



Two neutral atoms separated by R much larger than the atomic size, a limit that ensure that the corresponding wavefunctions are not overlapping

$$E = (K\hbar\omega_0\alpha_A\alpha_B) R^{-6}$$

LDA/GGA Semilocal Density Functionals

DFT within LDA and GGA functionals has been extremely successful in predicting structural, elastic, vibrational properties of materials bound by metallic, ionic, covalent bonds.

These functionals focus on the properties of the electron gas around **a single point in space**.

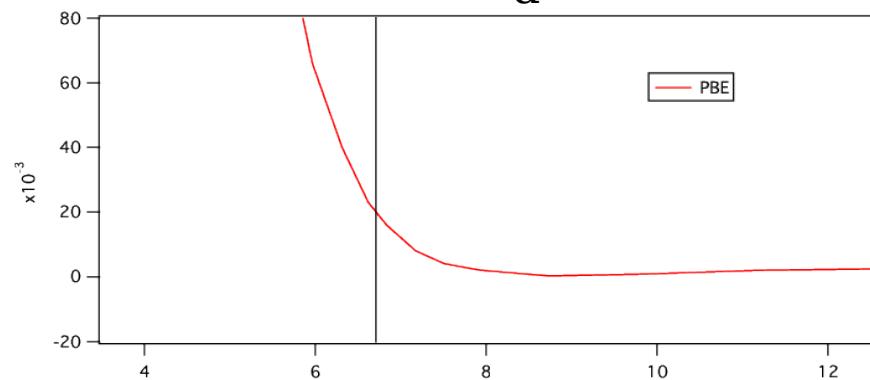
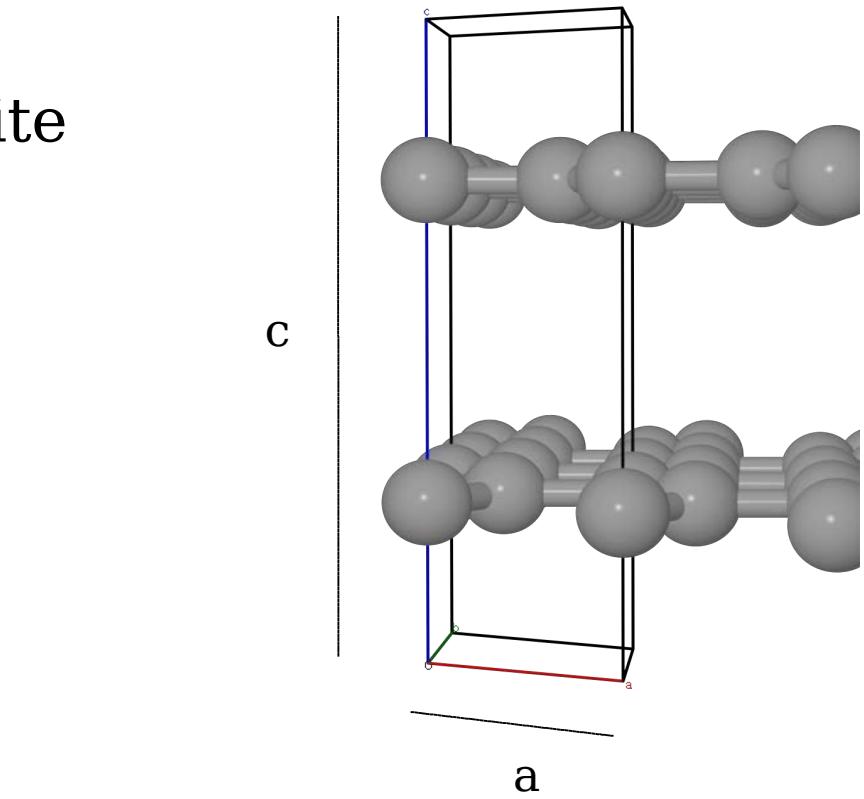
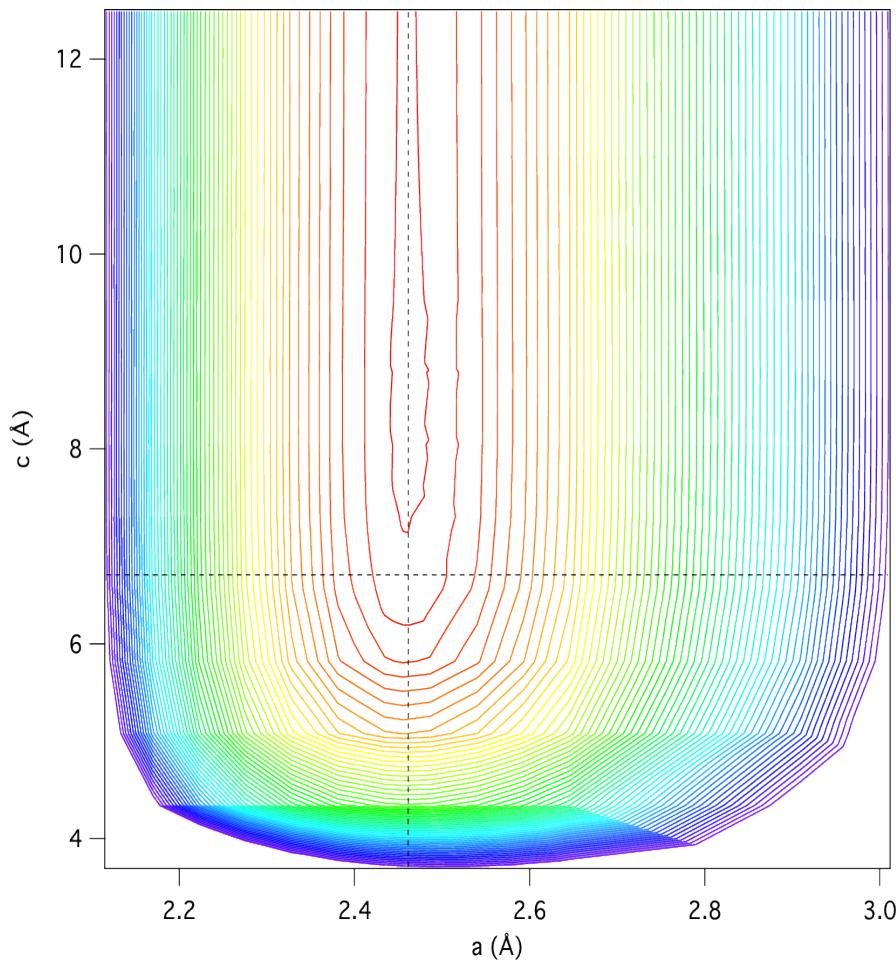
$$E_{xc}^{LDA} = \int n(r) \epsilon_{xc}^{hom}(n(r)) dr \quad E_{xc}^{GGA} = \int n(r) F_{xc}^{GGA}(n(r), |\nabla n(r)|) dr$$

