제 6회 전자구조계산 여름학교

Intro to Tutorial Wed.8

# Exchange-correlation functionals and corrections in QE

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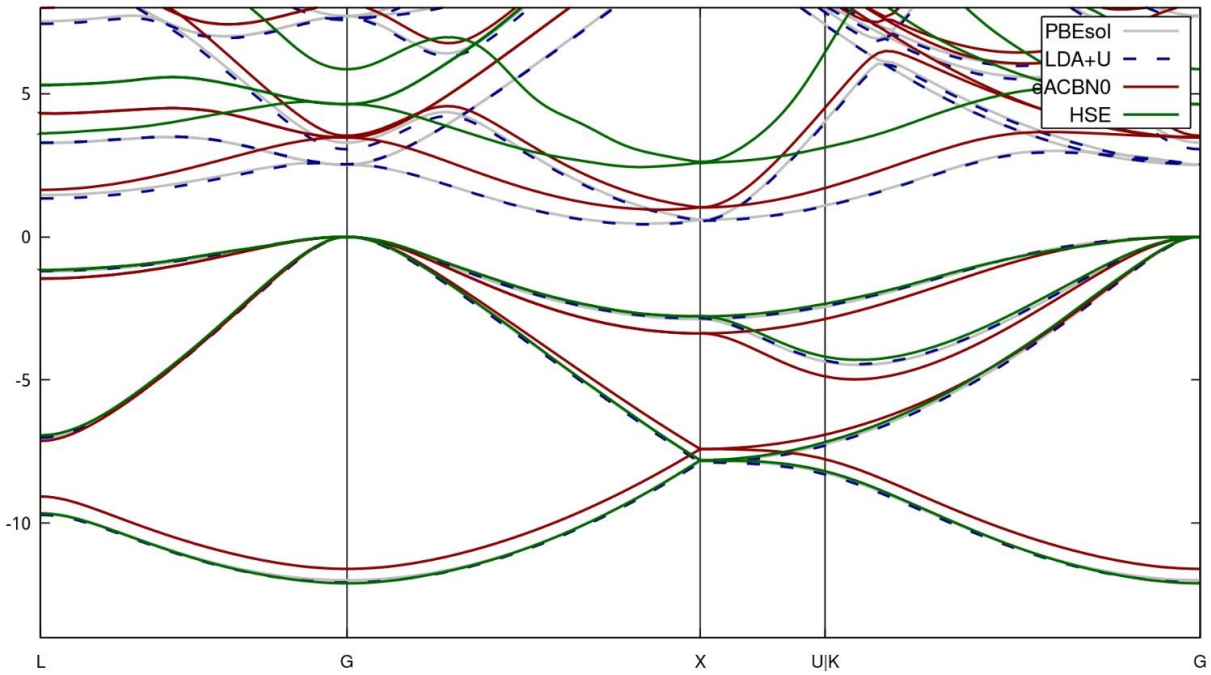
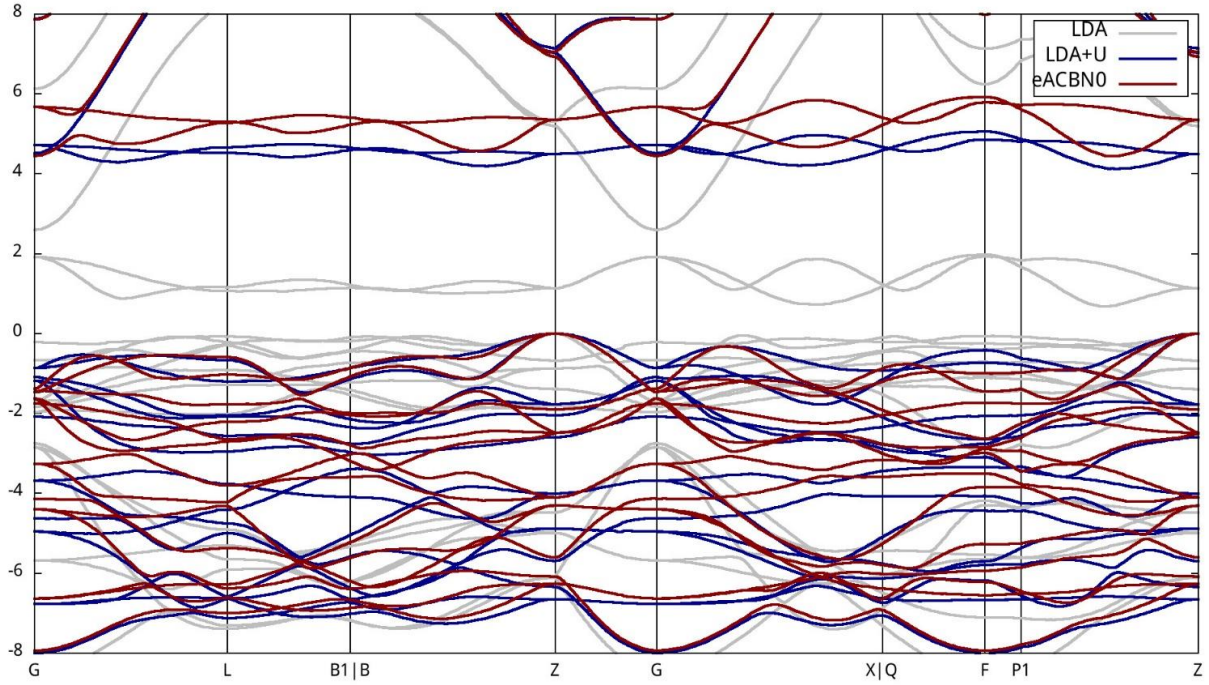
# Goal

