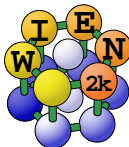


Methods available in WIEN2k for the treatment of the exchange and correlation effects

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WIEN2k Hands-On Workshop for New and Existing Users
8-19 April 2024
ICTP, Trieste, Italy



Outline of the talk

- ▶ Introduction to the DFT-(g)KS method
- ▶ (Semi)local functionals:
 - ▶ LDA
 - ▶ GGA
 - ▶ MGGA
 - ▶ Libxc
- ▶ Methods for van der Waals systems:
 - ▶ Atom-pairwise methods (e.g., DFT-D3)
 - ▶ Nonlocal functionals
- ▶ Potentials for band gaps:
 - ▶ (Local) modified Becke-Johnson
 - ▶ GLLB-SC
- ▶ On-site methods for strongly correlated d and f electrons:
 - ▶ DFT+ U
 - ▶ On-site hybrid functionals
- ▶ Hybrid functionals
- ▶ Recommendations

Total energy in Kohn-Sham DFT¹

$$E_{\text{tot}} = \underbrace{\frac{1}{2} \sum_i \int |\nabla \psi_i(\mathbf{r})|^2 d^3 r}_{T_s} + \underbrace{\frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r'}_{E_{ee}} + \underbrace{\int v_{\text{en}}(\mathbf{r})\rho(\mathbf{r}) d^3 r}_{E_{\text{en}}} + \underbrace{\frac{1}{2} \sum_{\substack{A,B \\ A \neq B}} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{E_{\text{nn}}} + E_{\text{xc}}$$

- ▶ T_s : kinetic energy of the non-interacting electrons
- ▶ E_{ee} : repulsive electron-electron electrostatic Coulomb energy
- ▶ E_{en} : attractive electron-nucleus electrostatic Coulomb energy
- ▶ E_{nn} : repulsive nucleus-nucleus electrostatic Coulomb energy
- ▶ $E_{\text{xc}} = E_x + E_c$: exchange (x) and correlation (c) energy

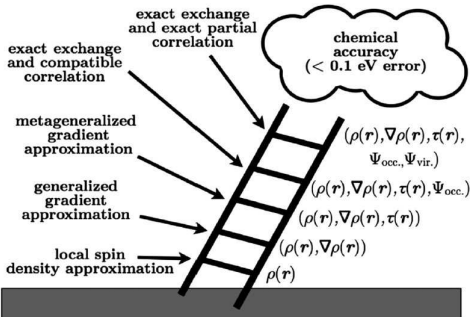
Approximations for E_{xc} have to be used in practice.
The reliability of the results depends mainly on E_{xc}

¹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

Approximations for E_{xc} (Jacob's ladder¹)

$$E_{xc} = \int \epsilon_{xc}(\mathbf{r}) d^3\mathbf{r}$$

The XC energy density ϵ_{xc} depends on various quantities (electron density $\rho = \sum_i |\psi_i|^2$, kinetic-energy density $\tau = \frac{1}{2} \sum_i |\nabla\psi_i|^2$)



When climbing up Jacob's ladder, the functionals are more and more

- ▶ accurate (in principle)
- ▶ mathematically sophisticated (complicated formulas)
- ▶ difficult to implement
- ▶ expensive to evaluate (time and memory)

¹J. P. Perdew *et al.*, J. Chem. Phys. **123**, 062201 (2005)

(Generalized) Kohn-Sham Schrödinger equations

Minimization of E_{tot} leads to

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ee}}(\mathbf{r}) + v_{\text{en}}(\mathbf{r}) + \hat{v}_{\text{xc}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Two types of exchange-correlation potentials \hat{v}_{xc} :

- ▶ Multiplicative (1st and 2nd rungs): $\hat{v}_{\text{xc}} = \delta E_{\text{xc}} / \delta \rho = v_{\text{xc}}$ (KS¹), simple to calculate and implement.
 - ▶ LDA
 - ▶ GGA
- ▶ Non-multiplicative (3rd and higher rungs): $\hat{v}_{\text{xc}} = (1/\psi_i)\delta E_{\text{xc}}/\delta\psi_i^* = v_{\text{xc},i}$ (generalized KS²), more complicated implementation.
 - ▶ MGGA
 - ▶ Hartree-Fock
 - ▶ Hybrid (mixing of GGA and Hartree-Fock)
 - ▶ LDA+ U
 - ▶ Self-interaction corrected (Perdew-Zunger)

¹ W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

² A. Seidl *et al.*, Phys. Rev. B **53**, 3764 (1996)

Local density approximation (LDA)

- ▶ LDA is the first and most simple approximation for the XC energy.¹
- ▶ The XC energy density is a function depending solely on the electron density.
 - ▶ Non-spin-polarized case:

$$\epsilon_{xc}^{\text{LDA}}(\mathbf{r}) = f(\rho(\mathbf{r}))$$

- ▶ Spin-polarized case:

$$\epsilon_{xc}^{\text{LDA}}(\mathbf{r}) = f(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}))$$

- ▶ The LDA was used until the beginning of the 90s, especially in solid-state physics. It has never really been used in chemistry.
- ▶ **The accuracy of LDA is in general quite bad.**

¹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

Semilocal functionals: GGA

- ▶ The first GGA functionals are from the mid 80s.¹
- ▶ They are usually expressed as

$$\epsilon_{\text{xc}}^{\text{GGA}}(\rho, \nabla\rho) = \epsilon_{\text{x}}^{\text{LDA}}(\rho)F_{\text{xc}}(r_s, s)$$

where F_{xc} is the **enhancement factor** and

$$r_s = \frac{1}{\left(\frac{4}{3}\pi\rho\right)^{1/3}} \quad (\text{Wigner-Seitz radius, related to } \rho)$$

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}} \quad (\text{reduced density gradient, related to } \nabla\rho)$$

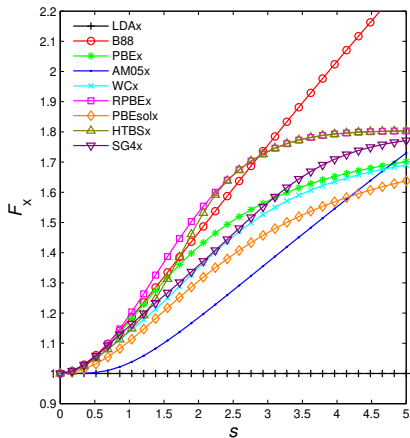
- ▶ Generally improve over LDA.