As such they **do not describe** vdW interaction.

The same is true for Hybrids, DFT+U and SIC etc...

Failure of semilocal functionals

Graphite

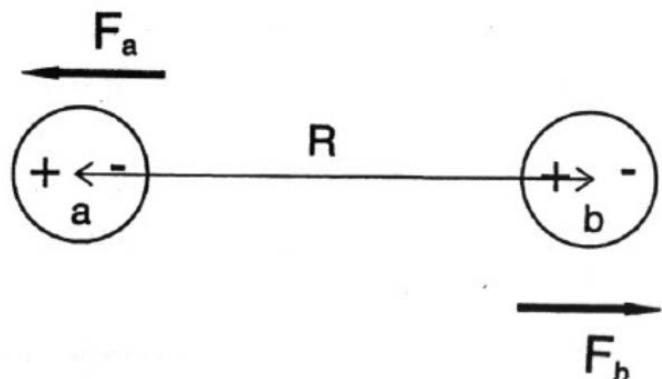


Functionals for weak (vdW) interactions

None of the above-mentioned functionals properly accounts for van der Waals (or “dispersive”) forces. No functional based on the local charge/gradients/kinetic energy and/or exact exchange can contain vdW interactions, whose nature is *nonlocal*

Possible solutions include:

- Ignore van der Waals interactions altogether! sometimes not possible, though
- Add them as a *semi-empirical* correction: very cheap, not very elegant, but often good enough for practical purposes
- Introduce a truly *non-local* functional: more elegant and more computationally demanding, but still feasible



Semi-empirical van der Waals interactions

- **DFT+D** (Grimme): the vdW energy term is added to plain GGA as a semi-empirical correction,

$$E_{DFT+D} = E_{DFT} + E_{vdW}, \quad E_{vdW} = -\frac{s_6}{2} \sum_{i \neq j} \frac{C_6^{ij}}{R_{ij}^6} f_{damp}(R_{ij})$$

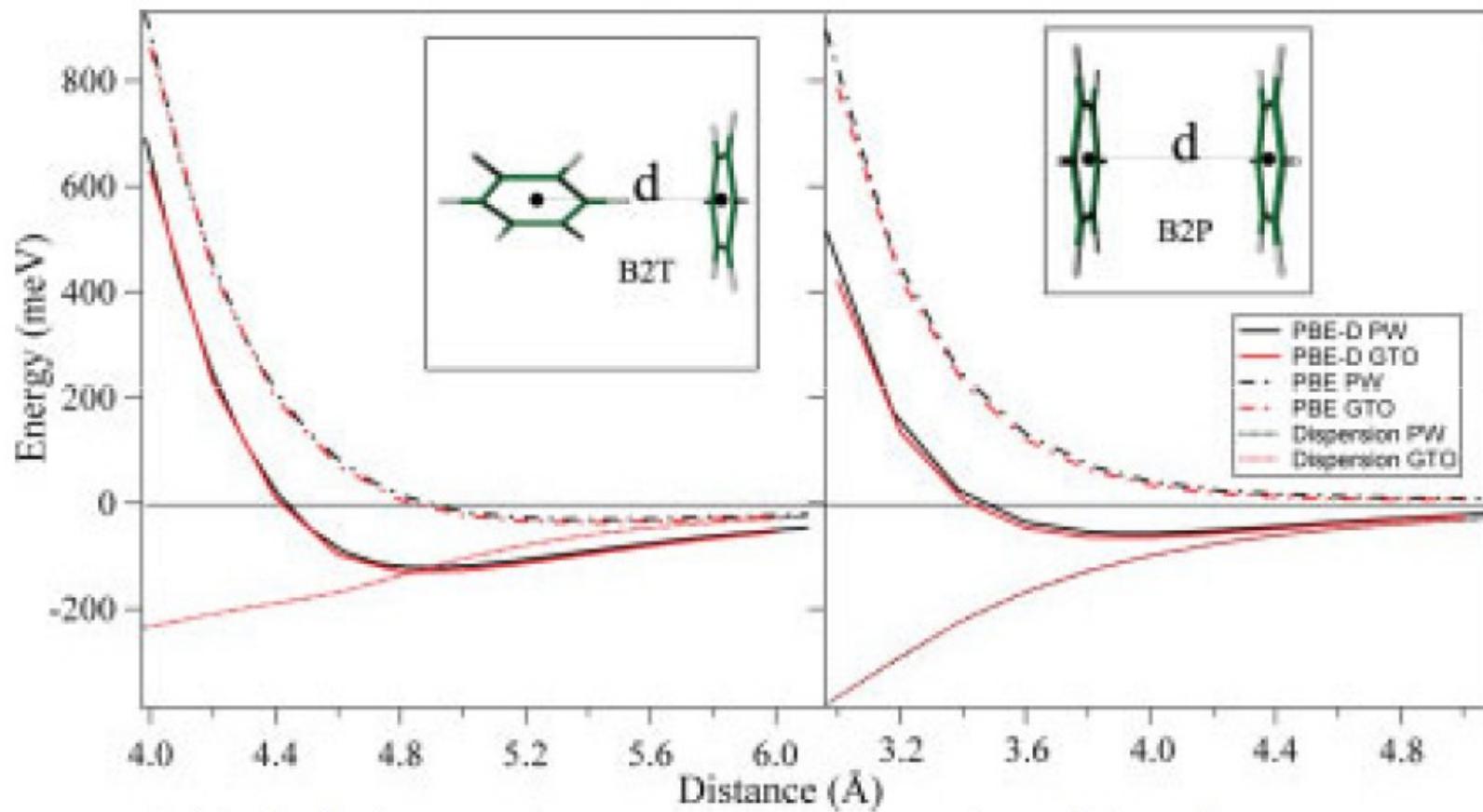
where s_6 is a global scaling factor depending upon the specific GGA;