✓ Explore different XC functionals (LDA/GGA)
and advanced corrections (DFT+*U* and Hybrid functionals).

Silicon




NiO



# Recap: Inaccuracy of Density functional theory

Total energy:

$$E_{\text{total}}[n(\vec{r})] = E_K + E_{\text{ext}} + E_{\text{Hartree}} + E_{\text{XC}}$$

Exact form is unknown.

A single particle Kohn-Sham equations:

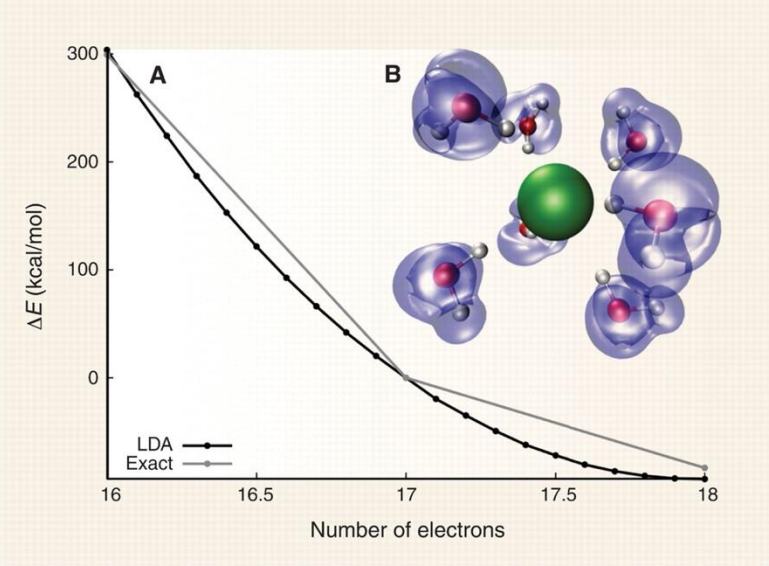
$$H_{KS}\psi_{nk}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_I(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\psi_{nk}(\mathbf{r}) = \epsilon_{nk}\psi_{nk}(\mathbf{r})$$

Approximate functionals for XC such as LDA or GGA are **fast** but makes **self-interaction error**.

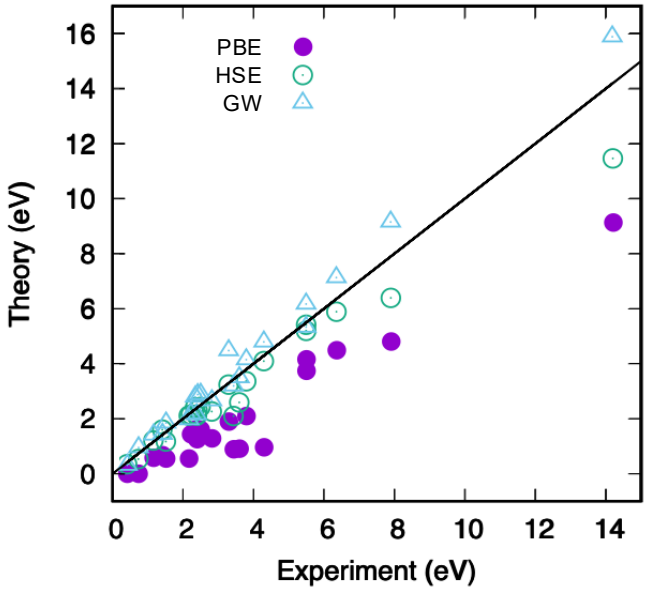
[1] P. Hoenberg, *et al.*, Phys. Rev. **136**, B864 (1964)
[2] W. Kohn, *et al.*, Phys. Rev. **140**, A1133 (1965)