¹J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); A. D. Becke, J. Chem Phys. **84**, 4524 (1986)

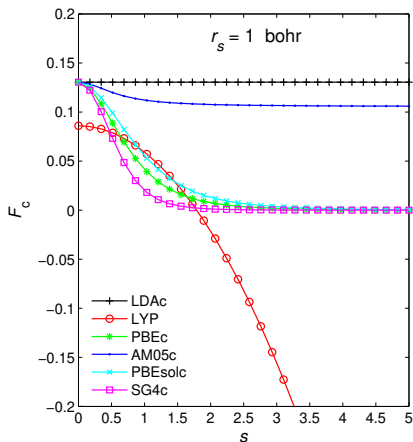
GGA: Comparison of enhancement factors

$$F_{xc}(\mathbf{r}) = \frac{\epsilon_{xc}^{GGA}(\mathbf{r})}{\epsilon_x^{LDA}(\mathbf{r})} = \frac{\epsilon_x^{GGA}(\mathbf{r}) + \epsilon_c^{GGA}(\mathbf{r})}{\epsilon_x^{LDA}(\mathbf{r})} = \underbrace{\frac{\epsilon_x^{GGA}(\mathbf{r})}{\epsilon_x^{LDA}(\mathbf{r})}}_{F_x(\mathbf{r})} + \underbrace{\frac{\epsilon_c^{GGA}(\mathbf{r})}{\epsilon_x^{LDA}(\mathbf{r})}}_{F_c(\mathbf{r})} = F_x(\mathbf{r}) + F_c(\mathbf{r})$$

F_x corrects for the too small magnitude of LDA exchange

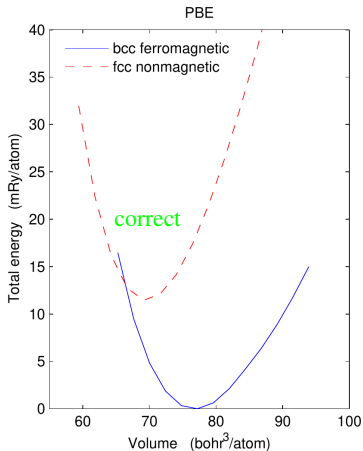
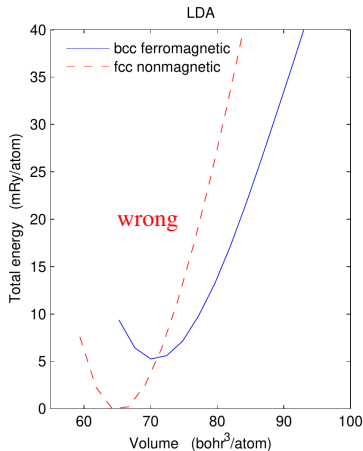


F_c corrects for the too large magnitude of LDA correlation



GGA: The historical success for solid iron (1990)

- ▶ From experiment the ground state of Fe is known to be bcc ferromagnetic
- ▶ LDA wrongly gives fcc nonmagnetic as the ground state
- ▶ GGA (e.g. PW91 or PBE) provides the correct answer¹



¹B. Barbiellini, E. G. Moroni, and T. Jarlborg, *J. Phys.: Condens. Matter* **2**, 7597 (1990)

Illustration of the limit of GGA

Mean absolute error for molecular properties¹

	Atomization energy ^a	Barrier height ^b
LDA	83.7	15.4
PBEsol (worst GGA)	58.8	11.5
PBE	22.2	9.2
BLYP (best GGA)	9.5	7.9

^a 223 molecules. Values in kcal/mol.

^b 76 chemical reactions. Values in kcal/mol.

Mean absolute error for solid-state properties²

	Lattice constant ^a	Bulk modulus ^b
LDA	0.071	11.5
PBEsol (best GGA)	0.030	7.8
PBE	0.061	12.2
BLYP (worst GGA)	0.120	25.2

^a 44 solids. Values in Å.

^b 44 solids. Values in GPa.

No GGA exists that is good for molecular properties and solid-state properties at the same time

¹ J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015)

² F. Tran, J. Stelzl, and P. Blaha, J. Chem. Phys. **144**, 204120 (2016)

Semilocal functionals: MGGA

- ▶ Started to appear in the mid 90s³:
- ▶ Dependency on the kinetic-energy density $\tau = \frac{1}{2} \sum_i |\nabla\psi_i|^2$:

$$\epsilon_{\text{xc}}^{\text{MGGA}}(\rho, \nabla\rho, \tau) = \epsilon_{\text{x}}^{\text{LDA}}(\rho) F_{\text{xc}}(r_s, s, \alpha)$$

- ▶ $\alpha = \frac{\tau - \tau_{\text{W}}}{\tau_{\text{TF}}}$
 - ▶ $\alpha = 1$ (region of constant electron density)
 - ▶ $\alpha \approx 0$ (in one- and two-electron regions very close and very far from nuclei)
 - ▶ $\alpha \gg 1$ (region between closed shell atoms)
- ▶ Thanks to their dependency on τ , MGGA functionals are more flexible than GGAs
- ▶ Example: **SCAN**¹ is currently the most used MGGA
 - ▶ as good as the best GGA for the atomization energy of molecules
 - ▶ as good as the best GGA for the lattice constant of solids

³T. Van Voorhis and G. E. Scuseria, *J. Chem. Phys.* **109**, 400 (1998)

¹J. Sun *et al.*, *Phys. Rev. Lett.* **115**, 036402 (2015)

MGGA functionals: more broadly accurate than GGA

Mean absolute error for molecular properties¹

	Atomization energy ^a	Barrier height ^b
LDA	83.7	15.4
PBESol (worst GGA)	58.8	11.5
PBE	22.2	9.2
BLYP (best GGA)	9.5	7.9
SCAN	5.7	7.7

^a223 molecules. Values in kcal/mol.

^b76 chemical reactions. Values in kcal/mol.