$C_6^{ij} = \sqrt{C_6^{(i)} C_6^{(j)}}$ where $C_6^{(i)}$ are dispersion coefficients for the i -th atom;
a damping function

$$f_{damp}(R) = \frac{1}{1 + e^{-d(R/R_r - 1)}}$$

prevent singularities for $R \rightarrow 0$. Parameters are fitted to experimental or accurate theoretical data. Very cheap and simple, but hardly a first-principle approach.
QUANTUM ESPRESSO implements Grimme's DFT-D2.

- **Tkatchenko-Scheffler**: the C_6 coefficients are computed from first principles, that is, from the charge density. Recent versions of QUANTUM ESPRESSO implement this approach (not yet available for Ultrasoft PP and PAW).



$C_6H_6-C_6H_6$ interaction energy as a function of the distance between centers of mass: red (black) lines refer to Gaussian (PWscf) calculations. GTO results were not corrected for BSSE.

Nonlocal vdW functionals

Nonlocal functionals account for van der Waals (dispersive) forces:

$$E_{nl} = \frac{1}{2} \int n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad \Phi(\mathbf{r}, \mathbf{r}') \equiv \Phi(n(\mathbf{r}), \nabla n(\mathbf{r}), n(\mathbf{r}'), \nabla n(\mathbf{r}'), |\mathbf{r} - \mathbf{r}'|)$$

Can be computed with a reasonable computational overhead (Soler's technique) yielding generally good results, but often overestimating binding.

QUANTUM ESPRESSO implements several flavors of such functional, notably:
vdW-DF (Dion *et al.*, Thonhauser *et al.*), vdW-DF2 (Lee *et al.*),
revised VV10 (Sabatini *et al.*, Vydrov and van Voorhis)

For practical usage, the kernel Φ should be computed and stored in a file.

- vdW-DF, vdW-DF2: run auxiliary code `generate_vdW_kernel_table.x`, store file `vdW_kernel_table` in the directory where pseudopotentials (PP) are read from;
- rVV10: run auxiliary code `generate_rVV10_kernel_table.x`, store file `rVV10_kernel_table` in the same directory as above.

Truly non-local functionals

$$E^{(2)} = -\frac{3\hbar}{\pi} \int_0^\infty du \int_A dr \int_B dr' \frac{\alpha(r, iu)\alpha(r', iu)}{|r - r'|^6}$$

$$\overline{\alpha}(iu) = \int \alpha(r, iu)$$

$$u \rightarrow \infty : \overline{\alpha}(iu) = Ne^2/mu^2$$

$$\alpha(r, iu) = \frac{e^2}{m} \frac{n(r)}{\omega_0^2(r) + u^2}$$

$$E^{(2)} = -\frac{3\hbar e^4}{2m^2} \int dr \int dr' \frac{n(r)n(r')}{\omega_0(r)\omega_0(r')[\omega_0(r) + \omega_0(r')]|r - r'|^6}$$

$$E_c = E_c^0 + E_c^{nl}$$

$$E_c^{nl} = \frac{\hbar}{2} \int dr \int dr' n(r)\Phi(r, r')n(r')$$

**6 dim
integral !**

$$\Phi \rightarrow -\frac{3e^4}{2m^2} \frac{1}{\omega_0(r)\omega_0(r')[\omega_0(r) + \omega_0(r')]|r - r'|^6}$$

How to deal with van der Waals in DFT?