# Recap: Quantitative errors in DFT-LDA and DFT-GGA

## Chlorine atom

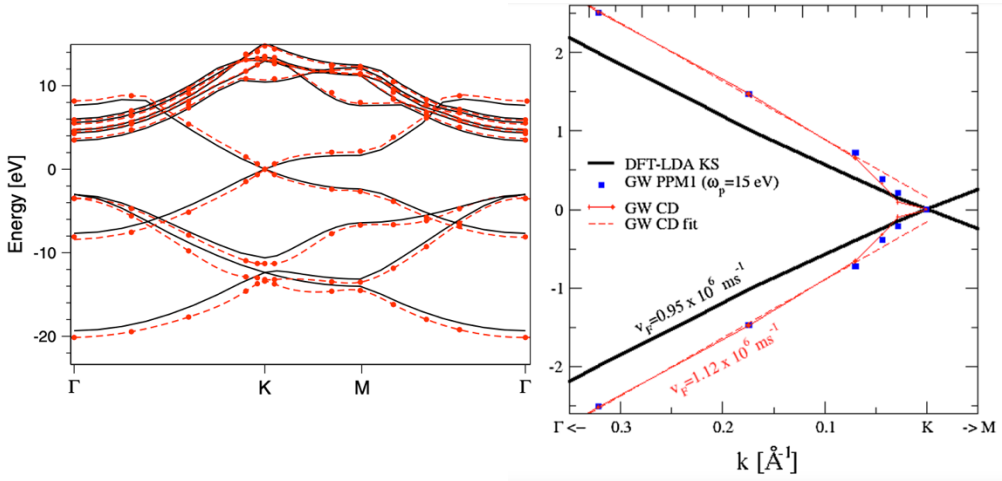



Delocalization error




Bandgap underestimation

## Monolayer graphene

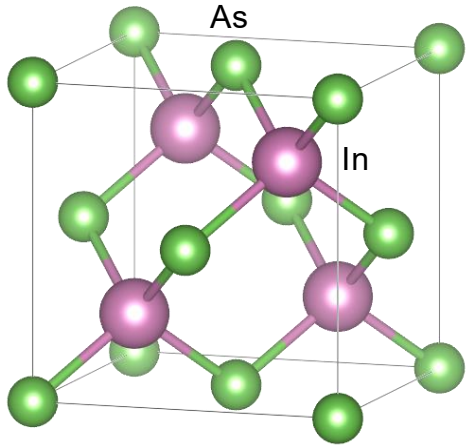



Inaccurate Fermi velocity

[1] A. J. Cohen, *et al.*, Science **321**, 792 (2008)
[2] S.-H. Lee, *et al.*, Phys. Rev. Research **2**, 043410 (2020)
[3] P. E. Trevisanutto, *et al.*, Phys. Rev. Lett. **101**, 226405 (2008)

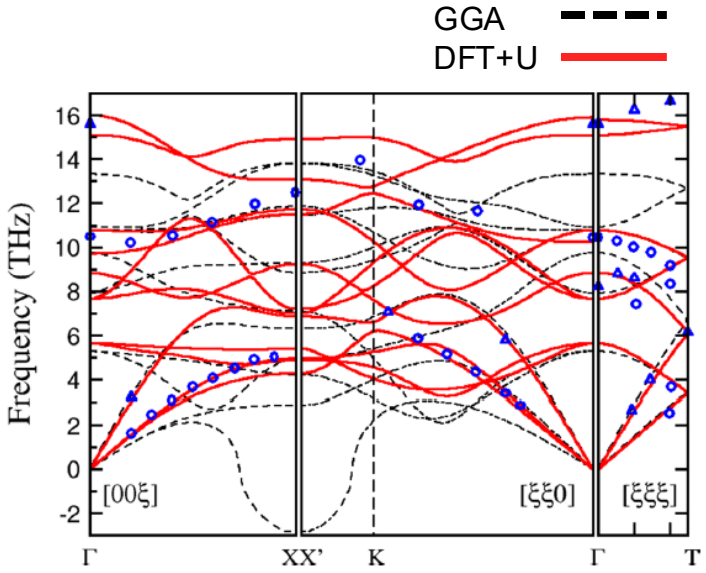
# Recap: Qualitative errors in DFT-LDA and DFT-GGA

