

Notes for users of DFT+ U (+ J) in ONETEP

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DFT+ U is fully and self-consistently implemented in ONETEP, together with a number of advanced ancillary functionalities. The method is linear-scaling with respect to system size, exhibiting no systematic tendency to slow convergence to the ground-state. DFT+ U in its conventional fixed-projector form introduces only a small increase in computational pre-factor with respect to the underlying exchange-correlation functional [1].

PLEASE NOTE: Seven columns are now required in the Hubbard block in order to allow for + J calculations. Older input files with six columns will not yield incorrect results, but the code will exit.

A very short introduction to DFT+ U

DFT+ U [2, 3, 4], also known as LDA+ U or LSDA+ U , is a method used to improve the description of so-called strongly correlated materials offered by DFT within conventional approximations for exchange-correlation (XC) such as the LSDA and σ -GGA, quantitatively and even qualitatively. These functionals, based on the locally-evaluated density and its gradients, can sometimes fail to reproduce the physics associated with localised orbitals of $3d$ and $4f$ character characteristic of conventionally-classed strongly correlated materials, a category consisting of not only first-row transition metals and their oxides, but also lanthanoid oxide materials, and other materials such as certain magnetic semiconductors and organometallic molecules.

Typically, the LDA and its extensions underestimate local magnetic moments and the tendency to favour high-spin ground-states in such materials, and the insulating gap in cases where it is related to electron localisation. Underestimation of the gap due to the absence, in the LDA, of the derivative discontinuity with respect to orbital occupancy in the exact XC-functional may be confounded by an underestimation of the exchange splitting induced by local magnetic moments.

The DFT+ U correction term is usually thought of as an explicit mean-field treatment of the exchange-correlation energy contributed by the correlated sites (subspaces projected out with functions of $3d$ and or $4f$ character)

within the Hubbard model, including a double-counting correction for that contribution already included in the LDA term. The flavour implemented in ONETEP is the basis-set independent, rotationally invariant quadratic penalty functional of Ref [5], defined by the additive energy correction

$$E_{DFT+U} [n^{(I)(\sigma)}] = \sum_{I\sigma} \frac{U^{(I)}}{2} \text{Tr} \left[\mathbf{n}^{(I)(\sigma)} \left(1 - \mathbf{n}^{(I)(\sigma)} \right) \right]. \quad (1.1)$$

Here, U is an estimate of the scalar screened density-density Coulomb repulsion between localised orbitals. The occupancy matrix of the correlated site I , for spin channel σ , is defined, in the case of orthonormal projector functions $\{|\varphi_m^{(I)}\rangle\}$, and density-matrix $\hat{\rho}^{(\sigma)}$, by

$$n_{mm'}^{(I)(\sigma)} = \langle \varphi_m^{(I)} | \hat{\rho}^{(\sigma)} | \varphi_{m'}^{(I)} \rangle. \quad (1.2)$$

Put simply, if the system under study comprises open $3d$ or $4f$ sub-shells, then there is a good chance that the LDA will find a minimum energy by partly occupying and leaving degenerate the Kohn-Sham orbitals strongly overlapping with these states, rather than splitting them into occupied and virtual Hubbard bands. This leads to an underestimation of the insulating gap and any associated magnetic order. In this case, the DFT+ U method can be used to penalise the non-integer occupancy of these orbitals, tending to fill states with occupancy greater than 0.5 and empty states with occupancy less than 0.5, as can be seen from the expression for the DFT+ U potential

$$\hat{V}_{DFT+U}^{(\sigma)} = \sum_I U^{(I)} |\varphi_m^{(I)}\rangle \left(\frac{1}{2} \delta_{mm'} - n_{mm'}^{(I)(\sigma)} \right) \langle \varphi_{m'}^{(I)}|. \quad (1.3)$$

The DFT+ U term may be considered as a correction which cancels the contribution to the energy arising due to the spurious self-interaction of a partially occupied orbital [5]. In this case, the U parameter is the curvature of the total energy with respect to the occupancy of the correlated manifold - which should be a piece-wise linear curve were Janak's theorem satisfied [6] - which can be computed using linear-response theory (among other methods such as constrained DFT) according to the prescription given in Refs. [5, 7].

