

DFT+ U modified code description

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I. BRIEF SUMMARY OF DFT+ U FORMALISM

The general form of DFT+ U (It has also been conventionally referred to as LDA+ U . However, to strictly distinguish LDA+ U and LSDA+ U , we used a term ‘‘DFT+ U ’’.) energy correction for a certain orbital can be expressed as:

$$E^U = E^{\text{int}} - E^{\text{dc}}, \quad (1)$$

where E^{int} and E^{dc} refers to the interaction energy and the double-counting term, respectively.

The E^{int} reads (for noncollinear scheme) [1, 2]:

$$E^{\text{int}} = \frac{1}{2} \sum_{\{m_i\}, \sigma, \sigma'} \{n_{m_1 m_2}^{\sigma\sigma} \langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle n_{m_3 m_4}^{\sigma'\sigma'} - n_{m_1 m_2}^{\sigma\sigma'} \langle m_1, m_3 | V_{ee} | m_4, m_2 \rangle n_{m_3 m_4}^{\sigma'\sigma} \}, \quad (2)$$

where $n_{m_1 m_2}^{\sigma\sigma'}$ are the elements of on-site density matrix (DM) \mathbf{n} for orbitals $\{m_i\}$ and spins σ, σ' ($\sigma, \sigma' = \uparrow$ or \downarrow). Simplification to collinear case is straightforward by taking $n_{m_1 m_2}^{\sigma\sigma'} = 0$ for $\sigma \neq \sigma'$.

The elements of on-site Coulomb interaction tensor can be expressed as [1, 3]:

$$\langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle = \sum_{\{m'_i\}} [S_{m_1 m'_1} S_{m_3 m'_3} \left\{ \sum_{k=0} \alpha_k(m'_1, m'_3, m'_2, m'_4) F^k \right\} S_{m'_2 m_2}^{-1} S_{m'_4 m_4}^{-1}], \quad (3)$$

with

$$\alpha_k(m'_1, m'_3, m'_2, m'_4) = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle Y_{l, m'_1} | Y_{k, q} Y_{l, m'_2} \rangle \langle Y_{l, m'_3} Y_{k, q} | Y_{l, m'_4} \rangle, \quad (4)$$

where α_k and F^k refers to Racah-Wigner numbers and Slater integrals, respectively [1, 3], and S is a transformation matrix from spherical harmonics (m'_i) to the predefined local basis (PAOs in OpenMX). Here $\langle Y_{l, m'_1} | Y_{k, q} Y_{l, m'_2} \rangle$ corresponds to the Gaunt coefficients and can be calculated by using Wigner-3j symbols. Conventional expression of Slater integrals which we follow are $U = F^0$, $J = (F^2 + F^4)/14$, and $F^4/F^2 = 0.625$ for d -orbitals. (U : Hubbard U / J : Hund’s coupling J).

There are several variations of double-counting term (E^{dc}). Most widely used are so-called ‘‘FLL’’ and ‘‘AMF’’ forms. For their detailed functional expressions, refer to Ref. 4 and references therein.

Once Eqs. 2 – 4 are computed, all the other processes are very similiar to the case of Dudarev’s scheme [5, 6].

II. SHORT EXPLANATION TO NEWLY ADDED AND MODIFIED CODES

Newly added source code is `Coulomb_Interaction.c` to generate Coulomb interaction tensor (Eq. 3). Modified codes are `Allocate_Arrays.c`, `Free_Arrays.c`, `Input_std.c`, `Occupation_Number_LDA_U.c`, `Total_Energy.c`, `openmx_common.h`, `outputfile.c`, `Set_Vpot.c`, `Set_XC_Grid.c`, `SetPara_DFT.c`, `Stress.c`, `XC_CA_LSDA.c`, `XC_PBE.c`, and `XC_PW92C.c`. I note that there are minor modifications in `Set_Vpot.c`, `Set_XC_Grid.c`, `SetPara_DFT.c`, `Stress.c`, `XC_CA_LSDA.c`, `XC_PBE.c`, and `XC_PW92C.c`. All modifications I made are traced with keyword, “S.Ryee”.

A. New input keywords

Followings are the newly added keywords for general DFT+ U calculations [4] and are compatible with the existing keywords, `scf.Hubbard.U` and `scf.Hubbard.Occupation`.

