Introduction to Density Functional Theory

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Take-Home Message

As for any other QM-based method the important message to keep in mind is : Accuracy is less important than Pertinence...

Be aware of each method **strength** and **weakness** is crucial

- to choose the appropriate method for the system / property of interest
- not to over-interpret the (non exact) results

Schrödinger Equation (1926)

- Born-Oppenheimer approximation : $\hat{H}(r_i, R_\alpha) \equiv \hat{H}^{el}_{R_\alpha}(r_i)$

- Time-independent (non-relativistic) Schrödinger equation

$$\hat{H}^{el} \psi_n(x_1, x_2, \ldots, x_n) = E_n \psi_n(x_1, x_2, \ldots, x_n)$$

$$\hat{H}^{el} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i=1}^{n} \sum_{j>i} \frac{1}{r_{ij}}$$

- $\psi_n(x_1, x_2, \ldots, x_n)$: n-particles wave function $\qquad x_i = r_i(x_i, y_i, z_i) \otimes \sigma_i(\pm\frac{1}{2})$

- Electronic energy : functional of ψ_n

$$E_n[\psi_n] = \frac{\langle \psi_n(x_1, \ldots, x_n) \mid \hat{H}^{el} \mid \psi_n(x_1, \ldots, x_n) \rangle}{\langle \psi_n(x_1, \ldots, x_n) \mid \psi_n(x_1, \ldots, x_n) \rangle}$$

- ψ_n and $E_n[\psi_n] \longrightarrow$ all thermodynamic properties

How to Solve Schrödinger Equation?

- Mono-electronic approximation

  $\psi_n(x_1, \ldots, x_n)$: antisymmetrized product of mono-electronic functions ϕ_i (MOs)

  $$\psi_n(x_1, \ldots, x_n) \sim \mathcal{A} \prod_i^n \phi_i(x_i)$$

  $$\psi_n(x_1, x_2, \ldots, x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \ldots & \phi_n(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \ldots & \phi_n(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(x_n) & \phi_2(x_n) & \ldots & \phi_n(x_n) \end{vmatrix} = \mid \phi_1, \phi_3, \ldots, \phi_n \mid$$

- Mean-Field approximation

  $$\hat{H}^{el} = \sum_{i=1}^{n} \left(-\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \frac{1}{2}\sum_{j \neq i} \frac{1}{r_{ij}} \right) = \sum_{i=1}^{n} \left(\hat{h}_i + \frac{1}{2}\sum_{j \neq i} \hat{v}_{ij} \right) = \sum_{i=1}^{n} \hat{F}_i$$

  $\longrightarrow$ The Hartree-Fock method (1928 - 1930)

The Hartree-Fock method 1928-1930

$$H^{el} \;=\; \sum_{i=1}^{n} \left(\hat{h}_i + \frac{1}{2} \sum_{j \neq i} \hat{V}_{ij} \right) \;=\; \sum_{i=1}^{n} \left(\hat{h}_i + \frac{1}{2} \sum_{j \neq i} \left\{ \hat{J}_j - \hat{K}_j \right\} \right)$$

▷ Coulomb ($\hat{J}_j$) and Exchange ($\hat{K}_j$) space operators

$$\hat{J}_2 \; \phi_i(r_1) = \int \phi_j^*(r_2) \frac{1}{r_{12}} \phi_j(r_2) dr_2 \; \phi_i(r_1) \qquad J_{12} = \int \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{r_{12}} \phi_i(r_1) \phi_j(r_2) dr_2 dr_1$$

$$\hat{K}_2 \; \phi_i(r_1) = \int \phi_j^*(r_2) \frac{1}{r_{12}} \phi_i(r_2) dr_2 \; \phi_j(r_1) \qquad K_{12} = \int \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{r_{12}} \phi_j(r_1) \phi_i(r_2) dr_2 dr_1$$

▷ two-electron integrals : tough and time-consuming task !
▷ more important : action depends on the solution !
  → self-consistent solution (iterative procedure)

• Energy Decomposition

$$E_n^{HF}[\psi_n] = \sum_{i=1}^{n} \epsilon_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i} (J_{ij} - K_{ij})$$

Strength & Weakness of HF method(s)