How to activate DFT+ U in ONETEP

In order to activate the DFT+ U functionality, the **hubbard** block is added to the input file. For example, in the case of a system containing iron and cerium atoms incorrectly described by the exchange-correlation functional, which we suspect could benefit from the DFT+ U correction to improve the description of localisation, we might use the **hubbard block**:

!! species ¹	l ²	$U(\text{eV})$ ³	$J(\text{eV})$ ⁴	Z ⁵	$\alpha(\text{eV})$ ⁶	$\sigma(\text{eV})$ ⁷
% block hubbard						
Fe1	2	4.0	0.0	-10.0	0.00	1.0
Fe2	2	4.0	0.0	-10.0	0.00	-1.0
Ce1	3	6.0	0.0	-10.0	0.5	0.0
% endblock hubbard						

The columns of the **hubbard block** are described as follows:

1. The species label, e.g. *Fe1* for iron atoms of a first type in the cell, *Fe2* for iron atoms of a second kind, etc. Only the species to which orbitals to be corrected by DFT+ U are assigned should be listed in this block.
2. The angular momentum channel of the projectors used to delineate the strongly correlated sites on Hubbard atoms this type, e.g. $l = 2$ for *Fe1*. Conventionally, the radial quantum number $r = l + 1$ is used to generate atom-centred atomic projectors, so that $l = 2$ gives $3d$ orbitals, $l = 3$ gives $4f$ orbitals etc. (please get in contact if you need to use a $r \neq l + 1$ combination, or multiple sub-shells per atom).
3. The value of the Hubbard U for this sub-shell, in electron-volts. Most users will simply work with the value for U that they find corrects the band-gap or bond-lengths in the system they wish to study. Methods do, however, exist to estimate its value, for example the linear-response technique [5, 7], which is implemented in ONETEP.
4. The value of the Hund's exchange J for this sub-shell, in electron-volts. The rotationally invariant exchange corrective term described in detail in Ref. [8] is fully implemented in ONETEP (including forces etc), and activated for any $J \neq 0$.
5. This number Z selects how the radial part of the projector functions used to describe the $1s$, $2p$, $3d$ or $4f$ atomic orbitals entering the DFT+ U functional are defined. In the case that $\mathbf{Z} < \mathbf{0}$, a subset of the orbitals generated by solving the atomic problem subject to the pseudopotential for the species in question are chosen (in which case the projectors form a subset of the initial guesses for the ONETEP NGWFs); here the magnitude of the negative \mathbf{Z} makes no difference. In the case that $\mathbf{Z} > \mathbf{0}$, for more advanced users, this number is the effective charge divided by the ratio of effective masses used to generate projectors in the form of solutions to the hydrogenic Schrödinger equation. A good guess for this number might be the Clementi-Raimondi effective charge, tabulated in Refs. [9, 10], and the choice of radial profile does matter [11]. In both cases, the projectors are effectively

renormalised within an atom-centred sphere with the same radius as the NGWFs on that atom.

6. An additional potential acting on the subspace in question, the prefactor α is here entered in electron-volts. This is needed, for example, in order to locally vary the potential in order to determine the value of U which is consistent with the screened response in the system with linear-response theory [5, 7], or to break a spatial symmetry, such as in a mixed-valence system. In the example given, we are additionally penalising the occupancy on cerium $4f$ atomic orbitals.
7. The spin-splitting factor, in electron-volts, which is deducted from the α factor for the spin-up channel and added to α for the spin-down channel. In the example shown here we're promoting spin-up magnetisation for iron atoms $Fe1$, and spin-down for $Fe2$. This can be very useful for appropriately breaking magnetic symmetries in antiferromagnetic solids or open-shell singlet molecules, or for estimating the magnetic susceptibility or exchange coupling.

N.B. Users may find the DFT+ U functionality useful in cases of systems even when the DFT+ U correction is not needed (setting the all U parameters to zero does not disable the functionality). The implementation offers a very inexpensive method for carrying out carefully-defined atom-centred atomic population analysis, or breaking symmetries in spin or charge ordered systems.