Mean absolute error for solid-state properties²

	Lattice constant ^a	Bulk modulus ^b
LDA	0.071	11.5
PBESol (best GGA)	0.030	7.8
PBE	0.061	12.2
BLYP (worst GGA)	0.120	25.2
SCAN	0.030	7.4

^a44 solids. Values in Å.

^b44 solids. Values in GPa.

MGGA can be good for molecular properties and solid-state properties at the same time

¹J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015)

²F. Tran, J. Stelzl, and P. Blaha, J. Chem. Phys. **144**, 204120 (2016)

MGGA functionals: Lattice constant, cohesive energy and band gap

- ▶ Can a MGGA functional be accurate for the **lattice constant**, **cohesive energy** and **band gap**?
- ▶ We recently tried to answer this question by training the following exchange functional form¹

$$F_x = \frac{\sum_{i=0}^N \sum_{j=0}^{N-i} c_{ij} p^i t^j}{\sum_{i=0}^N \sum_{j=0}^{N-i} d_{ij} p^i t^j} \quad \left(p \propto \frac{|\nabla\rho|^2}{\rho^{8/3}}, t \propto \frac{\tau}{\rho^{5/3}} \right)$$

- ▶ $N = 2$ was chosen, leading to 11 independent empirical parameters c_{ij} and d_{ij} . SCAN for correlation.
- ▶ mGGA23 and mGGA23' have well-balanced accuracy:

	Lattice constant ^a	Cohesive energy ^b	Band gap ^c
PBE	0.06	0.19	1.10
SCAN	0.03	0.19	0.76
mGGA23	0.03	0.22	0.63
mGGA23'	0.06	0.36	0.54
TASK ²	0.23	1.34	0.54

^a 44 solids. Values in Å.

^b 44 solids. Values in eV/atom.

^c 440 solids. Values in eV.

It is possible to construct a MGGA that is reasonably accurate for the three properties

¹ P. Kovács, F. Tran, P. Blaha, and G. K. H. Madsen, J. Chem. Phys. **157**, 094110 (2022)

² T. Aschebrock and S. Kümmel, Phys. Rev. Res. **1**, 033082 (2019)

Libxc: a library of exchange-correlation and kinetic energy functionals¹

- ▶ External library of basically all existing semilocal (LDA, GGA and MGGA) functionals
- ▶ Number of exchange-correlation functionals in Libxc version 6.2.2 (latest version):
 - ▶ LDA: 65
 - ▶ GGA: 315
 - ▶ MGGA: 210
- ▶ Calculates the XC energy density and derivatives
- ▶ Written in C, but with Fortran and Python bindings
- ▶ Supported by 41 DFT codes (WIEN2k is among them)
- ▶ Installation in WIEN2k: `LIBXCROOT` (in the Makefile in `SRC_lapw0`) is the path to the Libxc installation

¹M. A. L. Marques *et al.*, *Comput. Phys. Commun.* **183**, 2272 (2012); S. Lehtola *et al.*, *SoftwareX* **7**, 1 (2018); <https://libxc.gitlab.io>

Some facts about GGA and MGGA functionals

- ▶ About 300 GGA and 200 MGGA functionals exist.¹ This is a real jungle!
- ▶ They can be divided into two categories:
 - ▶ **Empirical**: parameters fitted to accurate (i.e., experimental) data
 - ▶ **Ab initio (i.e., from first-principles)**: all parameters were determined such that known mathematical conditions are obeyed (e.g., PBE or SCAN)
- ▶ Computational speed:
 - ▶ GGA is barely slower than LDA
 - ▶ MGGA is slower than GGA, but moderately
 - ▶ It may be more difficult to achieve self-consistency with MGGA
 - ▶ **LDA, GGA and MGGA are clearly (much) faster than more advanced methods like hybrid or GW**
- ▶ GGA and MGGA are widely used for total energy calculation (i.e., geometry), especially in solid-state physics

¹<https://libxc.gitlab.io/functionals>

Input file case.in0: keywords for the xc-functional

The functional is specified at the 1st line of **case.in0**. Three different ways:

1. Specify a global keyword for E_x , E_c , v_x , v_c :
 - ▶ TOT *XC_NAME*
2. Specify a keyword for E_x , E_c , v_x , v_c individually:
 - ▶ TOT *EX_NAME1 EC_NAME2 VX_NAME3 VC_NAME4*
3. Specify keywords to use functionals from **Libxc**:
 - ▶ TOT *XC_TYPE_X_NAME1 XC_TYPE_C_NAME2*
 - ▶ TOT *XC_TYPE_XC_NAME*

where *TYPE* is the family name: **LDA**, **GGA** or **MGGA**

Input file case.in0: examples

▶ PBE:

TOT XC_PBE

or

TOT EX_PBE EC_PBE VX_PBE VC_PBE

or (Libxc keyword)

TOT XC_GGA_X_PBE XC_GGA_C_PBE

▶ MGGA_MS2:

TOT XC_MGGA_MS 0.504 0.14601 4.0
 κ, c, b

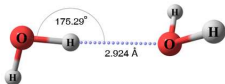
All available functionals are listed in tables of the user's guide and in `$WIENROOT/SRC_lapw0/xc_funcs.h` (or on the Libxc website¹) for **Libxc**

¹<https://libxc.gitlab.io/functionals>

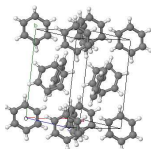
van der Waals systems

A system (dimer, molecular complex, solid) is called a van der Waals system if the cohesion is essentially due to weak interactions (e.g., dispersion) and not by covalent or ionic bonds.

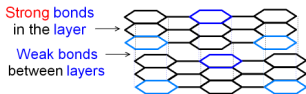
- ▶ van der Waals bonds are much weaker ($\sim 10^{-5} - 30$ kcal/mol) than covalent or ionic bonds ($\sim 50 - 250$ kcal/mol)
- ▶ van der Waals interactions are of several types: Pauli repulsion (repulsive), electrostatic (attractive or repulsive), induction (attractive), **dispersion (attractive and always present)**



water dimer
binding energy ~ 4 kcal/mol



benzene crystal
lattice energy ~ 10 kcal/mol



graphite
interlayer binding energy ~ 1 kcal/mol/atom

The semilocal and hybrid functionals do not account for the dispersion forces \implies these approximations are very unreliable for van der Waals systems. This was one of the most important problems in DFT until the middle of the 2000s.

