

The Hubbard Correction May Not Be Needed Where It Is Commonly Used and May Be Useful Where One Would Not Expect

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Commonly used GGA DFT functionals often fail to correctly describe the electronic structure of strongly correlated materials like transition metal oxides (TMO). Even in materials not considered as strong correlated, erroneous band gaps, ordering of states and ordering of energies of different polymorphs can result. This issue is well known, and Hubbard (U) correction is often employed to adjust for the strong on-site electron-electron repulsion. The values for U, frequently chosen to match experimental properties, are not transferable between codes due to the different projection operators employed. The bulk of ab initio results in particular on TMOs are obtained with plane-wave bases, often applying Hubbard corrections of several eV on TM *d* orbitals.

We used an established approach to tune U to reproduce experimental TMO thermochemistry with localized pseudo-atomic orbitals and a GGA density functional. We find the values for U to be significantly lower than their commonly reported plane-wave counterparts, only mildly affecting electronic structure and energetics compared to the uncorrected GGA results, *and we obtained qualitatively correct electronic structure without the U correction* including localized gap states in several oxides [1-3] and correct ordering of valence band states in NiO (the classic test case for GGA errors) [3]. This was observed with different codes, with or without (full-potential) pseudopotentials. The ubiquitous use of plane wave DFT codes may therefore have distorted the perception of functional behavior and of the need for U.

On the other hand, the Hubbard correction maybe useful (with plane wave or localized basis sets) on *s* or *p* states to effectively correct bandstructure errors in GGA functionals which may lead to incorrect ordering of states or of energies between phases. This will be shown on the examples of organic molecules and phases of tin [4-5].

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