- **Hartree-Fock solution**
  - ⊕ Truly *ab initio* : start from scratch
  - ⊕ Reasonable first-order solution
  - ⊖ Mono-electronic & <u>mono-determinantal</u> wf
  - ⊖ Electronic repulsions treated as "mean-field"
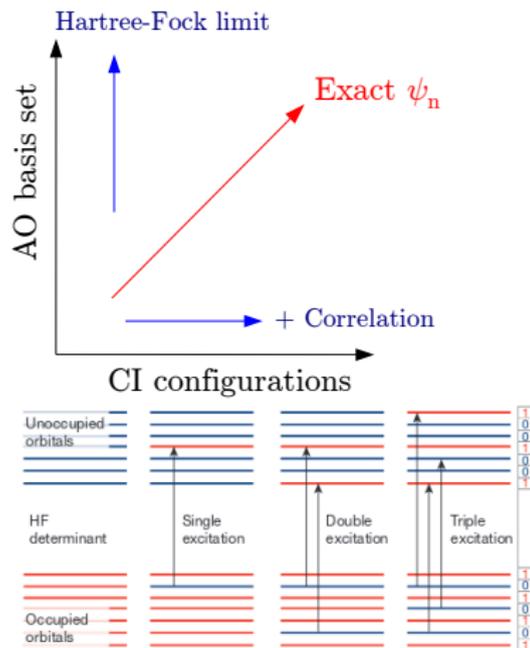
    ⟶ NO electron correlation ! ...almost no

- **Post-Hartree-Fock methods**

  Configuration Interaction (CI)

  $$\Psi_n^{ex}(x_1, x_2, \ldots, x_n) = \psi_n^{HF} + \sum_i C_i \psi_n^*$$

  with ψ_i^* : single-, di-, . . . excitations

  - ⊕ Correlated method $E_c = E^{ex} - E^{HF}$
  - ⊖ Restricted to "small" systems
    CPU-time increases in n^{5-7} (or even $n!$)
  - ⊖ No explicit CI procedure for solid state

Hartree-Fock limit

Exact ψ_n

AO basis set

+ Correlation

CI configurations

Main idea of DFT

Use the electron density $\rho(r) = \rho(\vec{r})$ as the basic variable, instead of the n-electron wave-function $\psi_n(x_1, \ldots, x_n)$

- The electron density is defined as :

$$\rho(r_1) = n \int \ldots \int \mid \psi_n(x_1, \ldots, x_n) \mid^2 d\sigma_1, dx_2, \ldots, dx_n$$

- It corresponds to the probability of finding one electron of arbitrary spin in the volume element dr around r_1 whatever is the position / spin of all other electrons.
- It is an observable that can be measured experimentally

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- It integrates to the total number of electrons $\int \rho(r) dr = n$.

- It vanishes at infinity : $\rho(r \longrightarrow \infty) = 0$

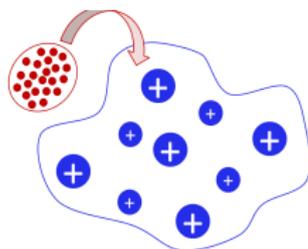- Its asymptotic exponential decay away from all nuclei is linked to the Ionization Potential

Hohenberg and Kohn (1964)

The GROUND-STATE properties of any system of *n*-interacting particles are rigourously deduced from the electron density distribution $\rho(r)$

- <u>Theorem HK1</u> There is a unique correspondence $v(r) \longleftrightarrow \rho(r)$

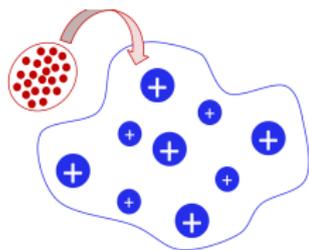$$\boxed{E_v[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho]}$$

$$\downarrow$$

Universal function ($T[\rho] + V_{ee}[\rho]$)

- <u>Theorem HK2</u> $\rho_{ex}(r)$ minimizes $E[\rho]$

$$\boxed{E_v[\rho] = \min_{\rho} \left\{ F_{HK}[\rho] + \int \rho(r)v(r) \right\}}$$

$$E[\rho] = \underbrace{\hat{T}[\rho] + \hat{V}_{ee}[\rho]}_{\downarrow} + \int v(r)\rho(r)dr$$

$$F_{HK}[\rho]$$

▷ Expression of $F_{HK}[\rho]$?

$$\langle \psi_n[\rho] \mid \hat{T} \mid \psi_n[\rho] \rangle = T[\rho]$$

$$\langle \psi_n[\rho] \mid \hat{V}_{ee} \mid \psi_n[\rho] \rangle = V_{ee}[\rho]$$

▷ Need a link between $\psi_n[\rho]$ and $\rho(\vec{r})$

Link between ψ_n and $\rho(\vec{r})$: the Density Operator $\hat{\gamma}_n$

$$\hat{\gamma}_n = \mid \psi_n(x_1, x_2, \ldots, x_n) \rangle \langle \psi_n(x'_1, x'_2, \ldots, x'_n) \mid$$