Approximations for E_{xc} specific for van der Waals systems

The solution to remedy the problem of semilocal/hybrid methods for van der Waals is to add a term that is specific (\sim contains the physics) for the dispersion interactions:

$$E_{xc} = E_{xc}^{\text{semilocal/hybrid}} + E_{c,\text{disp}}$$

Two types of dispersion terms have been proposed:

- ▶ Atom-pairwise (computationally cheap)¹:

$$E_{c,\text{disp}}^{\text{PW}} = - \sum_{A < B} \sum_{n=6,8,10,\dots} f_n^{\text{damp}}(R_{AB}) \frac{C_n^{AB}}{R_{AB}^n}$$

R_{AB} is the distance between atoms A and B , C_n^{AB} are dispersion coefficients and f_n^{damp} is a damping function that prevents too large values of the energy when $R_{AB} \rightarrow 0$.

- ▶ Nonlocal (slightly expensive because of the double integral)²:

$$E_{c,\text{disp}}^{\text{NL}} = \frac{1}{2} \int \int \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d^3r d^3r'$$

Φ is a kernel which depends on ρ , $\nabla\rho$ and $|\mathbf{r} - \mathbf{r}'|$.

¹ S. Grimme, *J. Comput. Chem.* **25**, 1463 (2004)

² M. Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004)

DFT-D3: the most popular atom-pairwise method¹

► Features:

- Computationally cheap. Add little time.
- C_n^{AB} depend on positions of the nuclei (via coordination number)
- Energy, forces and stress tensor
- 3-body term available (can be important for solids)

► Installation for WIEN2k:

- Not included in WIEN2k
- Download and compile the DFTD3 package.² Then, copy the `dftd3` executable in `$WIENROOT`

► Usage:

- Input file `case.indftd3` (if not present a default one is copied automatically by `x.lapw`)
- `run_lapw -dftd3 ...`
- `case.scfdftd3` is included in `case.scf`

¹ S. Grimme *et al.*, *J. Chem. Phys.* **132**, 154104 (2010)

² <https://www.chemie.uni-bonn.de/grimme/de/software/dft-d3>

DFT-D3: input file case.indftd3

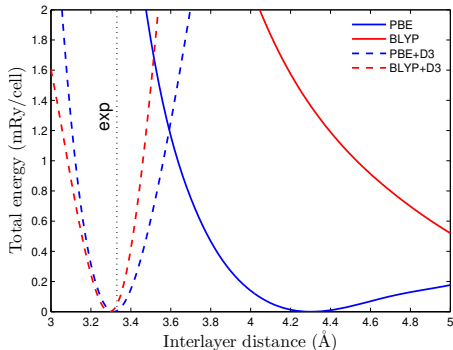
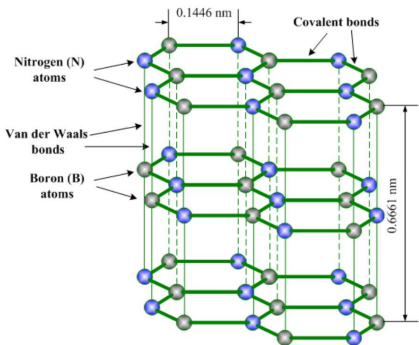
Default (and recommended) input file:

<code>method</code>	<code>bj</code>	damping function f_n^{damp}
<code>func</code>	<code>default</code>	the one in case.in0*
<code>grad</code>	<code>yes</code>	forces
<code>pbcc</code>	<code>yes</code>	periodic boundary conditions
<code>abc</code>	<code>yes</code>	3-body term
<code>cutoff</code>	<code>95</code>	interaction cutoff
<code>cnthr</code>	<code>40</code>	coordination number cutoff
<code>num</code>	<code>no</code>	numerical gradient

* `default` will work for PBE, PBEsol, BLYP and TPSS. For other functionals, the functional name has to be specified (see `dftd3.f` of DFTD3 package)

DFTD-D3: application to hexagonal boron nitride

The GGA BLYP and PBE lead to too large interlayer distance and (nearly) no interlayer bonding
Adding the atom-pairwise correction D3 leads to good agreement with experiment



Interlayer binding energy (in meV/atom):

Experiment	40
PBE	2
BLYP	No binding
PBE-D3	41
BLYP-D3	58

Nonlocal vdW functionals

$$E_{c,\text{disp}}^{\text{NL}} = \frac{1}{2} \int \int \rho(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d^3 r d^3 r'$$

Families of kernels Φ proposed in the literature:

- ▶ **DRSLL**¹, **LMKLL**²:
 - ▶ Derived from (adiabatic-connection-fluctuation-dissipation theorem) ACFDT
 - ▶ Parameter: Z_{ab}
- ▶ **VV10**³, **rVV10**⁴, **rVV10L**⁵:
 - ▶ Parameters: b and C
- ▶ **vdW-DF3-opt1/vdW-DF3-opt2**⁶:
 - ▶ Parameters: α and γ

¹ M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004)

² K. Lee *et al.*, Phys. Rev. B **82**, 081101(R) (2010)

³ O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. **133**, 244103 (2010)

⁴ R. Sabatini *et al.*, Phys. Rev. B **87**, 041108(R) (2013)

⁵ H. Peng and J. P. Perdew, Phys. Rev. B **95**, 081105(R) (2017)

⁶ D. Chakraborty *et al.*, J. Chem. Theory Comput. **16**, 5893 (2020)

Nonlocal vdW functionals in WIEN2k

► Features:

► Fast FFT-based method of Román-Pérez and Soler¹:

1. ρ is smoothed close to the nuclei (density cutoff ρ_c) $\rightarrow \rho_s$.²
2. ρ_s is expanded in plane waves in the whole unit cell. G_{\max} is the plane-wave cutoff of the expansion.