- develop a truly non local XC functional

$$E_c^{\text{nl}} = \frac{1}{2} \int d^3r d^3r' n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'),$$

$\Phi(n(r), \text{grad } n, n(r'), \text{ grad } n', |r-r'|)$

A number of functionals have been proposed

-vdw-DF : Dion et al, PRL **92**, 246401 (2006)

-vdW-DF2 : Lee et al, PRB **82**, 081101 (2010)

-VV09 : Vydrov and Van Voorhis, PRL **103**, 063004 (2009)

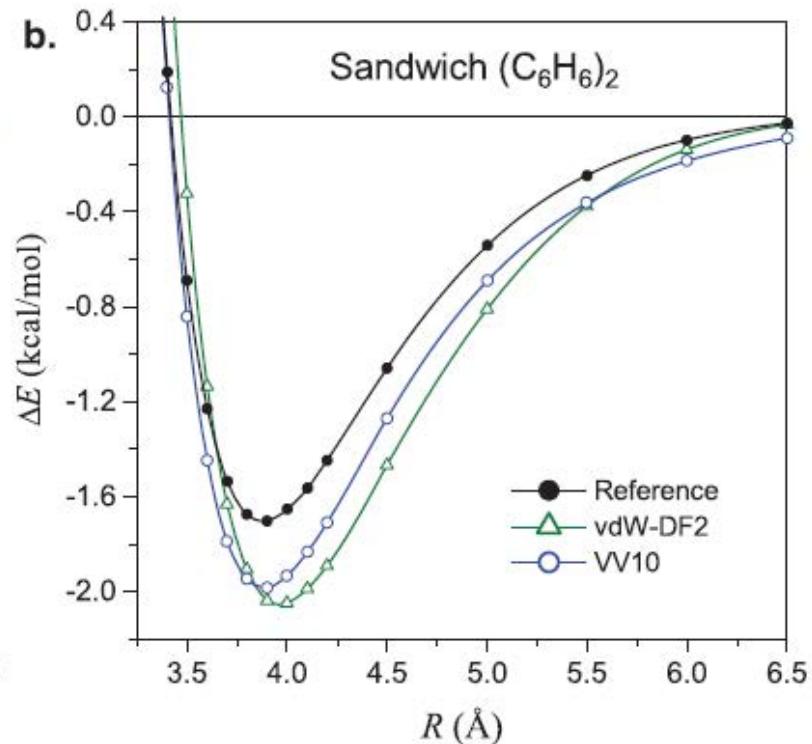
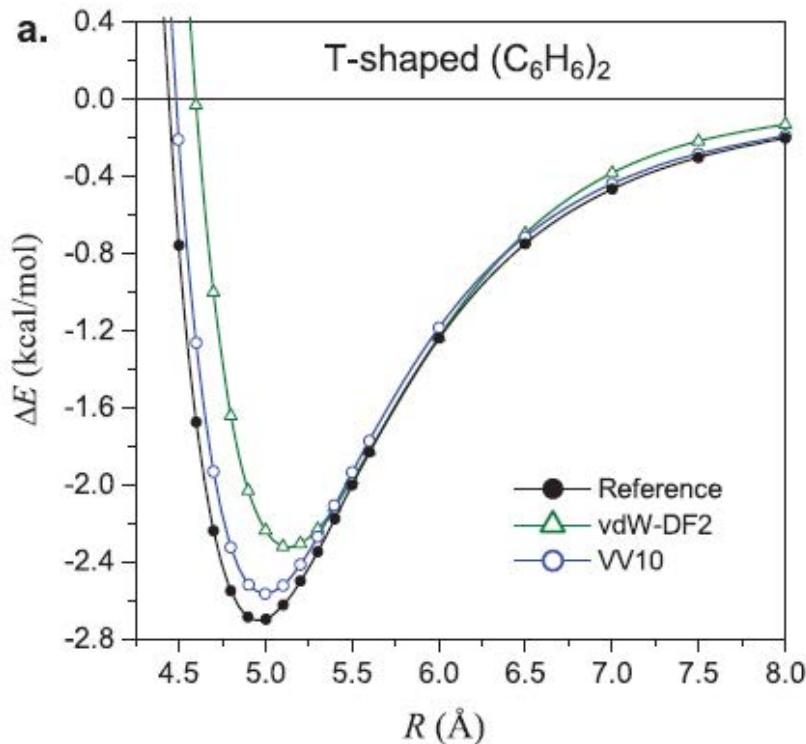
-VV10 : Vydrov and Van Voorhis, JCP **133**, 244103 (2010)

How to deal with van der Waals in DFT?