▷ Density matrix in the N-particles configurations space

$$\gamma_n = \psi_n(x_1, x_2, \ldots, x_n)\psi_n^*(x'_1, x'_2, \ldots, x'_n)$$

▷ 1-electron (1th-order) Reduced Density Matrix

$$\gamma_1(r_1; r'_1) = n \int \psi_n(x_1, x_2, \ldots, x_n)\psi_n^*(x'_1, x_2, \ldots, x_n)d\sigma_1, dx_2, \ldots, dx_n$$

$$\gamma_1(r_1; r_1) = n \int \mid \psi_n(x_1, x_2, \ldots, x_n) \mid^2 d\sigma_1, dx_2, \ldots, dx_n$$

$$\downarrow$$

Diagonal $\rho(r_1) = \rho_1(r_1)$: Probability to find one electron in r_1 with arbitrary spin σ_1

$$\boxed{\int \rho(r_1)dr_1 = n}$$

▷ 2-electron (2nd-order) Reduced Density Matrix:

$$\gamma_2(r_1, r_2; r_1', r_2') = \frac{n(n-1)}{2} \int \psi_n^*(x_1, x_2, \ldots, x_n)\psi_n(x_1', x_2', \ldots, x_n)d\sigma_1, d\sigma_2, dx_3, \ldots, dx_n$$

$$\gamma_2(r_1, r_2, r_1, r_2) = \frac{n(n-1)}{2} \int \mid \psi_n(x_1, x_2, \ldots, x_n) \mid^2 d\sigma_1, d\sigma_2, dx_3, \ldots, dx_n$$

$$\downarrow$$

Diagonal $\rho_2(r_1, r_2)$: Probability to find e-pair in r_1, r_2 with arbitrary spin σ_1, σ_2

$$\boxed{\int \int \rho_2(r_1, r_2)dr_1 \ dr_2 = \frac{1}{2}n(n-1)}$$

Energy Decomposition

$$E[\rho] = -\frac{1}{2} \int \left[\nabla^2 \gamma_1(r, r')\right]_{r=r'} dr \; + \; \int v(r)\rho(r)dr \; + \; \frac{1}{2} \int \int \frac{\rho_2(r, r')}{\mid r - r' \mid} dr \; dr'$$

$T[\rho]$ unknown $\qquad\qquad\qquad V_{ne}[\rho]$ known $\qquad\qquad\qquad V_{ee}[\rho]$ unknown

$\gamma_1(r, r')$ unknown $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \rho_2(r_1, r_2) \neq \rho_1(r_1)\rho_1(r_2)$!

We are still left with the many-body problem ...

We need a trick to solve this equation

Kohn-Sham Equations

- Use an auxiliary system of n <u>non-interacting</u> particles for which the kinetic energy is known

$$\psi_s(x_1, x_2, \ldots, x_n) = \mid \phi_1 \phi_2 \ldots \phi_n \mid \qquad \rho_s(\vec{r}) = \sum_{i=1}^{n} \mid \phi_i(\vec{r}) \mid^2$$

with $\phi_i(\vec{r})$ = Kohn-Sham orbitals (natural orbitals, occupancy $n_i = 1$ or 0)

$$\boxed{T_s[\rho] = \sum_{i=1}^{n} \langle \phi_i \mid -\frac{1}{2}\nabla_i^2 \mid \phi_i \rangle}$$

- The energy functional then writes:

$$E[\rho] = T_s[\rho] + (T[\rho] - T_s[\rho]) + \int v(\vec{r})\rho(\vec{r})dr + V_{ee}[\rho]$$

- The bielectronic part $V_{ee}[\rho]$

$$V_{ee}[\rho] \quad = \quad \frac{1}{2} \int \int \frac{\rho_2(r_1, r_2)}{\mid r_1 - r_2 \mid} dr_1 dr_2 = \frac{1}{2} \int \int \frac{\rho(r_1)\tilde{\rho}(r_2^{r_1})}{\mid r_1 - r_2 \mid} dr_1 dr_2$$

$\tilde{\rho}_1(r_2^{r_1}) =$ conditional probability ($e(2)$ in r_2 given that $e(1)$ in r_1)