<code>scf.DFTU.Type</code>	2	# 1:Simplified(Dudarev) 2:General, default=1
<code>scf.dc.Type</code>	cFLL	# sFLL sAMF cFLL cAMF, default=sFLL
<code>scf.Slater.Ratio</code>	0.625	# default=0.625
<code>scf.Yukawa</code>	off	# default=off

Only by setting to `scf.DFTU.Type=2`, the other keywords (`scf.dc.Type`, `scf.Slater.Ratio`, `scf.Yukawa`) can be used. Also, to use `scf.DFTU.Type=2`, `scf.SpinPolarization` should be on or NC.

`scf.DFTU.Type=1` corresponds to using the existing DFT+ U implementation [6].

B. New source code; `Coulomb_Interaction.c`

Part for Slater integrals. This part is basically categorized into two choices; when using 1) standard way and 2) Yukawa-type potential. The second choice is activated only when `scf.Yukawa=on` in ‘*.dat’ file. However, either choice has the same purpose: to generate Eq. 3 via Slater integrals and Eq. 4.

1) In the standard way, Slater integrals are expressed as $F^0 = U$, $F^2 = J * 14 / (1.0 + \text{scf.Slater.Ratio})$, and $F^4 = \text{scf.Slater.Ratio} * F^2$ for d -orbital.

2) When using Yukawa-type potential, $F^0 = U$, and F^2 and F^4 are estimated from U [4], thus not requiring input J values. This process is realized by three functions, namely, ‘static double

Bessel_j', 'static double Bessel_h', and 'static double Integrate_Bessel'. For formal details, please refer to Ref. 4 or Ref. 7.

Part for calculation of Racah-Wigner numbers. Calculation of Eq. 4 is realized by the two functions 'static double Wigner3j' and 'static double Gaunt_SR'.

Finally, with given Slater integrals and Racah-Wigner numbers, Eq. 3 is generated through 'static double Coulomb_Matrix' using transformation matrix S (in Eq. 3) as expressed in function 'static dcomplex StoR'. This process is performed for every orbital having nonzero U or J . The generated Coulomb interaction tensor is stored in array named 'Coulomb_Array'.

C. Short note on 'cFLL' and 'cAMF' double-counting

Setting `scf.dc.Type` to `cFLL` or `cAMF` requires *charge-only* exchange-correlation (xc) energy of LDA (or GGA). Therefore, if `scf.dc.Type=sFLL` or `cAMF`, OpenMX will automatically enforces zero spin-polarization when using xc subroutines such as `Set_XC_Grid.c`, `XC_CA_LSDA.c`, `XC_PBE.c`, and `XC_PW92C.c`. Moreover, ignoring spin-polarization in xc energy is constrained to be activated for `SCF_iter` ≥ 2 , as numerical instability was found when it was done from the very beginning (`SCF_iter` ≥ 1).

III. TEST CALCULATIONS

The input files are included in the directory 'example'.

A. NiO

B. MnO

C. FeO noncollinear

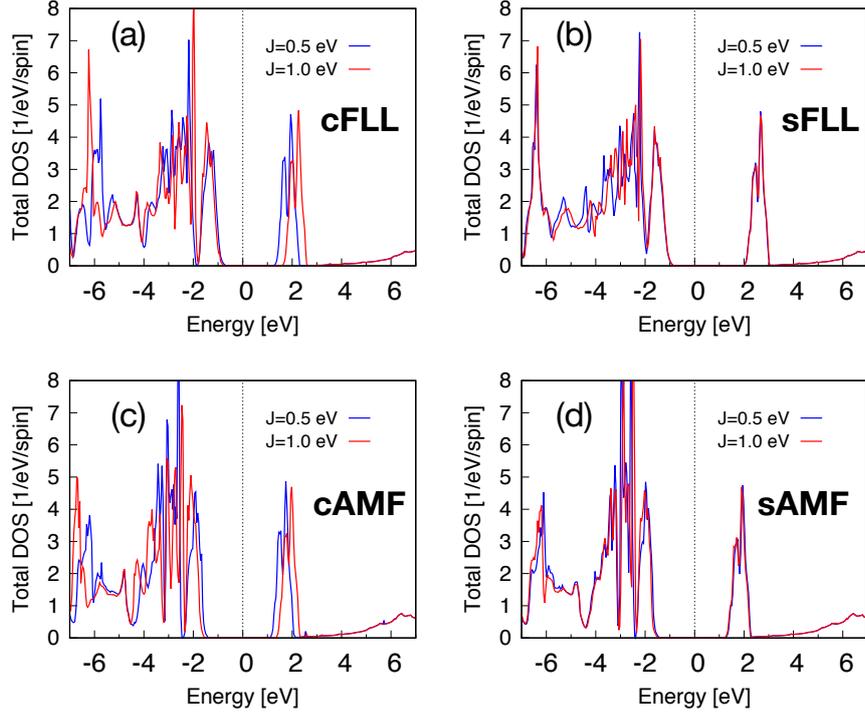


FIG. 1: The up-spin density of states of NiO by (a) cFLL, (b) sFLL, (c) cAMF, and (d) sAMF. U is fixed to 5 eV and $J = 0.5$ eV for blue lines and 1.0 eV for red lines.

