

The 2nd station to DMFT: DFT+U

(After you know what is Anderson impurity model.)

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When does the DFT not work?

Answer in short

The traditional density functional theory (DFT) calculation method is not working when processing strongly correlated materials, like Mott insulators.

Answer in bullshit

DFT is not working when it is not working.

Answer ask more questions

You must first know why the DFT is not working. Then we can determine when it will fail.

Why does the DFT not work?

Hartree-Fock (HF) approximation (without spin),

$$\begin{aligned} E_j^{\text{HF}} \phi_j(\mathbf{r}) = & \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi_j(\mathbf{r}) \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_k \int \frac{\phi_k^*(\mathbf{r}') \phi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \phi_j(\mathbf{r}) \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_k \int \frac{\phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \phi_k(\mathbf{r}) \end{aligned} \quad (1)$$

Delocalization error (i.e., many-body self-interaction error)

The LDA or GGA, which only uses the electron density's information, is insufficient for precisely describing the exchange effect. It will introduce some residual self-interaction energy, which will make the Coulomb interaction overestimate and the electrons tend to be more delocalized, especially in d/f orbitals.

Why does the DFT not work?

HF approximation (without spin),

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Static correlation error (HF method also has this problem)

DFT is based on the single-electron approximation and puts the complex many-body correlation into the exchange correlation term. Both LDA and GGA functionals are fitted from the numerical results of the homogeneous electron gas model, which only depend on the local density and the gradient of the local density, ignoring the time and space fluctuations of complex many-body correlations. **The dynamic correlation effect of strongly correlated d/f electrons cannot be described.**

What can we do when DFT fails?

Many approaches have been proposed to address these deficiencies, such as,

- self-interaction corrected DFT, [Phys. Rev. B 23, 5048 (1981)]
- hybrid functionals, [J. Chem. Phys. 98, 5648 (1993)]
- the localized orbital scaling correction, [Natl. Sci. Rev. 5, 203 (2018)]
- fractional spin correction. [Proc. Natl. Acad. Sci. U. S. A. 115, 9678 (2018)]
- ...

The most popular method

The most popular approaches in solid-state physics are the combination of L(S)DA and GGAs

- with a simpler mean-field-type correction based on the Hubbard model (DFT+ U), [Phys. Rev. B 44, 943 (1991)]
- and with the non-perturbative manybody technique-dynamical mean-field theory (DMFT). [Phys. Rev. Lett. 62, 324 (1989)]

The basic idea of DFT+ U method

$$E_{\text{DFT}+U} = E_{\text{DFT}} - E_{\text{dc}} + E_U \quad (2)$$

Pickup artist

- E_{DFT} is the energy of density functional approximations at the level of L(S)DA or GGA.
- E_U is the Coulomb interaction energy due to strongly correlated electrons given by the **Hartree-Fock approximation to the multi-orbital Hubbard model**.
- The double counting term E_{dc} is subtracted here to discount the Coulomb interaction energy that is already included in DFT at an average level.

The E_U term: multi-orbital Hubbard model

The full electron-electron interaction can be written as,

$$\hat{H}_{\text{Hub}} = \frac{1}{2} \sum_{\{m\}} \sum_{\sigma\sigma'} \langle mm' | v_{\text{sc}} | m''m''' \rangle \hat{c}_m^{\sigma\dagger} \hat{c}_{m'}^{\sigma'\dagger} \hat{c}_{m''}^{\sigma'} \hat{c}_{m'''}^{\sigma} \quad (3)$$

Where the Coulomb interaction matrix elements are,

$$\langle mm' | v_{\text{sc}} | m''m''' \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_{m'}^*(\mathbf{r}') v_{\text{sc}}(\mathbf{r}, \mathbf{r}') \phi_{m''}(\mathbf{r}) \phi_{m'''}(\mathbf{r}') \quad (4)$$

And v_{sc} is the statically screened Coulomb potential, $\{m\}$ represent m, m', m'', m''' are the local orbital indices for d or f subshell.

The E_U term: Hartree-Fock approximation

Neglecting the spin-orbit coupling (SOC) effect, the **Hartree-Fock approximation** to the Hubbard Hamiltonian can be obtained by evaluating its expectation value within the symmetrical Kohn-Sham (KS) ground state $|0\rangle$.

$$\begin{aligned} E_U &= \langle 0 | \hat{H}_{\text{Hub}} | 0 \rangle \\ &= \frac{1}{2} \sum_{\{m\}, \sigma} \left(\langle mm' | v_{\text{sc}} | m'' m''' \rangle - \langle mm' | v_{\text{sc}} | m''' m'' \rangle \right) n_{m''m}^{\sigma} n_{m'''m'}^{\sigma} \\ &\quad + \frac{1}{2} \sum_{\{m\}, \sigma} \langle mm' | v_{\text{sc}} | m'' m''' \rangle n_{m''m}^{\sigma} n_{m'''m'}^{-\sigma} \end{aligned} \quad (5)$$

Where the $n_{mm'}^{\sigma}$ is the local occupation matrix given by,

$$n_{mm'}^{\sigma} = \langle 0 | \hat{c}_m^{\sigma\dagger} \hat{c}_m^{\sigma} | 0 \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{n, \mathbf{k}} f_{n\mathbf{k}}^{\sigma} \langle \psi_{n\mathbf{k}}^{\sigma} | m' \sigma \rangle \langle m \sigma | \psi_{n\mathbf{k}}^{\sigma} \rangle \quad (6)$$

The E_U term: rotationally invariant and diagonalize

Observations

- Since the E_U is a observable quantity, Eq. (5) must be rotationally invariable.
- The occupation number matrix n^σ is hermitian, one can always introduce a unitary transformation to diagonalize it.

$$E_U = \frac{1}{2}U \sum_{mm',\sigma} n_m^\sigma n_{m'}^{-\sigma} - \frac{1}{2}(U - J) \sum_{m \neq m',\sigma} n_m^\sigma n_{m'}^\sigma \quad (7)$$

$$U = \langle mm' | v_{\text{sc}} | mm' \rangle \quad (8a)$$

$$J = \langle mm' | v_{\text{sc}} | m'm \rangle \quad (8b)$$

Note that the self-interaction is absent in both Eq. (5) and Eq. (7).