- The exchange-correlation hole : hole created around $e(1)$ to avoid $e(2)$

$$\rho(r_1)\tilde{\rho}(r_2^{r_1}) \quad = \quad \rho(r_1)\left\{\rho(r_2) + \rho_2^{\text{hole}}(r_1, r_2)\right\}$$

$$V_{ee}[\rho] \quad = \quad J[\rho] + \epsilon_{xc}^{\text{hole}}[\rho]$$

Kohn-Sham Equations

$$E[\rho] = T_s[\rho] + \int v(r)\rho(r)dr + J[\rho] + \left\{ T[\rho] - T_s[\rho] + \epsilon_{xc}^{\text{hole}}[\rho] \right\}$$

$$\boxed{T_s[\rho] + \int v(r)\rho(r)dr + J[\rho] + E_{xc}[\rho]}$$

- The KS linear equations :

$$\hat{H}^{el}\psi_n(r_1; \ldots, r_n) = E_n\psi_n(r_1, \ldots, r_n)$$

$$\sum_{i=1}^{n} \left(\frac{1}{2}\nabla_i^2 + \underbrace{V_{\text{eff}}(r)}_{\downarrow} \right) \phi_i = \sum_{i=1}^{n} e_i\,\phi_i(r)$$

$$\boxed{V_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{\mid r - r' \mid}dr' + v_{xc}(r)}$$

$$\boxed{v_{xc}(r) = \frac{\partial E_{xc}[\rho]}{\partial \rho(r)}}$$

- Local potential !
- Contains correction to $T_s[\rho]$
- If exact $\rightarrow \rho^{ex}, E_{KS}^{ex}[\rho]$
- Exact shape unkown ... but <u>limits know</u>

Kohn-Sham Equations

- **Why Kohn-Sham equations so interesting?**
  - Knowledge $\psi_{GS}(x_1, x_2, \ldots, x_n)$ is not required : gain in computational time
  - "Similar" to Hartree-Fock mono-electronic equations
  - Contain <u>all electronic effects</u> (Kinetic, Coulomb, Exchange and Correlation)

$$\sum_{i=1}^{n} \left\{ -\frac{1}{2}\nabla_i^2 + V_{\text{eff}}(r) \right\} \phi_i(r) = \sum_{i=1}^{n} \epsilon_i \, \phi_i(r)$$

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Applied to the *n*-independent particle system

$$\Downarrow$$

Ground-State energy $E_{GS}^{ex}[\rho]$ and density ρ_{GS}^{ex}
of the *n*-interacting particle system

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Applied to the *n*-independent particle system

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Ground-State energy $E_{GS}^{ex}[\rho]$ and density ρ_{GS}^{ex}
of the *n*-interacting particle system

- Why Kohn-Sham equations not so interesting?
  - Introduce an auxiliary system which can be far from realistic
  - KS DFT is mono-determinantal !!
  - DFT is a Ground-State theory

Different flavors of energy functionals (non exhaustive list)

So far, different classes of energy functionals have been developed which mainly differ from the way the exchange-correlation energy accounts (or not) for the shape of the electron density

$$E_{xc}[\rho] = \int \epsilon_{xc}[\rho]\rho(r)dr \qquad\qquad \epsilon_{xc}[\rho] = f(\rho, \nabla\rho, \Delta\rho, \ldots)$$

- Local Density Approximation (LDA) $E^{LDA}[\rho]$
- Generalized Gradient Approximation (GGA) $E^{GGA}[\rho, \nabla\rho]$
- Meta Generalized Gradient Approximation (meta-GGA) $E^{mGGA}[\rho, \nabla\rho, \Delta\rho]$
  . . .

Other classes of energy functionals have been developed to correct (at least partially) the inherent errors of DFT functionals due to $V_{eff}(r)$ such as the *self-interaction*, *dispersion*, . . .

- Hybrids functionals (DFT+HF, range-separated)
- Self-Interaction corrected functionals (DFT+U, SIC, DFT+HF, range-separated)
- Dispersion corrected functionals (Grimme D2, D3, Tatchenko-Scheffler ...)

- **Local Density Approximation (LDA)**

  The exchange-correlation energy of a given particle located at r only depends on the electron density at this point. LDA assumes a spherical ρ^{hole} for exchange and correlation.

  $$E_{xc}^{LDA}[\rho] = \int \epsilon_{xc}^{LDA}[\rho]\rho(r)dr = \int \left(\epsilon_{x}^{LDA}[\rho] + \epsilon_{c}^{LDA}[\rho] \right) \rho(r)dr$$

Pure DFT functionals

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  - The analytical expression of the exchange energy comes from the Thomas-Fermi-Dirac model (homogeneous electron gas)

    $$\epsilon_{x}^{LDA}[\rho] = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(r)dr$$

  - The analytical expression of the correlation energy comes from an interpolation of quantum Monte Carlo calculations by Ceperley and Alder (the "Vosko-Wilk-Nusair" functional)

    $$\epsilon_{c}^{LDA}[\rho] = f(\rho)$$

E_c^{LDA} Just for fun ...