- develop a truly non local XC functional

$$E_{\text{c}}^{\text{nl}} = \frac{1}{2} \int d^3r d^3r' n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'),$$

Phi($n(r)$, grad n , $n(r')$, grad n' , $|r-r'|$)



How to compute efficiently van der Waals functionals ?

- for

$$E_c^{\text{nl}} = \frac{1}{2} \int d^3 r d^3 r' n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'),$$

$$\Phi(n(r), \text{grad } n, n(r'), \text{grad } n', |r-r'|)$$

If the kernel depends separately on densities and gradients in the two points the integral is a 6-dimesional object very expensive to calculate

How to compute efficiently van der Waals functionals ?

- for

$$E_c^{\text{nl}} = \frac{1}{2} \int d^3r d^3r' n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'),$$

$$\Phi(n(r), \text{grad } n, n(r'), \text{grad } n', |r-r'|)$$

If the kernel does not depend separately on the densities and gradient in the two points but only through a combined function $q(n(r), \text{grad } n)$ (true for vDW-DF/vdW-dF2)

$$\Phi(q(n(r), \text{grad } n), q(n(r'), \text{grad } n'), |r-r'|)$$

one can precalculate the value of the kernel for a number of Points in a 2D **q-grid** and interpolate in between

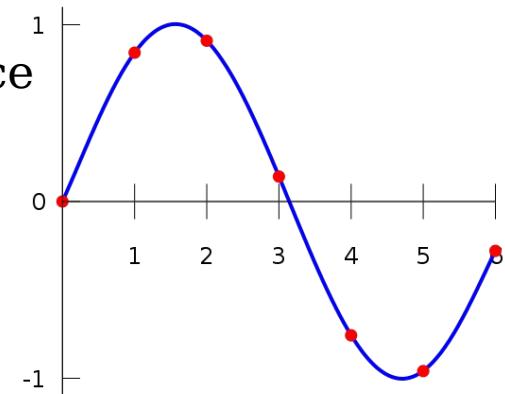
G. Roman-Perez & J.M. Soler, *PRL 103, 096102 (2009)*

an efficient integration

Roman-Perez & Soler interpolation scheme

If it's possible to express the complex density dependence on r, r' via a single $q(r)$ (and $q(r')$) function then ...

$$\Phi(q_1, q_2, r_{12}) \approx \sum_{\alpha, \beta} \Phi(q_\alpha, q_\beta, r_{12}) P_\alpha(q_1) P_\beta(q_2)$$



$$E_c^{nl} = \frac{1}{2} \sum_{\alpha, \beta} \int \int \Theta_\alpha(r) \Phi(q_\alpha, q_\beta, |r - r'|) \Theta_\beta(r') dr dr'$$

$$= \frac{\Omega}{2} \sum_{\alpha, \beta} \sum_G \Theta_\alpha^*(G) \Phi(q_\alpha, q_\beta, |G|) \Theta_\beta(G)$$

$$\Theta_\alpha(r) = n(r) P_\alpha(q(r))$$

The vdW energy can be expressed as a sum of a number of convolutions i.e. simple 3d integrals