## Indium arsenide



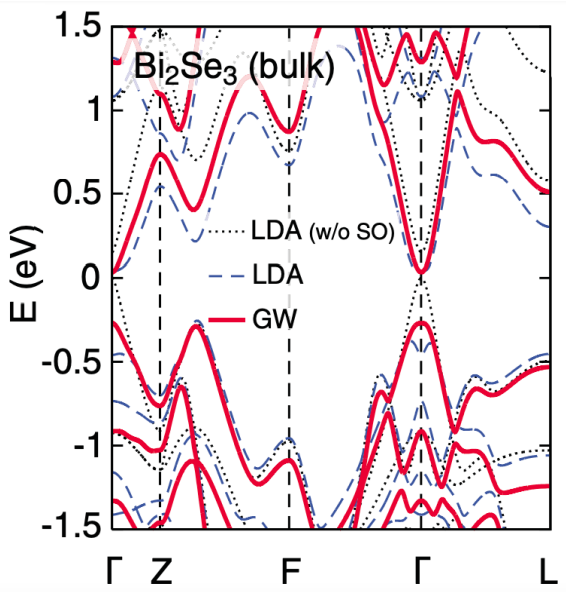

GGA: topological insulator
Expt.: normal insulator

## Cobalt oxide




Dynamically unstable in GGA

## Bismuth selenide




LDA: indirect band gap
GW: direct band gap

[1] J. Vidal, *et al.*, Phys. Rev. B **84**, 041109 (2011)
[2] A, Floris, *et al.*, Phys. Rev. B **101**, 064305 (2020)
[3] O. V. Yazyev, *et al.*, Phys. Rev. B **85**, 161101(R) (2012)

# Various method for correction

$$H_{KS}\psi_{nk}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_I(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\psi_{nk}(\mathbf{r}) = \epsilon_{nk}\psi_{nk}(\mathbf{r})$$

Approximate functionals for XC such as LDA or GGA are **fast** but makes **self-interaction error**.

- Self-energy correction through GW approximation
- Dynamical mean-field theory + DFT
- Hybrid functional
- Local self-interaction error correction through DFT+*U*

and many others…

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Approximate functionals for XC such as LDA or GGA are **fast** but makes **self-interaction error**.

- Self-energy correction through GW approximation
- Dynamical mean-field theory + DFT

→ Beyond the one-body treatment

- Hybrid functional
- Local self-interaction error correction through DFT+*U*

→ Today's scope.