$$E_c^{LDA}[\rho] \quad \rightarrow \quad \epsilon_c^{VWN}[r_s] = \frac{A}{2} \left\{ ln \frac{x}{X(x)} + \frac{2b}{Q} tan^{-1} \frac{Q}{2x+b} \right.$$
$$\left. - \frac{bx_0}{X(x_0)} \left[ln \frac{(x-x_0)^2}{X(x_0)} + 2 \frac{(b+2x_0)}{Q} tan^{-1} \frac{Q}{2x+b} \right] \right\}$$

with r_s radius of the sphere defined by the effective volume occupied by an electron and

$$X(x) = x^2 + bx + c \qquad Q = (4c - b^2)^{1/2} \ldots \ldots$$

(meta) Generalized Gradients Approximation (GGA)

- **Introduction of density gradients**

  GGA functionals seek to improve LDA functionals by adding "non-local" properties of the electron density but still the exchange-correlation potential remains local $v_{xc}(r)$!!

$$E_x^{GGA} = E_x^{LDA} + f_{xc}[\rho, \nabla\rho]$$

$$E_x^{mGGA} = E_x^{LDA} + f_{xc}[\rho, \nabla\rho, \Delta\rho]$$

  f_{xc} either fitted on experimental results (wide series of molecules) or deduced from "more rational" results of full CI quantum mechanic calculations. Improvement of kinetic energy with meta-GGA ($\Delta\rho$)

- E_c^{GGA} much more difficult to express than E_x^{GGA}

  - BP and PBE
    Widely used in solid state chemistry/physics
  - Perdew-Wang 1991
    Known to better reproduce weak interactions
  - Lee-Yang-Par 1988
    In association with $E_x^{B3}[\rho]$ gives very good results in molecular systems

Limits of "local" DFT functionals

- **LDA**

  Suppose that $\rho(r)$ varies smoothly

  $\oplus$ Covalent and diamagnetic ionic solids with weak electron correlation (s, p-elements) and no Van der Waals interactions

  $\oplus$ Pretty good description of local properties and structures

  $\rightarrow$ relative errors wrt experiments generally less than $\pm 5 - 10\%$

  $\ominus$ Wrong near the nucleus but partial cancellation with $E_{cohesive}^{AB}$

  $\ominus$ Bad description of $E_{xc}[\rho]$ but partial error cancellation between E_x and E_c

  $\ominus$ Bad asymptotic behavior of $v_{xc}(\vec{r})$

  . . .

- **(metal)-GGA**

  Account for variations of $\rho(r)$

  $\oplus$ Iono-covalent solids with d or f elements with weak electron correlation and no Van der Waals interactions

  $\oplus$ Pretty good description of equilibrium structures even for correlated systems

  $\rightarrow$ relative errors wrt experiments generally less than $\pm 5\%$

  $\ominus$ Underestimated energy gaps in particular for strongly-correlated systems

  - Transition metal oxides are generally metals with GGA (oups ...) !

  - Bad reproduction of magnetic properties

  $\ominus$ Properties arising from the non locality of $V_{xc}[\rho]$ are generally not properly accounted / reproduced

  . . .

Beyond "local" DFT Functionals

- ## DFT+HF Hybrid functionals

  Hybrid functionals seek to improve GGA functionals by adding explicit non-local properties of the electron density through a mixing of E_x^{DFT} and E_x^{HF}

  $$E_{xc}^{Hyb} = a E_x^{DFT} + b E_x^{HF} + c E_c^{DFT}$$

$$
\begin{aligned}
E_{xc}^{B3LYP} &= E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) \\
&\quad + a_c(E_c^{GGA} - E_c^{LDA}) \\
E_x^{PBE0} &= \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_c^{PBE} \\
E_{xc}^{HSE06} &= \frac{1}{4} E_x^{HF,sr}(\mu) + \frac{3}{4} E_x^{PBE,sr}\mu) + E_x^{PBE,lr}(\mu) + E_c^{PBE}
\end{aligned}
$$
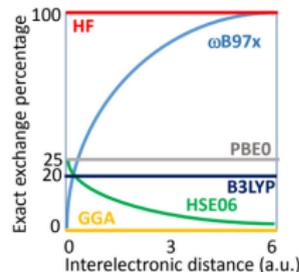
from Franck Rabilloud (https://sites.google.com/site/franckrabilloud/cours-hf-dft-tddft)

Beyond "local" DFT Functionals

- Limit of B3LYP

Why does the B3LYP hybrid functional fail for metals?