The grid dimension determines the accuracy: 20 x 20 is ok

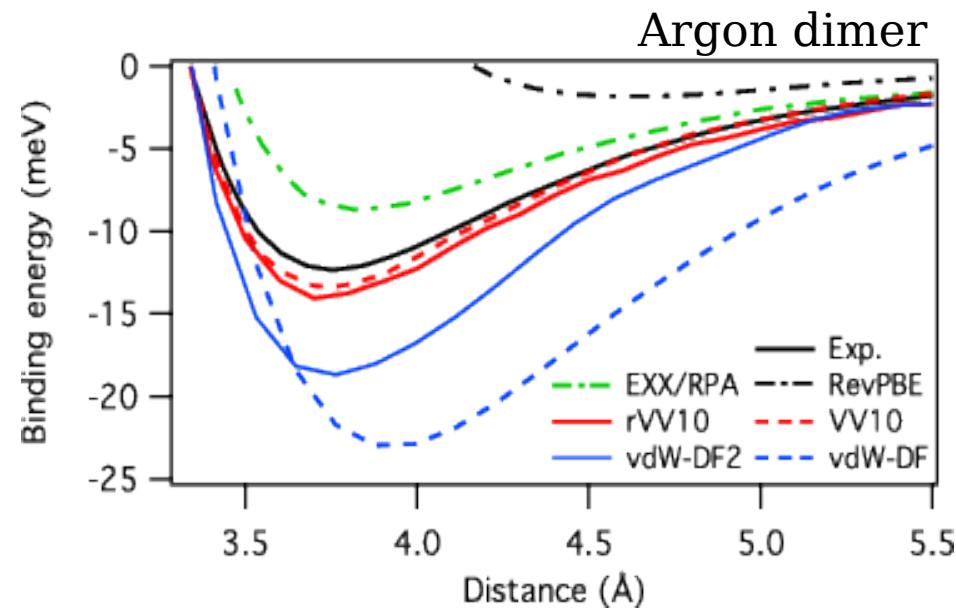
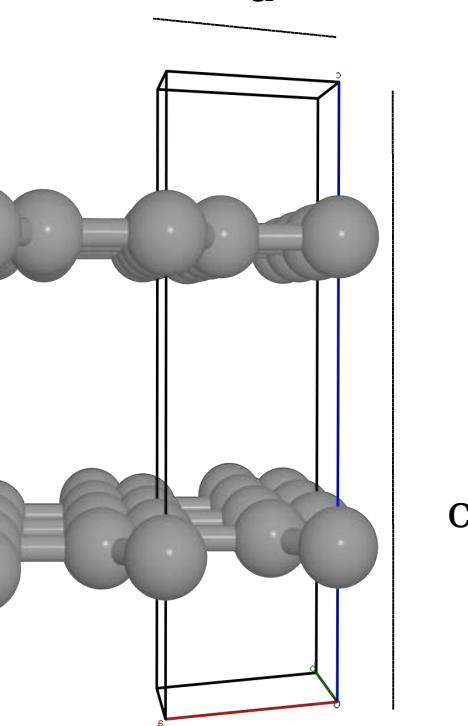
Several Non-Local Functionals

	ω_0 in $E_c^{(2)}$	$E_{xc}^{LDA/GGA}$	C_6 error
vdWDF	$\frac{9\hbar}{8\pi m} \left[k_F(1 + \mu s^2) \frac{4\pi}{3e^2} \varepsilon_c^{LDA} \right]$ with $\mu = 0.09434$	SLA+PW+RPBE-	18.5%
vdWDF2	$\frac{9\hbar}{8\pi m} \left[k_F(1 + \mu s^2) \frac{4\pi}{3e^2} \varepsilon_c^{LDA} \right]$ with $\mu = 0.20963$	SLA+PW+RPW86-	60.9%
vdWDF-09	$\frac{\hbar}{3m} k_F^2 (1 + \mu s^2)$ with $\mu = 0.22$	SLA+PW+RPBE-	10.4%
vv10	$\sqrt{\frac{\omega_p^2}{3} + C \frac{\hbar^2}{m^2} \left \frac{\nabla n}{n} \right ^4}$ with $C = 0.0089$	SLA+PW+RPW86+PBC	10.7%

vdWDF - functional can exploit the Roman-Perez Soler interpolation
 Vv10 - functional does not fulfill the needed conditions

rVV10 applications

Noble gas dimer are classical examples of dispersion dominated systems where the quality of different functionals can be explored.



Graphite cel parameters (Å)

	a	c
vdW-DF	2.48	7.19
vdW-DF2	2.47	7.06
rVV10	2.46	6.72
exp	2.46	6.71

Advanced exchange and correlation functionals

The accuracy of density functional theory depends crucially on the choice of the approximated functional for exchange and correlation

Advanced solutions:

- DFT+U
- Hybrid functionals
- van der Waals functionals