Compatibility

The DFT+ U functionality is fully compatible with almost all other parts of the ONETEP code, such as listed below, since it simply involves an additional term in the Hamiltonian and ionic forces. Please get in touch first if you would like to use a more exotic combination of these functionalities:

1. Total-energy minimisation and ionic forces
2. Geometry optimisation, molecular dynamics and phonon calculations
3. All other functionals including hybrids and Van der Waals functionals
4. Implicit solvation
5. The PAW formalism and ultrasoft pseudopotentials
6. Constrained DFT
7. Local density of states (including a correlated subspace decomposition)
8. Natural bond orbital calculations

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9. Conduction-band optimisation and Fermi’s Golden Rule spectra
 10. Calculations of changes in electric polarisation
 11. Time-dependent DFT
 12. Electronic transmission calculations

The extension of the DFT+ U implementation to cluster Dynamical mean-field theory has also been implemented in ONETEP; for an example of its capabilities see Ref. [12].

Using NGWFs and projector self-consistency

Any reasonable set of localised atomic-like functions may, in principle, be used for the projectors defining the correlated subspaces in DFT+ U ; the choice is somewhat arbitrary and the description “atomic orbitals” does not uniquely define them. One possible approach is to use Wannier functions for the Kohn-Sham orbitals, so that the correlated subspaces are proper subspaces of the Kohn-Sham Hilbert space. Indeed, there is numerical evidence to suggest that Maximally Localised Wannier Functions (MLWFs) [13, 14], in particular, provide a basis that maximises a particular measure of the on-site Coulomb repulsion [15], and MLWFs are in common use as a minimal basis with which to construct tight-binding models from first-principles.

In ONETEP, a set of variationally-optimised nonorthogonal generalised Wannier functions (NGWFs) are generated as a by-product of total-energy minimisation. NGWFs exhibit some similar properties to MLWFs and other flavours of localised Wannier functions, and, for example, can be used to calculate finite-difference response properties in a similar way [16]. As they are conveniently available in ONETEP, we have made it possible to re-use the NGWFs from the end of a ground-state calculation as a set of Hubbard projectors with which to define the DFT+ U correction. For this, it was necessary to develop a tensorially-consistent formulation of DFT+ U in order to accommodate nonorthogonal projector functions [17]; projector nonorthogonality for a given subspace is automatically compensated for.

In order to ensure that NGWFs with appropriate symmetry are chosen as Hubbard projectors for a given atom, those n NGWFs $|\phi_\alpha\rangle$ that maximise $\sum_{m,\alpha}^n \langle \varphi_m | \phi_\alpha \rangle \langle \phi_\alpha | \varphi_m \rangle$, for a given set of n hydrogenic orbitals $|\varphi_m\rangle$, defined in the **hubbard** block, are selected for the task. The keyword **hubbard_max_iter**, (defaulting to 0), sets the task to **HUBBARDSCF**, which performs a self-consistency cycle over the Hubbard projectors, demonstrated in Refs. [11, 17]. The density from one minimisation is re-used at the beginning of the next, and setting **hubbard_max_iter** to 2 one can carry out a DFT+ U calculation using the LDA NGWFs as projectors.

The keywords `hubbard_energy_tol`, `hubbard_conv_win`, and `hubbard_proj_mixing` are used to manage the Hubbard projector self-consistency cycle. For convergence, the ground state energy must deviate less than `hubbard_energy_tol` (defaulting to $10^{-8}Ha$) from one `HUBBARDSCF` iteration to the next, over `hubbard_conv_win` (defaulting to 2) iterations. A fraction `hubbard_proj_mixing` (defaulting to 0.0) of the previous Hubbard projectors may be mixed with the new ones in order to accelerate the procedure, although this has never been found to be necessary. Setting `hubbard_proj_mixing` to a negative value causes the projectors to be read in from a `.tightbox_hub_projs` file, for restarting a `HUBBARDSCF` calculation or for a variety of post-processing tasks.

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