Joachim Paier, Martijn Marsman, and Georg Kresse

Faculty of Physics, Universität Wien and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Wien, Austria

The B3LYP hybrid functional has shown to successfully predict a wide range of molecular properties. For periodic systems, however, the failure to attain the exact homogeneous electron gas limit as well as the semiempirical construction turns out to be a major drawback of the functional. We rigorously assess the B3LYP functional for solids through calculations of lattice parameters, bulk moduli, and thermochemical properties (atomization energies and reaction energies). The theoretical lattice constants overestimate the experimental ones by approximately 1%, and hence behave similarly to the PBE gradient-corrected exchange-correlation functional. B3LYP atomization energies of solids are drastically worse than those of nonempirical hybrid Hartree-Fock/density functionals (HF/DFT) such as PBE0 and HSE03. These large errors can be traced back to the lack of a proper description of "free-electron-like" systems with a significant itinerant character (metals and small gap semiconductors). Similar calculations using the popular semiempirical B3PW91 hybrid functional, which fulfills the uniform electron gas limit, show a clear improvement over B3LYP regarding atomization energies. Finally, theoretical values for heats of formation for both the B3LYP as well as the B3PW91 functionals are presented. These document a most likely fortuitously good agreement with experiment for the B3LYP hybrid functional. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2747249]

- **DFT+U formalism**
  - Large self-interaction error for strongly correlated electrons (d and f)
  - Effective on-site correction added to the $3d$-orbitals $\rightarrow U_{eff} = U - J$ to penalize fractional/double occupancy of d, f-orbitals $\rightarrow$ high-spin configurations

$$E^{LDA+U}[\rho, \tilde{n}] = E^{LDA}[\rho] + E^{Hub}[\tilde{n}] - E_{dc}[\tilde{n}] = E^{LDA}[\rho] + E^{U_{eff}}[\tilde{n}]$$
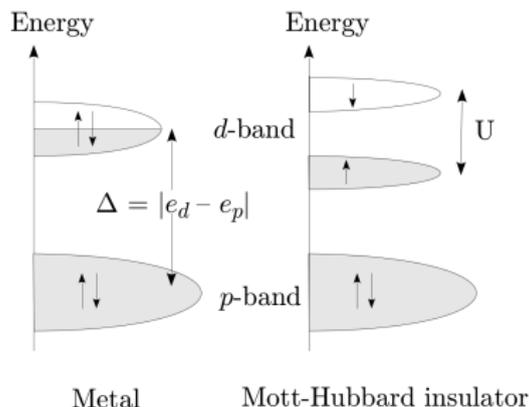
$$E_{dc}[\tilde{n}] = \frac{U-J}{2} Tr\tilde{n}\{Tr\tilde{n} - 1\}$$

$$E_{U_{eff}}[\tilde{n}] = \frac{U-J}{2} Tr\{\tilde{n}(1 - \tilde{n})\}$$

$\tilde{n}(1 - \tilde{n})$: deviation from idempotence

Metal   Mott-Hubbard insulator

Limits of "hybrid" functionals

- **DFT / HF**

  Introduce exact HF exchange

  - $\oplus$ Various flavors of hybrid functionals - Just play with them !
  - $\ominus$ All parameterized ! even those that are claimed to be "parameter-free" !
  - $\ominus$ Quite expensive compared to pure DFT functionals due to bi-electron integrals
  - $\oplus$ Generally much better than pure-DFT functionals for strongly correlated systems

- **DFT / Hubbard**

  Introduce the U_{eff} parameter

  - $\oplus$ Mainly used to correct energy gaps of transition metal oxides
  - $\ominus$ Also parameterized ! but with a physically meaningfull parameter
  - $\oplus$ As cheap as pure DFT functionals
  - $\oplus$ Generally much better than pure-DFT functionals for strongly correlated systems

Be careful about over-interpretation

- Density of States - Gaps
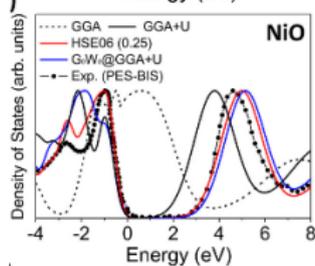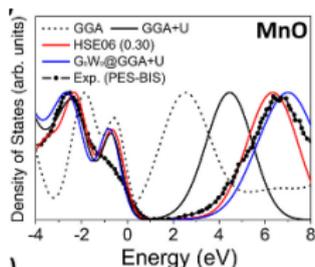
PRB 92, 115118 (2015)
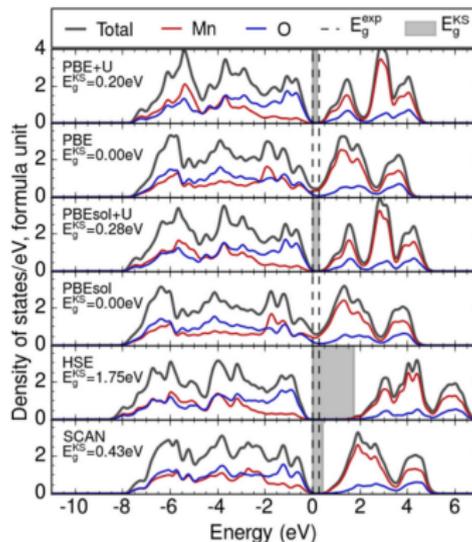
PRB 93, 045132 (2016)