► More expensive than atom-pairwise methods

► Many of the vdW functionals from the literature are available (see list in user's guide)

► Usage:

► Input file `case.innlvdw` (`$WIENROOT/SRC_templates`)

► `run_lapw -nlvdw ...`

¹ G. Román-Pérez and J. M. Soler, Phys. Rev. Lett. **103**, 096102 (2009)

² F. Tran *et al.*, Phys. Rev. B **96**, 054103 (2017)

Nonlocal vdW functionals: input file case.innlvdw

1	kernel type
-0.8491	parameters of the kernel
20	plane-wave expansion cutoff GMAX
0.3	density cutoff rhoc
T	calculation of the potential (T or F)

line 1 : “1” for DRSSL/LMKLL or “2” for rVV10(L)

line 2 : “-0.8491” for DRSSL, “-1.887” for LMKLL

“6.3 0.0093” for rVV10

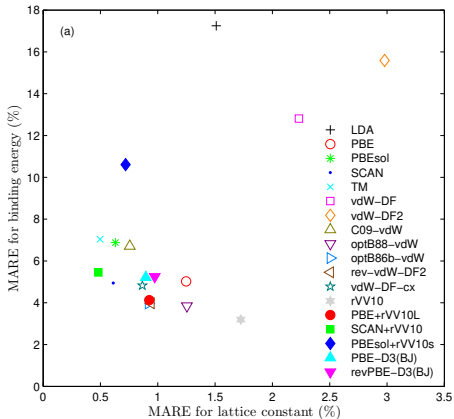
line 3 : Use $G_{\max} = 25$ or 30 in case of numerical noise

line 4 : Eventually repeat with larger ρ_c (e.g, 0.6)

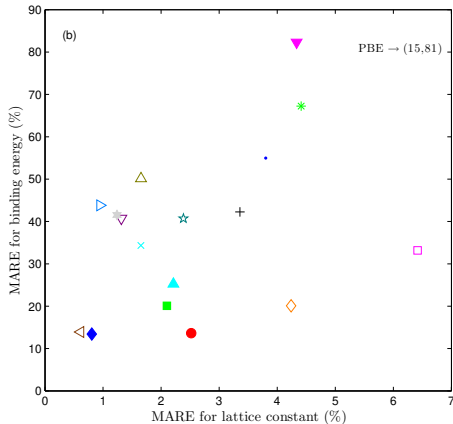
line 5 : Potential is necessary only for forces. Save computational time if set to “F”

van der Waals interactions: tests on solids¹

44 strongly bound solids



17 weakly bound solids



Conclusion: rev-vdW-DF2² is a good choice for solids

¹ F. Tran *et al.*, Phys. Rev. Materials **3**, 063602 (2019)

² I. Hamada, Phys. Rev. B. **89**, 121103(R) (2014)

mBJ: a MGGA potential for reliable band gap calculations

- ▶ The standard semilocal functionals (PBE, SCAN, etc.) underestimate the band gap of solids. It is a well-know problem in DFT.
- ▶ The modified Becke-Johnson (mBJ) potential was designed to be accurate for the band gap:¹

$$v_x^{\text{mBJ}}(\mathbf{r}) = cv_x^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{6}} \sqrt{\frac{\tau(\mathbf{r})}{\rho(\mathbf{r})}} \quad c = \alpha + \beta \left(\frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})} d^3r \right)^{1/2}$$

where v_x^{BR} is the Becke-Roussel potential²

- ▶ It is a potential that has no associated exchange energy E_x
- ▶ It depends on ρ , $\nabla\rho$, $\nabla^2\rho$ and τ and is therefore of the MGGA type
- ▶ $\alpha = 1.023$ and $\beta = -0.012$ were fitted such that the experimental band gap of 22 solids are reproduced at best¹
- ▶ The average of $|\nabla\rho|/\rho$ in the unit cell makes the mBJ potential unapplicable for systems with vacuum or interfaces. A solution is to fix c or to use the local mBJ potential³.

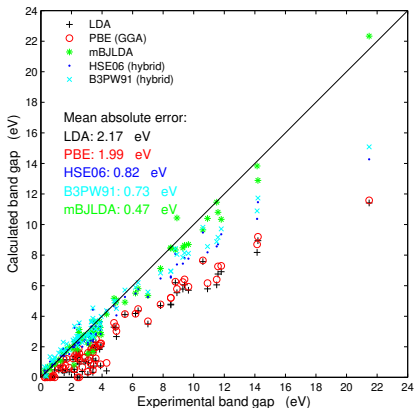
¹ F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

² A. D. Becke and M. R. Roussel, Phys. Rev. A **39**, 3761 (1989)

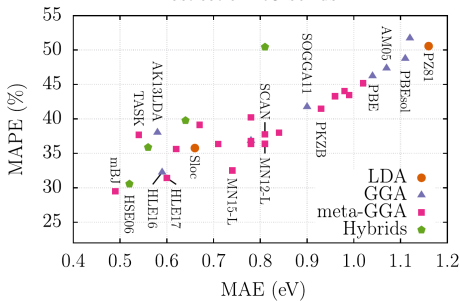
³ T. Rauch, M. A. L. Marques, and S. Botti, J. Chem. Theory Comput. **16**, 2654 (2020)

mBJ: a MGGA potential for reliable band gap calculations

Test set of 76 solids¹



Test set of 473 solids²



mBJ is more accurate than the usual hybrid functionals and much faster since it is a semilocal method. 5500 citations.