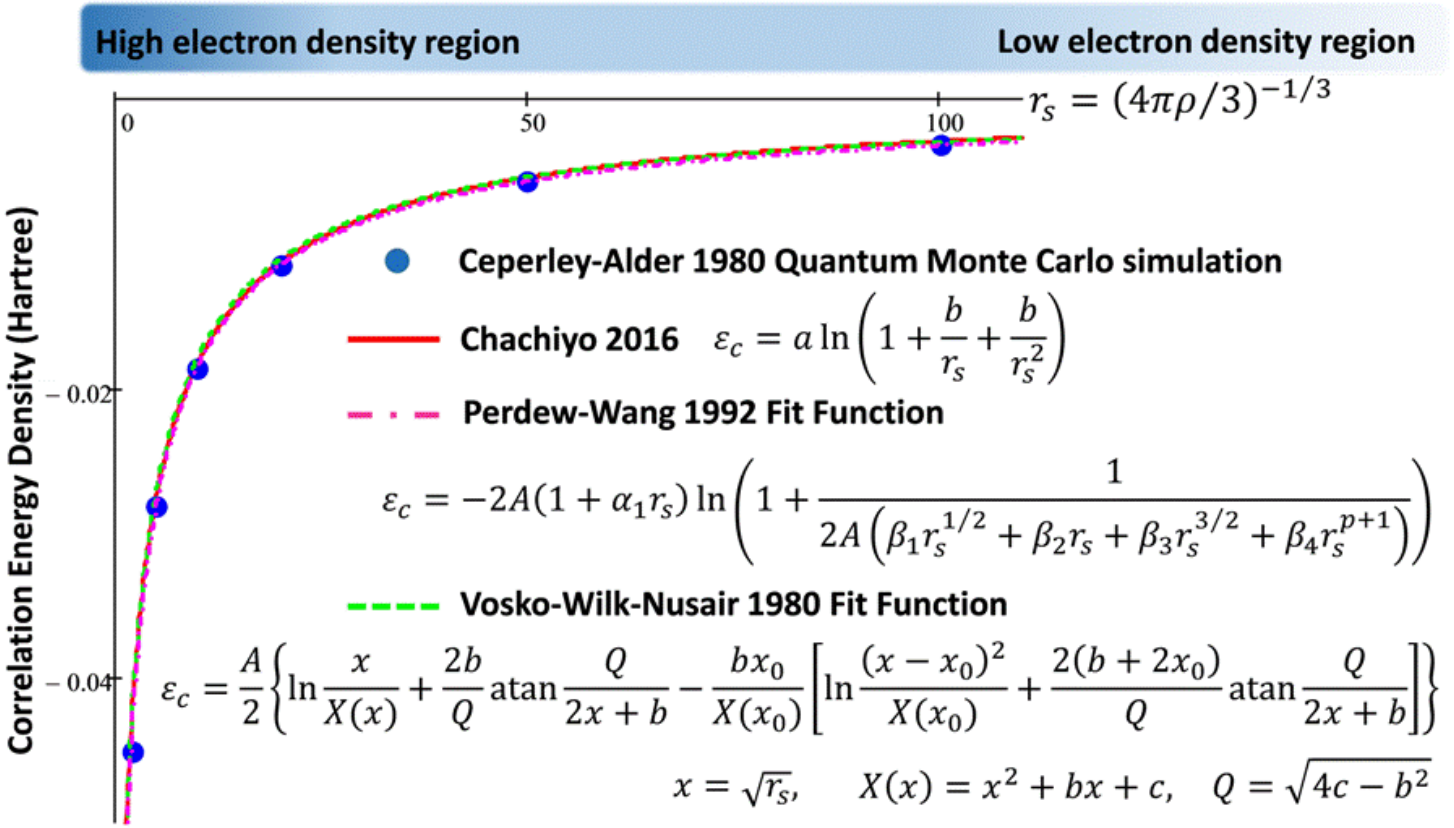
and many others…

# Local Density Approximation (LDA)

- ✓ Derived from the homogeneous electron gas (HEG) model.
- ✓ The XC energy is calculated purely based on the local density $n(r)$ at each point.

$$E_{xc}^{LDA}[n(\boldsymbol{r})] = \int n(\boldsymbol{r})\varepsilon_{xc}\big(n(\boldsymbol{r})\big)d\boldsymbol{r}$$

$$E_{x}^{LDA}[n(\boldsymbol{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int n(\boldsymbol{r})^{\frac{4}{3}}d\boldsymbol{r}$$



# Generalized Grandient Approximation (GGA)

✓ An improvement over LDA. Considering $n(r)$ and its gradient $\nabla n(r)$. (Semi-local)

$$E_{xc}^{GGA}[n(\boldsymbol{r})] = \int n(\boldsymbol{r})\varepsilon_{xc}(n, \nabla n)d\boldsymbol{r}$$

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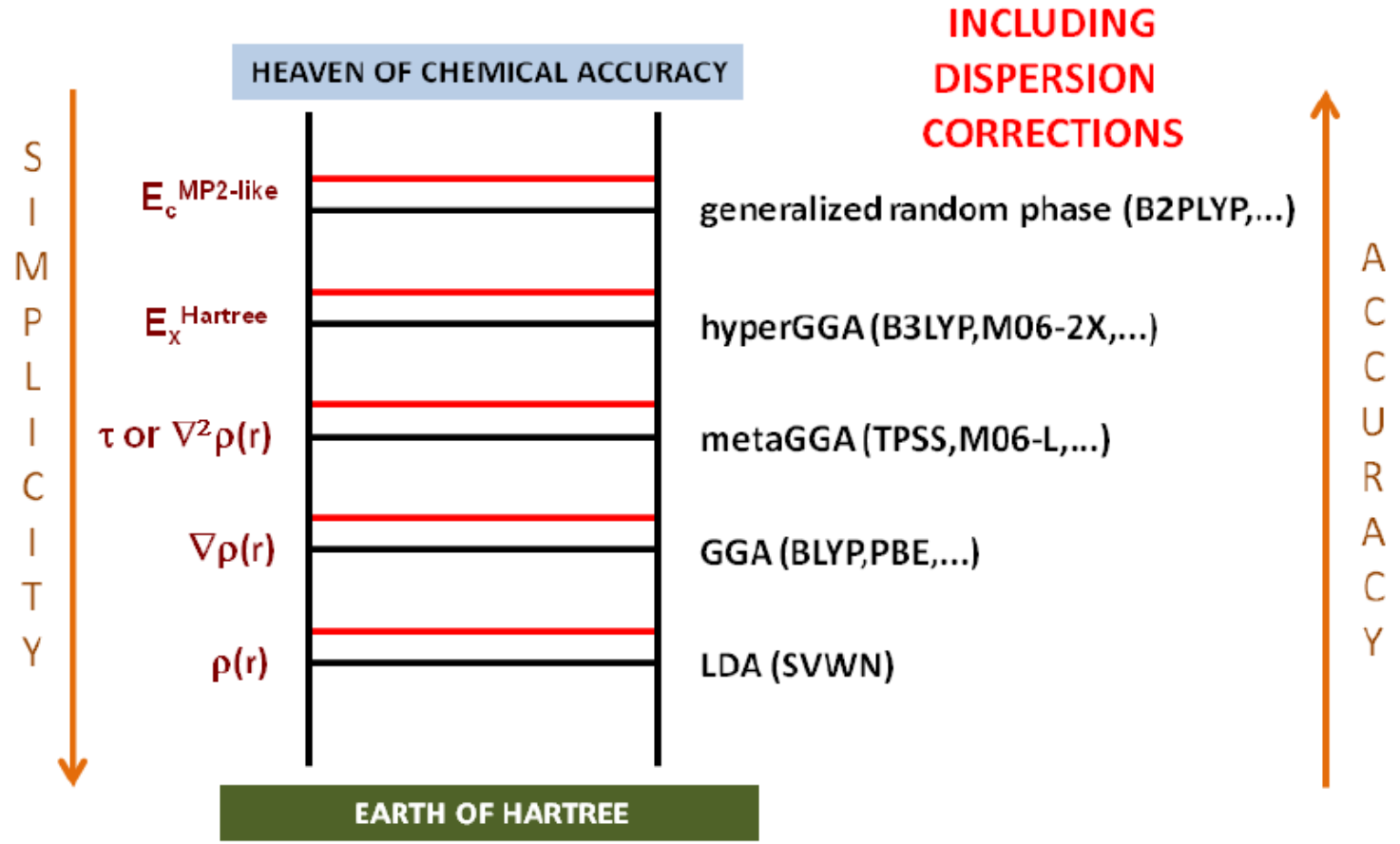
Beyond the GGA