The E_{dc} term: fully localized limit (FLL) scheme

The double counting term E_{dc} is an important portion of the DFT+ U theory. But the local/semi-local DFT are not orbit-resolved theories. Contributions from individual orbitals cannot be well separated.

Double counting schemes

By now, there are two main E_{dc} schemes used in DFT+ U calculation.

- One is called “around mean field (AMF)” scheme, which gives a better description for metallic system. [Phys. Rev. B 44, 943 (1991)]
- The other is called “fully localized limit (FLL)” scheme, which is more suitable for insulating system. [Phys. Rev. B 79, 035103 (2009)]

$$E_{\text{dc}}^{\text{FLL}} = \frac{1}{2}UN(N-1) - \frac{1}{2}J \sum_{\sigma} N^{\sigma}(N^{\sigma}-1). \quad (9)$$

The final expression for DFT+ U method

$$E_{\text{DFT}+U} = E_{\text{DFT}} - E_{\text{dc}} + E_U$$

$$E_U = \frac{1}{2}U \sum_{mm',\sigma} \mathbf{n}_m^\sigma \mathbf{n}_{m'}^{-\sigma} - \frac{1}{2}(U - J) \sum_{m \neq m',\sigma} \mathbf{n}_m^\sigma \mathbf{n}_{m'}^\sigma,$$

$$E_{\text{dc}} = \frac{1}{2}UN(N-1) - \frac{1}{2}J \sum_{\sigma} N^{\sigma}(N^{\sigma}-1).$$

Note that, $N = \sum_{\sigma} N^{\sigma} = \sum_{m,\sigma} \mathbf{n}_m^{\sigma}$. Then,

$$\begin{aligned} \Delta E_{\text{DFT}+U} &= E_{\text{DFT}+U} - E_{\text{DFT}} \\ &= \frac{1}{2}(U - J) \sum_{m,\sigma} (\mathbf{n}_m^{\sigma} - \mathbf{n}_m^{\sigma} \mathbf{n}_m^{\sigma}) \end{aligned} \quad (10)$$

Wait, are they?

If the parameters U and J are exact, then the self-interaction will be greatly eliminated.

What about the value of U and J ?

$$U = \langle mm' | v_{\text{sc}} | mm' \rangle, \quad J = \langle mm' | v_{\text{sc}} | m'm \rangle$$

Theoretically, U and J can be evaluated through Slater integrals, but the detailed form of the screened Coulomb interaction v_{sc} remains unknown.

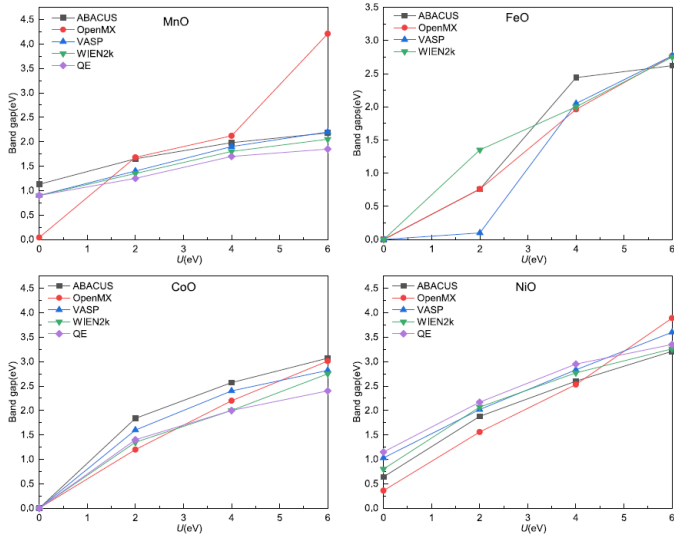
One may argue that we could set the v_{sc} as the Yukawa potential, $v_{\text{sc}} = e^{-\lambda|\mathbf{r}-\mathbf{r}'|}/|\mathbf{r}-\mathbf{r}'|$. But the thing is, there still will be one parameter λ that needs to be determined...

U and J in practical

In practical calculations, U and J are

- most commonly treated as adjustable parameters,
- or obtained via pragmatic schemes, such as
 - constrained DFT, [Phys. Rev. B 39, 1708 (1989)]
 - constrained random-phase approximation (RPA), [Phys. Rev. B 87, 165118 (2013)]
 - or linear-response approach. [Phys. Rev. B 71, 035105 (2005)]

DFT+ U in different packages



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- The traditional DFT calculation method has two errors, (i) delocalization error (DE), and (ii) static correlated error (SCE).
- The DE, which also called self-interaction error (SIE), is induced by the fact that density information alone cannot accurately describe the exchange term.
- In short, the $\text{DFT}+U$ is to make a HF approximation to the Hubbard model. It is simple, and efficient, but unrobust.
- The SCE is caused by the influence of quantum fluctuations with space and time. HF or $\text{DFT}+U$ method cannot avoid it. Only the DMFT method can solve this kind of error.