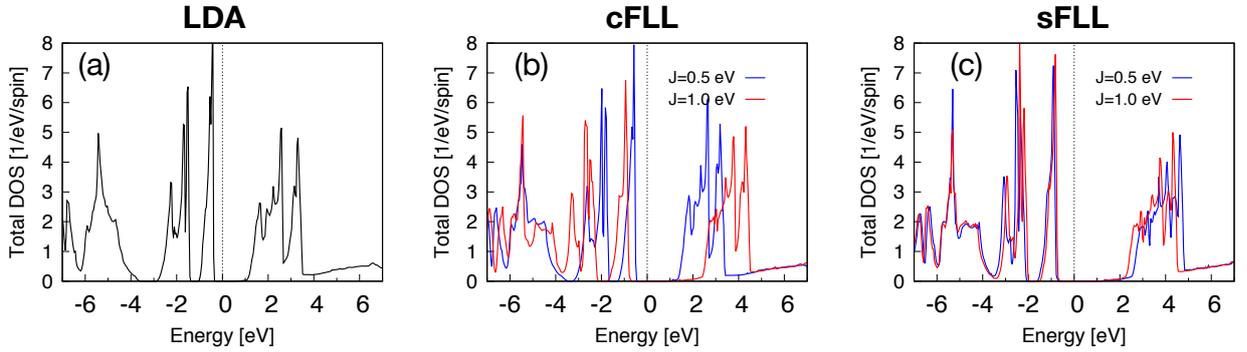


FIG. 2: The up-spin density of states of MnO by (a) LDA, (b) cFLL, and (c) sFLL. U is fixed to 3 eV and $J = 0.5$ eV for blue lines and 1.0 eV for red lines.

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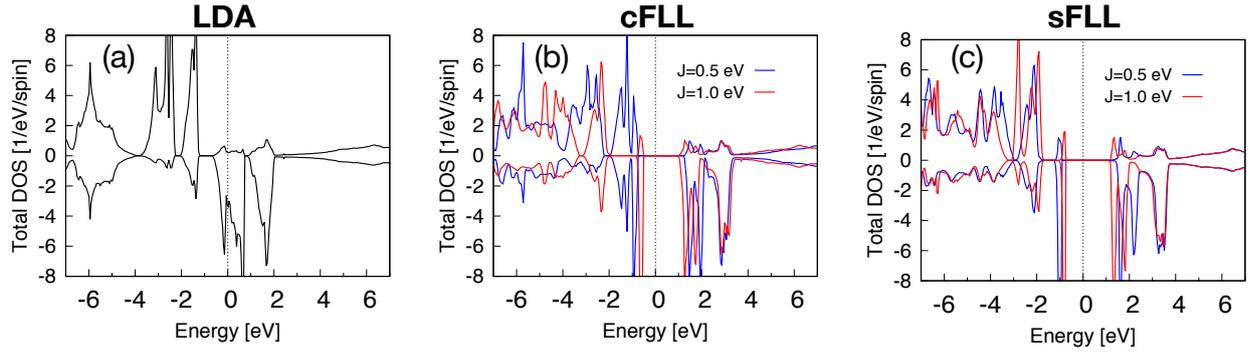


FIG. 3: The noncollinear up- and down-spin density of states of FeO by (a) LDA, (b) cFLL, and (c) sFLL. U is fixed to 4 eV and $J = 0.5$ eV for blue lines and 1.0 eV for red lines.

Type	J [eV]	spin moment [μ_B/Fe]	orbital moment [μ_B/Fe]
LDA	-	3.60	0.11
cFLL	0.5	3.80	0.85
	1.0	4.09	0.81
sFLL	0.5	3.99	0.79
	1.0	3.82	0.66

TABLE I: Calculated spin- and orbital-moment of FeO by LDA, cFLL, and sFLL. $U = 4$ eV for cFLL and sFLL. Mulliken population was used for all cases.

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