# Hybrid functional

✓ The exchange component consists of a mixing of GGA and Hartree-Fock exchange:

Unscreened hybrid functionals

$$E_{xc}^{HF} = \alpha E_x^{HF} + (1-\alpha)\, E_x^{GGA} + E_c^{GGA}$$

Range-separated hybrid functionals

$$E_{xc}^{HF} = \alpha E_x^{HF,SR}(\mu) + (1-\alpha)\, E_x^{GGA,SR}(\mu) + E_x^{GGA,LR}(\mu) + E_c^{GGA}$$

$$E_{xc}^{HSE} = \frac{1}{4} E_x^{HF,SR}(\mu) + \frac{3}{4} E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}(\mu) + E_c^{PBE}$$

HSE06: $\mu = 0.2\ \text{Å}^{-1}$

# Hybrid functional related input variables

| input_dft | CHARACTER |
|---|---|
| *Default:* | read from pseudopotential files |

```
Exchange-correlation functional: eg 'PBE', 'BLYP' etc
See Modules/funct.f90 for allowed values.
Overrides the value read from pseudopotential files.
Use with care and if you know what you are doing!
```

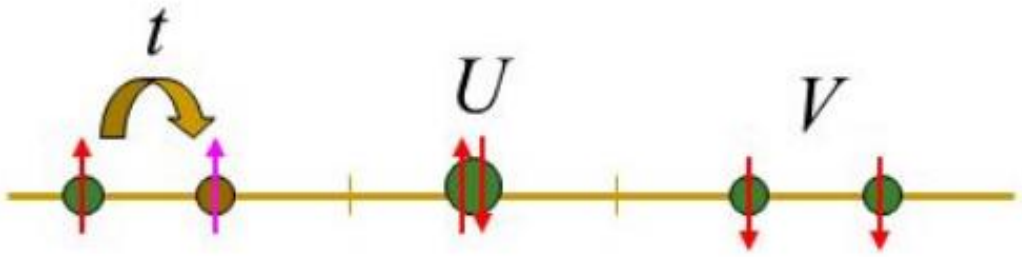
```
"tpss"   = "sla+pw+tpss+tpss"   = TPSS Meta-GGA
"m06l"   = "nox+noc+m6lx+m6lc"  = M06L Meta-GGA
"tb09"   = "sla+pw+tb09+tb09"   = TB09 Meta-GGA
"pbe0"   = "pb0x+pw+pb0x+pbc"   = PBE0
"b86bx"  = "pb0x+pw+b86x+pbc"   = B86bPBE hybrid
"bhahlyp"="pb0x+pw+b88x+blyp"   = Becke half-and-half LYP
"hse"    = "sla+pw+hse+pbc"     = Heyd-Scuseria-Ernzerhof (HSE 06, see note below)
"b3lyp"                         = B3LYP
"b3lyp-v1r"                     = B3LYP-VWN1-RPA
"x3lyp"                         = X3LYP
```

| nqx1, nqx2, nqx3 | INTEGER |
|---|---|

```
Three-dimensional mesh for q (k1-k2) sampling of
the Fock operator (EXX). Can be smaller than
the number of k-points.

Currently this defaults to the size of the k-point mesh used.
In QE =< 5.0.2 it defaulted to nqx1=nqx2=nqx3=1.
```

# DFT+U




Original Hubbard Hamiltonian: $$H = -t \sum_{\langle i,j \rangle, \sigma} \left( c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma} \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

On-site *U* correction: $$E_{\mathrm{DFT}+U}[\{\mathbf{n}\}] = E_{\mathrm{DFT}} + \sum_{I,\sigma} \frac{U_{\mathrm{eff}}^{I}}{2} \mathrm{tr}\left[\mathbf{n}^{I\sigma}\left(1 - \mathbf{n}^{I\sigma}\right)\right]$$