Performances differ from one system to another...

Be careful about over-interpretation

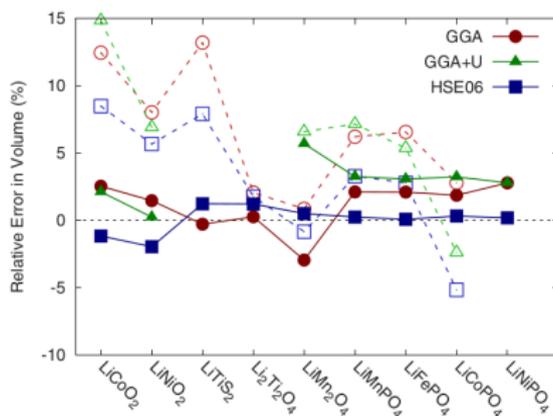- Density of States - Gaps KS or Δ !
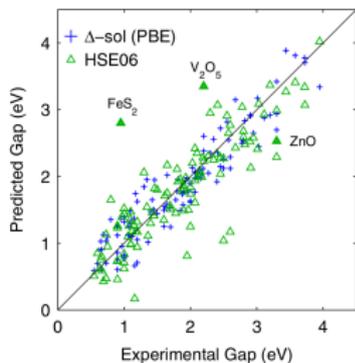
PRL 105, 196403 (2010)
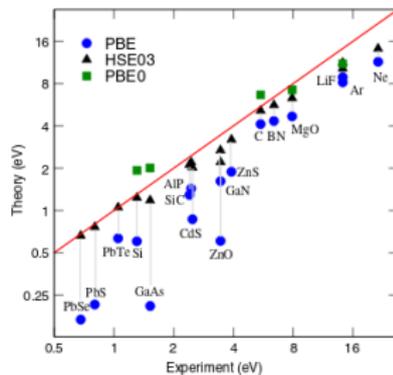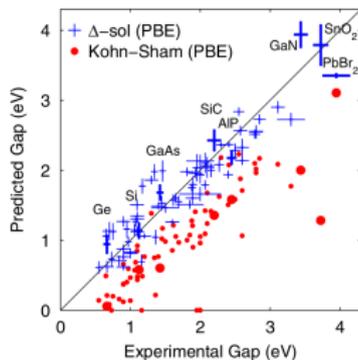
Kresse et al.

Results strongly depend on the way one computes energy band gaps !
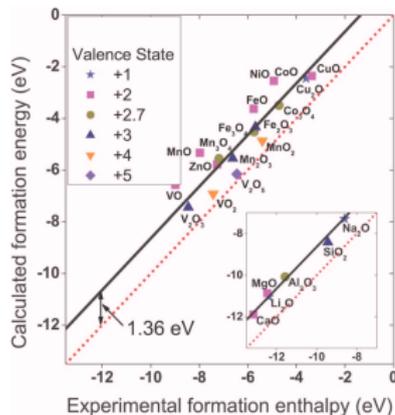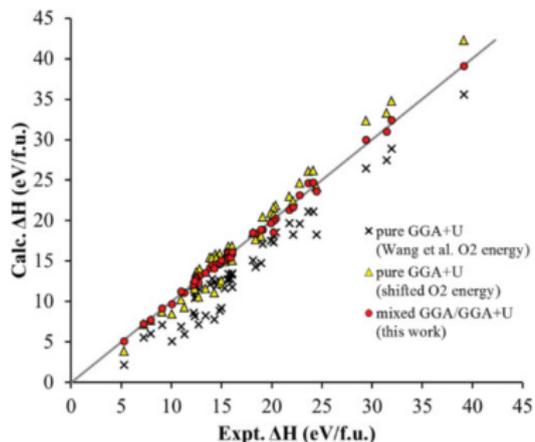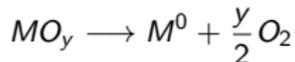
- Reaction enthalpies with DFT

$$MX + Li \longrightarrow LiMX \qquad V(x) = -\frac{1}{nF}\Delta_r G(x)$$

PRB 82, 075122 (2010)