¹ F. Tran and P. Blaha, *J. Phys. Chem. A* **121**, 3318 (2017)

² P. Borlido *et al.*, *npj Comput. Mater.* **6**, 96 (2020)

Local mBJ potential for systems with vacuum or interfaces

- ▶ The average of $|\nabla\rho|/\rho$ in the unit cell makes the mBJ potential unapplicable for systems with vacuum or interfaces
- ▶ To remedy this problem, a **local average** of $|\nabla\rho|/\rho$ is used¹:

$$v_{\mathbf{x}}^{\text{mBJ}}(\mathbf{r}) = \mathbf{c}(\mathbf{r})v_{\mathbf{x}}^{\text{BR}}(\mathbf{r}) + (3\mathbf{c}(\mathbf{r}) - 2) \frac{1}{\pi} \sqrt{\frac{5}{6}} \sqrt{\frac{\tau(\mathbf{r})}{\rho(\mathbf{r})}} \quad \mathbf{c}(\mathbf{r}) = \alpha + \beta\bar{g}(\mathbf{r})$$

$$\bar{g}(\mathbf{r}) = \frac{1}{(2\pi\sigma^2)^{3/2}} \int g(\mathbf{r}') e^{-\frac{|\mathbf{r}-\mathbf{r}'|^2}{2\sigma^2}} d^3r' \quad (\text{local average around each point } \mathbf{r})$$

$$g(\mathbf{r}) = \frac{1-\alpha}{\beta} \left[1 - \text{erf}\left(\frac{\rho(\mathbf{r})}{\rho_{\text{th}}}\right) \right] + \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})} \text{erf}\left(\frac{\rho(\mathbf{r})}{\rho_{\text{th}}}\right)$$

- ▶ Parameters: $\alpha = 0.488$, $\beta = 0.5$, $\sigma = 3.78$, and $\rho_{\text{th}} = 6.96 \times 10^{-4}$
- ▶ Error in the DFT band gap with respect to the G_0W_0 reference values for 298 2D materials (monolayers)²:

	MAE (eV)	MARE (%)
PBE	1.50	51
HSE06	0.78	29
r^2 SCAN	1.18	39
TASK	0.66	25
GLLB-SC	0.42	21
LMBJ ($\beta = 0.5$)	0.78	35
LMBJ ($\beta = 0.6$)	0.50	32

¹ T. Rauch, M. A. L. Marques, and S. Botti, *J. Chem. Theory Comput.* **16**, 2654 (2020)

² F. Tran *et al.*, *J. Chem. Phys.* **155**, 104103 (2021)

How to run a calculation with the mBJ potential?

1. `init_lapw` (choose LDA or PBE)
2. `init_mbj_lapw` (modifies `case.in0` and creates `case.inm_tau`)
3. `run_lapw -i 1 -NI` (creates `case.r2v` and `case.tausum`)
4. `save_lapw case_PBE_1_iteration`
5. `init_mbj_lapw` again and choose mBJ or local mBJ:
 - 1: mBJ
 - 2: lmBJ

and one of the parameterizations for α and β :

- 0: Original mBJ values¹
 - 1: New parametrization²
 - 2: For band gaps up to 7 eV²
 - 3: Original BJ potential³
 - 4: For perovskites (heavy atom, SOC)⁴
6. `run_lapw ...`

¹F. Tran and P. Blaha, *Phys. Rev. Lett.* **102**, 226401 (2009)

²D. Koller *et al.*, *Phys. Rev. B* **85**, 155109 (2012)

³A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **124**, 221101 (2006)

⁴R. A. Jishi *et al.*, *J. Phys. Chem. C* **118**, 28344 (2014)

GLLB-SC potential for band gaps

- ▶ Like mBJ, GLLB-SC is a potential (no energy functional)¹:

$$v_{xc,\sigma}^{\text{GLLB-SC}} = 2\varepsilon_{x,\sigma}^{\text{PBEsol}} + K_x^{\text{LDA}} \sum_{i=1}^{N_\sigma} \sqrt{\epsilon_{\text{H}} - \epsilon_{i\sigma}} \frac{|\psi_{i\sigma}|^2}{\rho_\sigma} + v_{c,\sigma}^{\text{PBEsol}}$$

- ▶ Leads to a **derivative discontinuity**:

$$\Delta = \int \psi_L^* \left[\sum_{i=1}^{N_{\sigma_L}} K_x^{\text{LDA}} (\sqrt{\epsilon_{\text{L}} - \epsilon_{i\sigma_L}} - \sqrt{\epsilon_{\text{H}} - \epsilon_{i\sigma_L}}) \frac{|\psi_{i\sigma_L}|^2}{\rho_{\sigma_L}} \right] \psi_L d^3r$$

Comparison with experiment: $E_g = E_g^{\text{KS}} + \Delta$

- ▶ Much better than LDA/GGA for band gaps
- ▶ Not as good as mBJ for strongly correlated systems²
- ▶ Seems interesting for electric field gradient²
- ▶ Implemented in WIEN2k²: See user's guide for usage

¹M. Kuisma *et al.*, Phys. Rev. B **82**, 115106 (2010)

²F. Tran, S. Ehsan, and P. Blaha, Phys. Rev. Materials **2**, 023802 (2018)

Strongly correlated solids

- ▶ Typically, these are magnetic solids with an **open-shell of 3d, 4f or 5f** electrons that are **well localized** (the opposite of itinerant) around the (transition metal, rare earth, actinide) atom
- ▶ The most known are antiferromagnetic oxides:
 - ▶ MnO, FeO, CoO, NiO, La₂CuO₄, YBa₂Cu₃O₆
 - ▶ Ce, Ce₂O₃, PrO₂
 - ▶ UO₂, PuO₂
- ▶ **These are very difficult cases for semilocal functionals**, which lead to qualitatively wrong results:
 - ▶ Too small magnetic moment or, even worse, wrong magnetic structure (nonmagnetic instead of antiferromagnetic)
 - ▶ Too small band gap or, even worse, metallic character instead of insulator

One **reason**: The strong onsite correlation among the 3d/4f/5f electrons is not well described. In particular, **the self-interaction error (the interaction of an electron with itself)** inherent to semilocal functionals is important for these systems.