- ✓ Empirical to fit experiments
- ✓ Linear response theory [M. Cococcioni, *et al.*, Phys Rev B **71**, 035105 (2005)]
- ✓ Constraint random phase approximation [F. Aryasetiawan, et al., Phys Rev B **70**, 195104 (2004)]
- ✓ Hartree-Fock-based formalism [L. A. Agapito, *et al.*, Phys. Rev. X **5**, 011006 (2015)]

# DFT+U related input variables in official QE

Within input file,

```
HUBBARD {ortho-atomic}
U     Ni1-3d    7.3751
U     Ni2-3d    7.3751
U     O-2p      9.3543
U     O-2p      9.3543
```

Parameter value

Atom species-Manifold

**Card's options:** atomic | ortho-atomic | norm-atomic | wf | pseudo

**HUBBARD** options are:

**atomic** :
use atomic orbitals (read from pseudopotential) to build the Hubbard projectors

**ortho-atomic** :
use Lowdin orthogonalized atomic orbitals. This option is recommended to be used whenever possible instead of atomic because it allows to avoid applying Hubbard corrections twice in the orbital overlap regions.

**norm-atomic** :
Lowdin normalization of atomic orbitals. Keep in mind: atomic orbitals are not orthogonalized in this case. This is a "quick and dirty" trick to be used when atomic orbitals from the pseudopotential are not normalized (and thus produce occupation whose value exceeds unity).

**wf** :
use Wannier functions to built Hubbard projectors. The information about the Wannier functionas are read from file "prefix".hub that must be generated using pmw.x (see PP/src/poormanwannier.f90 for details). Note: these are not maximally localized Wannier functions. (see PP/examples/example05)

**pseudo** :
use the pseudopotential projectors. The charge density outside the atomic core radii is excluded. N.B.: for atoms with +U, a pseudopotential with the all-electron atomic orbitals are required (i.e., as generated by ld1.x with lsave_wfc flag).

# DFT+U(+V) related input variables in official QE

Within input file,

```
HUBBARD {ortho-atomic}
U     Ni1-3d     7.3751
U     Ni2-3d     7.3751
U     O-2p       9.3543
U     O-2p       9.3543
```

Parameter value

Atom species-Manifold

```
HUBBARD {ortho-atomic}
V     Ni1-3d    Ni1-3d    1     1     7.3751
V     Ni1-3d      O-2p    1    20     0.3532
V     Ni1-3d      O-2p    1    55     0.3532
V     Ni1-3d      O-2p    1    47     0.3532
V     Ni1-3d      O-2p    1    44     0.3532
V     Ni1-3d      O-2p    1    23     0.3532
V     Ni1-3d      O-2p    1    12     0.3532
V     Ni2-3d    Ni2-3d    2     2     7.3751
V     Ni2-3d      O-2p    2    91     0.3532
V     Ni2-3d      O-2p    2    59     0.3532
```

***Card's options:*** **atomic | ortho-atomic | norm-atomic | wf | pseudo**

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**pseudo** :
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# DFT+U(+V) related input variables for eACBN0

```
lda_plus_v = .true., acbn0_type = 2, ehub_nn_distance = 3.0, ehub_conv_thr = 1.0D-08,
lacbn0 = .true., ehub_mixing = 0.8,
ehub_l_choice(1,1) = 1,  ehub_l_choice(1,2) = 1
ehub_l_choice(2,1) = 1,  ehub_l_choice(2,2) = 1
remove_ehub_u(1,1) = 0,  remove_ehub_u(2,1) = 0
```

1. lda_plus_v = .true. (default: .false.)

   Specify 'lda_plus_v = .true.' to enable DFT+*U*+*V* calculaitons

2. acbn0_type = 2 (default: 1)

   1: original ACBN0 (for *U* only), 2: extended ACBN0 (for *U* and *V*)

3. ehub_nn_distance = 2.4 (default: 3.0 angstrom)

   Specify a cut-off inter-atomic disance $d_{IJ}$ defined in our paper.
   (S. Lee and Y-W. Son, Phys. Rev. Res. **2**, 043410 (2020))

4. ehub_conv_thr = 1.0D-8 (default: 1.0D-8)

   Convergence threshold on Hubbard energy *U* & *V* (a.u) for ACBN0 calculation.

# DFT+U(+V) related input variables for eACBN0

```
lda_plus_v = .true., acbn0_type = 2, ehub_nn_distance = 3.0, ehub_conv_thr = 1.0D-08,
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ehub_l_choice(2,1) = 1,  ehub_l_choice(2,2) = 1
remove_ehub_u(1,1) = 0,  remove_ehub_u(2,1) = 0
```

5.lacbn0 = .true. (default: .false.)

Specify 'lacbn0 = .true.' to calculate eACBN0 energy for self-consistent Hubbard parameters.