Sometimes misleading to check the performance of XC-functionals on $\Delta_r G$ ...
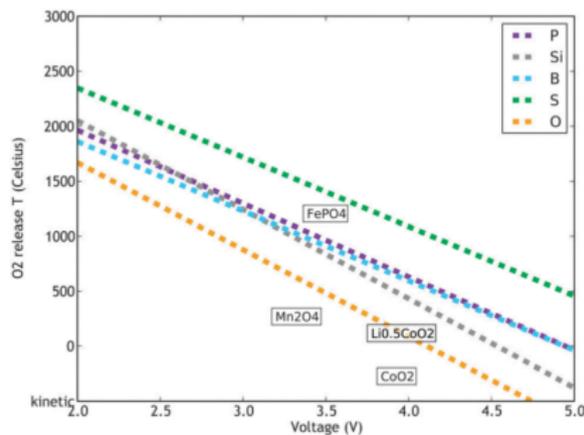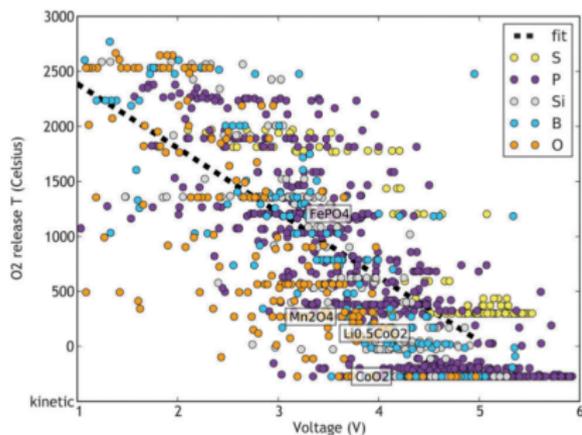
- Formation energies

$$MO_y \longrightarrow M^0 + \frac{y}{2}O_2$$

PRB 73, 195107-1-6 (2006)

Several successive approximations ...

- Average voltage calculations (Nernst)

$$V(x) = -\frac{1}{nF}\Delta_r G(x)$$

PCCP 17, 5942-5953 (2015)

Does one need so many calculations?...(see tomorrow)

Conclusion

- Never forget that DFT is a GROUND-STATE theory
  - Widely used in condensed matter
  - Numerically efficient (several hundreds of atoms/unit cell)
  - Quite accurate equilibrium properties

- Never forget that XF-functionals are not exact but non-local or parameterized ...
  - Check trends rather than seeking for absolute energies / properties
  - Compare DFT results with experiments ONLY IF they are comparable...

Never forget that low-energy properties of materials are mainly governed / dictated by crystal structures and local chemical bonding !

Interesting paper

Fig. 1 The historical trends in maximal deviation of the density produced by various DFT methods from the exact one.
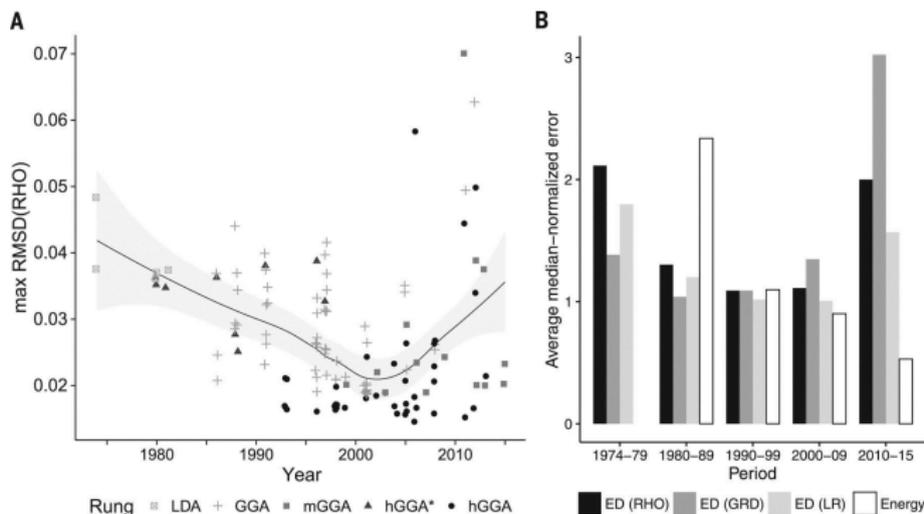
Michael G. Medvedev et al. Science 2017;355:49-52