More accurate methods for strongly correlated solids:

- ▶ **mBJ potential** (cheap)
- ▶ **On-site DFT+U¹** (cheap)
- ▶ **On-site hybrid functionals** (cheap)
- ▶ **Hybrid functionals** (expensive)
- ▶ **LDA+DMFT** (expensive, beyond-DFT method)

¹V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991)

On-site DFT+ U and hybrid methods in WIEN2k

- ▶ For solids, the hybrid functionals are computationally **very expensive**.
- ▶ In WIEN2k the **on-site** DFT+ U ¹ and **on-site** hybrid^{2,3} methods are available. These methods are approximations of the Hartree-Fock/hybrid methods:
Applied only inside atomic spheres of selected atoms and electrons of a given angular momentum ℓ .
- ▶ As cheap as semilocal functionals

¹ V. I. Anisimov *et al.*, Phys. Rev. B **44**, 943 (1991)

² P. Novák *et al.*, Phys. Stat. Sol. (b) **243**, 563 (2006)

³ F. Tran *et al.*, Phys. Rev. B **74**, 155108 (2006)

On-site DFT+ U and hybrid methods

The exchange-correlation functional is

$$E_{\text{xc}}^{\text{DFT}+U/\text{hybrid}} = E_{\text{xc}}^{\text{semilocal}}[\rho] + E_{\text{onsite}}[n_{mm'}]$$

$n_{mm'}$ is the density matrix of the correlated electrons

- ▶ For DFT+ U both exchange and correlation/Coulomb are corrected:

$$E_{\text{onsite}}^U = \underbrace{E_{\text{xc}}^{\text{screened HF}}}_{\text{correction}} - \underbrace{E_{\text{xc}}}_{\text{d. count.}}$$

Depends on parameters U and J

There are several versions of the double-counting term

- ▶ For the hybrid methods only exchange is corrected:

$$E_{\text{onsite}}^{\text{hybrid}} = \underbrace{\alpha E_{\text{x}}^{\text{HF}}}_{\text{corr.}} - \underbrace{\alpha E_{\text{x}}^{\text{semilocal}}}_{\text{d. count.}}$$

α (fraction of HF exchange) is a parameter $\in [0, 1]$

How to run DFT+ U and on-site hybrid calculations?

1. Create the input files:

- ▶ `case.inorb` and `case.indm` for DFT+ U
- ▶ `case.ineece` for on-site hybrid functionals (`case.indm` created automatically):

2. Run the job (can only be run with `runsp_lapw`):

- ▶ DFT+ U : `runsp_lapw -orb ...`
- ▶ Hybrid: `runsp_lapw -ecee ...`

For a calculation without spin-polarization ($\rho_{\uparrow} = \rho_{\downarrow}$): `runsp_c_lapw -orb/ecee ...`

Input file case.inorb

DFT+ U applied to the $4f$ electrons of atoms No. 2 and 4:

```
1 2 0          nmod, natorb, ipr
PRATT, 1.0     mixmod, amix
2 1 3         iatom, nlorb, lorb
4 1 3         iatom, nlorb, lorb
1             nsic (LDA+U(SIC) used)
0.61 0.07    U J (Ry)
0.61 0.07    U J (Ry)
```

nsic=0 for the AMF method (less strongly correlated electrons)

nsic=1 for the SIC method

nsic=2 for the HMF method

Review article : [E. R. Ylvisaker *et al.*, Phys. Rev. B **79**, 035103 \(2009\)](#)

Input file case.ineece

On-site hybrid functional applied to the 4*f* electrons of atoms No. 2 and 4:

```
-12.0 2          emin, natorb  
2 1 3          iatom, nlorb, lorb  
4 1 3          iatom, nlorb, lorb  
HYBR          HYBR/EECE  
0.25          fraction of exact exchange  $\alpha$ 
```

SCF cycle of DFT+ U in WIEN2k

lapw0

$\rightarrow v_{xc,\sigma}^{\text{DFT}} + v_{ee} + v_{en}$ (case.vspup(dn), case.vnsup(dn))

orb -up

$\rightarrow v_{mm'}^{\uparrow}$ (case.vorbup)

orb -dn

$\rightarrow v_{mm'}^{\downarrow}$ (case.vorbdn)

lapw1 -up -orb

$\rightarrow \psi_{n\mathbf{k}}^{\uparrow}, \epsilon_{n\mathbf{k}}^{\uparrow}$ (case.vectorup, case.energyup)

lapw1 -dn -orb

$\rightarrow \psi_{n\mathbf{k}}^{\downarrow}, \epsilon_{n\mathbf{k}}^{\downarrow}$ (case.vectordn, case.energydn)

lapw2 -up -orb

$\rightarrow \rho_{\text{val}}^{\uparrow}$ (case.clmvalup), $n_{mm'}^{\uparrow}$ (case.dmatup)

lapw2 -dn -orb

$\rightarrow \rho_{\text{val}}^{\downarrow}$ (case.clmvaldn), $n_{mm'}^{\downarrow}$ (case.dmatdn)

lcore -up

$\rightarrow \rho_{\text{core}}^{\uparrow}$ (case.clmcorup)

lcore -dn

$\rightarrow \rho_{\text{core}}^{\downarrow}$ (case.clmcordn)

mixer

\rightarrow mixed ρ^{σ} and $n_{mm'}^{\sigma}$

Hybrid functionals

- ▶ **On-site** hybrid functionals can be applied only to localized electrons
- ▶ **Full** hybrid functionals are necessary (but expensive) for solids with delocalized electrons (e.g., in *sp*-semiconductors)

Two types of full hybrid functionals available in WIEN2k¹:

- ▶ unscreened:

$$E_{xc} = E_{xc}^{\text{DFT}} + \alpha \left(E_x^{\text{HF}} - E_x^{\text{DFT}} \right)$$

- ▶ screened (short-range), $\frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow \frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$:

$$E_{xc} = E_{xc}^{\text{DFT}} + \alpha \left(E_x^{\text{SR-HF}} - E_x^{\text{SR-DFT}} \right)$$

screening leads to faster convergence with \mathbf{k} -points sampling

¹F. Tran and P. Blaha, Phys. Rev. B **83**, 235118 (2011)

Hybrid functionals: technical details

- ▶ 10-1000 times more expensive than semilocal functionals
- ▶ **k**-point and MPI parallelizations
- ▶ Approximations to speed up the calculations:
 - ▶ **Reduced k-mesh** for the HF potential. Example:
For a calculation with a $12 \times 12 \times 12$ **k**-mesh, the reduced **k**-mesh for the HF potential can be:
 $6 \times 6 \times 6$, $4 \times 4 \times 4$, $3 \times 3 \times 3$, $2 \times 2 \times 2$ or $1 \times 1 \times 1$
 - ▶ **Non-self-consistent** calculation of the band structure
- ▶ Use **run_bandplothf_lapw** for band structure
- ▶ Can be combined with spin-orbit coupling