6. ehub_mixing = 0.8 (default: 0.7)

We use a simple linear mixing. [$U_{new}$ = (1 – ehub_mixing)*$\Delta U$ + $U_{old}$]

7. ehub_l_choice(***a***,***b***) = 1 (default: 0)

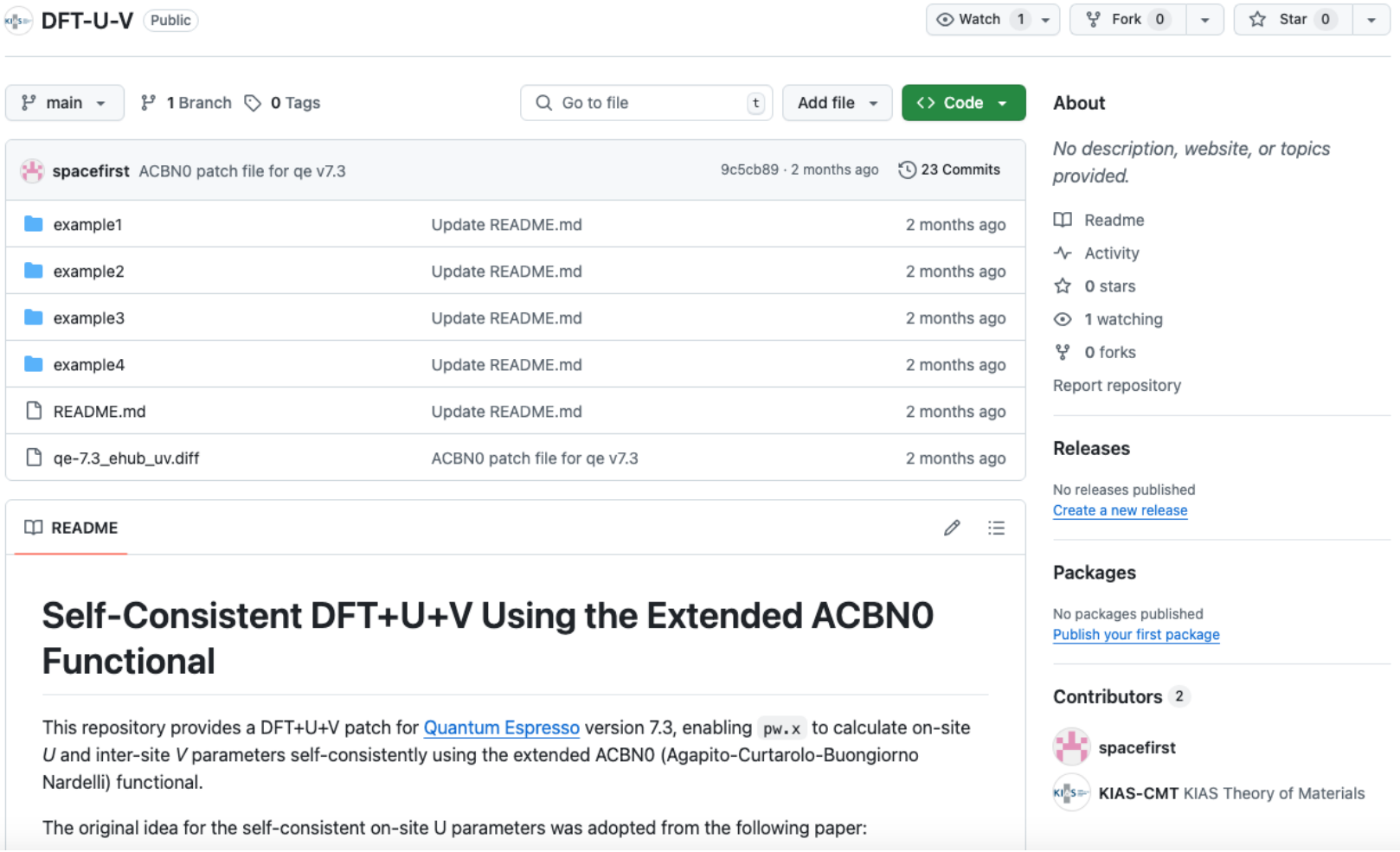
***a***: a type of atom in atomic species card
***b***: orbital index (1: *s* orbital, 2: *p* orbital, 3: *d* orbital, *f*-orbital is not available yet.)
Set "ehub_l_choice(***a***,***b***) = 1": DFT+*U*+*V* calculation for the ***b*** orbital of and atom with type ***a***.

8. remove_ehub_u(***a***,***b***) = 0, (default: 1)

Set "remove_ehub_u(***a***,***b***) = 0" : *U* for the ***b*** orbital of an atom with type ***a*** is forced to 0.

# Code availability for eACBN0

✓ Patch file is accessible via github (https://github.com/KIAS-CMT/DFT-U-V).

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