Hybrid functionals: input file case.inhf

Example for YS-PBE0 (similar to HSE06 from Heyd, Scuseria and Ernzerhof¹)

0.25	fraction α of HF exchange
T	screened (T, YS-PBE0) or unscreened (F, PBE0)
0.165	screening parameter λ
20	number of bands for the 2nd Hamiltonian
6	GMAX
3	lmax for the expansion of orbitals
3	lmax for the product of two orbitals
1d-3	radial integrals below this value neglected

Important: The computational time will depend strongly on the number of bands, GMAX, lmax and the number of k-points

¹A. V. Krukau *et al.*, J. Chem. Phys. **125**, 224106 (2006)

Hybrid functionals: input file case.inhf

Example for YS-PBE0 (similar to HSE06 from Heyd, Scuseria and Ernzerhof¹)

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Important: The computational time will depend strongly on the number of bands, GMAX, lmax and the number of k-points

¹A. V. Krukau *et al.*, J. Chem. Phys. **125**, 224106 (2006)

How to run hybrid functionals?

1. `init_lapw`
2. `run_lapw` for the semilocal functional (recommended), `save_lapw`
3. `init_hf_lapw` (this will create/modify input files)
 - 3.1 adjust `case.inhf` according to your needs
 - 3.2 reduced **k**-mesh for the HF potential? Yes or no
 - 3.3 specify the **k**-mesh
4. `run_lapw -hf` (-redklist) (-diaghf) ...

SCF cycle of hybrid functionals in WIEN2k

lapw0 -grr $\rightarrow v_x^{\text{DFT}} \text{ (case.r2v)}, \alpha E_x^{\text{DFT}} \text{ (:AEXSL)}$

lapw0 $\rightarrow v_{xc}^{\text{DFT}} + v_{ee} + v_{en} \text{ (case.vsp, case.vns)}$

lapw1 $\rightarrow \psi_{nk}^{\text{DFT}}, \epsilon_{nk}^{\text{DFT}} \text{ (case.vector, case.energy)}$

lapw2 $\rightarrow \sum_{nk} \epsilon_{nk}^{\text{DFT}} \text{ (:SLSUM)}$

hf $\rightarrow \psi_{nk}, \epsilon_{nk} \text{ (case.vectorhf, case.energyhf)}$

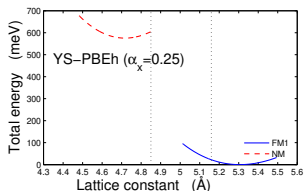
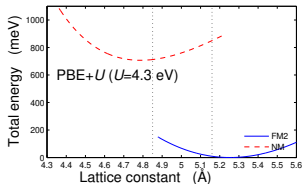
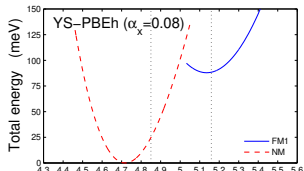
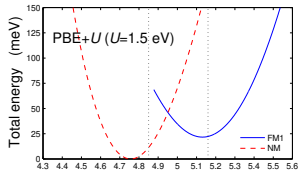
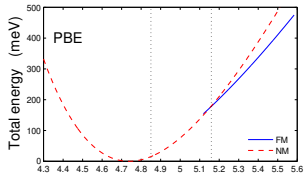
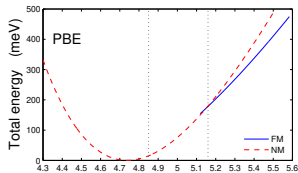
lapw2 -hf $\rightarrow \rho_{\text{val}} \text{ (case.clmval)}$

lcore $\rightarrow \rho_{\text{core}} \text{ (case.clmcor)}$

mixer $\rightarrow \text{mixed } \rho$

Nonmagnetic and ferromagnetic phases of cerium¹

Small U (1.5 eV) or α_x (0.08) leads to correct stability ordering



¹ F. Tran, F. Karsai, and P. Blaha, Phys. Rev. B **89**, 155106 (2014)

Antiferromagnetic transition-metal oxides (strongly correlated electrons)

TABLE I. Band gap (in eV).

Method	MnO	FeO	CoO	NiO	Cr ₂ O ₃	Fe ₂ O ₃
PBE	0.86	0.00	0.00	0.95	1.63	0.56
GLLB-SC	3.79	0.00	1.85	3.07	3.07	4.81
mBJ	2.94	1.84	3.13	4.14	3.68	2.35
HSE06	2.85	2.35	3.48	4.37	4.42	3.24
Expt.	3.90	2.40	2.50	4.30	3.40	2.20

TABLE II. Atomic spin magnetic moment μ_S (in μ_B) compared to the experimental total moment $\mu_S + \mu_L$. The orbital moment μ_L should be in the range 0.6-1 μ_B for FeO, 1-1.6 μ_B for CoO, 0.3-0.45 μ_B for NiO, and smaller for the other cases.

Method	MnO	FeO	CoO	NiO	CuO	Cr ₂ O ₃	Fe ₂ O ₃
PBE	4.17	3.39	2.43	1.38	0.38	2.44	3.53
GLLB-SC	4.56	3.74	2.73	1.65	0.55	2.99	4.43
mBJ	4.41	3.58	2.71	1.75	0.74	2.60	4.09
HSE06	4.36	3.55	2.65	1.68	0.67	2.61	4.08
Expt.	4.58	3.32,4.2,4.6	3.35,3.8,3.98	1.9,2.2	0.65	2.44,2.48,2.76	4.17,4.22

mBJ is as accurate as the hybrid functional HSE06 for antiferromagnetic oxides¹

¹F. Tran, S. Ehsan, and P. Blaha, Phys. Rev. Mater. 2, 023802 (2018)

Some recommendations

Before starting a calculation:

- ▶ Read a few DFT papers about your system or similar ones:
 - ▶ This should give you an idea which XC functional(s) should be the most reliable (or the least unreliable) for the **accuracy**.
 - ▶ **Do not apply DFT blindly!**
- ▶ Figure out which computational resources you have:
 - ▶ Hybrid functionals and *GW* require substantially more **computational resources** (and patience) than semilocal methods.
 - ▶ Do test calculations with reduced basis set size and number of *k*-points to have an idea of the computational time.

Thank you for your attention!