



The LSDA+ U Method

F. Essenberger, S. Sharma

The description of strongly correlated systems is a difficult task. Conventional density functional theory (DFT) calculations, using local/semi-local exchange-correlation functionals, cannot really capture strong Mott localizations [1]; Mott insulators when treated with these exchange-correlation-functionals and without any long range magnetic order, show a metallic ground state.

Over the years many ideas were developed to treat strongly correlated systems. Among them, most prominent within the frame-work of DFT are self-interaction-corrected local spin density approximation (SIC-LSDA) [2], hybrid functionals[3] and LSDA+ U . Out of these methods LSDA+ U is particularly useful as it is computationally less demanding and hence can easily be used for larger systems of modern day interest. Furthermore, with LSDA+ U it is possible to systematically increase the strength of the on-site repulsion U in order to gain insight into the effect of Coulomb correlations. The total energy in the LSDA+ U method consists of the LSDA total energy plus a ‘Hubbard-like’ term [4]:

$$E^{\text{LSDA}+U} = E^{\text{LSDA}}[\rho] + \frac{1}{2} \sum_I \sum_{\sigma} \sum_{\{m_i\}} [n_{m_1 m_3}^{I\sigma} n_{m_2 m_4}^{I-\sigma} \langle I, m_1 m_2 | \hat{v} | I, m_3 m_4 \rangle - n_{m_1 m_3}^{I\sigma} n_{m_2 m_4}^{I\sigma} (\langle I, m_1 m_2 | \hat{v} | I, m_4 m_3 \rangle - \langle I, m_1 m_2 | \hat{v} | I, m_3 m_4 \rangle)], \quad (1)$$

where $|I, m\sigma\rangle$ are localized atomic orbital at lattice site I , angular momentum m and spin component σ . The occupation number matrix elements, $n_{m_1 m_3}^{I\sigma}$, are defined as:

$$n_{mm'}^{I\sigma} := \sum_i^{\text{occ}} \langle \varphi_i | I, m\sigma \rangle \langle I, m'\sigma | \varphi_i \rangle. \quad (2)$$

A major problem within the LSDA+ U method is that the electronic interactions are already partially included in the LSDA energy thus a simple addition of the ‘Hubbard-like’ term to the LSDA energy would lead to double counting (DC) errors. Hence, a extra “DC term” is subtracted from the LSDA+ U total energy to avoid this error. An ideal DC term

should subtract the mean field part from the ‘Hubbard-like’ term; leaving only an orbital dependent correction to the orbital independent LSDA potential [5].

There is no rigorous way to construct a DC term, the usual approaches include the fully localized limit (FLL), around mean field (AMF) and interpolations between these two [5]. The FLL-DC term is derived from Eq. (1) by taking the limit of fully occupied orbitals *i.e.* $n_{mm'}^{I\sigma} = \delta_{mm'}$ and approximating the matrix elements by averaged values U^I and J^I , leading to the following energy correction ($N^I = \sum_{\sigma} N^{I\sigma} = \sum_m n_{mm}^{I\sigma}$):

$$E^{\text{FLL-DC}} = \sum_I \left[\frac{U^I}{2} N^I (N^I - 1) - \frac{J^I}{2} \sum_{\sigma} N^{I\sigma} (N^{I\sigma} - 1) \right]. \quad (3)$$

One could use the bare Coulomb interaction in the evaluation of the matrix elements in Eq. (1) and for the determination of U^I and J^I . But this would totally neglect screening effects, which are important in solid states. For the Coulomb interaction the matrix elements can be written as a product of real prefactors a_k and Slater integrals F_k^I :

$$\langle I, m_1 m_2 | \hat{v} | I, m_3 m_4 \rangle = \sum_{k=0}^{2l} a_k (m_1 m_3 m_2 m_4) F_k^I, \quad (4)$$

$$a_k (m_1 m_3 m_2 m_4) = \begin{cases} 0 & \text{if } k \text{ is odd} \\ \text{given by Eq. (7) in Ref. [10].} & \end{cases} \quad (5)$$

This means, that only the Slater integrals F_k^I with even k are needed in Eq. (4). The Slater integrals represent the radial part of the Coulomb interaction, which is mostly affected by screening effects. Hence, they are replaced by ‘‘screened Slater integrals’’ $\{S_0^I, S_2^I, \dots, S_{2l}^I\}$. These parameters are chosen in such a way that they allow for many body (screening) effects. In practice these screened Slater integrals are usually re-expressed in terms of only two parameters:

1. U^I the screened averaged Coulomb on site repulsion
2. J^I the screened exchange interaction.

Note, that the DC term in Eq. (3) is already expressed in terms of U^I and J^I . If the orbital quantum number l is two or greater, additional conditions are needed to ensure a unique map between $\{S_0^I, S_2^I, \dots, S_{2l}^I\}$ and $\{U^I, J^I\}$. The TMOs are such a case, because the

transition metals have partially filled d -shells ($l = 2$). For isolated transition metal atoms the ratio of the Slater integral $\frac{F_4^I}{F_2^I}$ is constant with good accuracy (between 0.62 and 0.63)[6]. Screening should effect F_4^I and F_2^I in equal measure, hence the ration $\frac{S_4^I}{S_2^I} = 0.625 = \frac{5}{8}$ is used to obtain the relations: $S_0^I = U^I$, $S_2^I = \frac{112}{13}J^I$ and $S_4^I = \frac{70}{13}J^I$. The two main approaches for determining the values of U^I and J^I are:

1. To chose the parameter in such a way to reproduce as many experimental observables as possible. This approach is frequently applied to large systems, where calculation of U^I and J^I is difficult.
2. To calculate the parameters U^I and J^I *ab-initio*. This brings the ‘first principle’ character back to the LSDA+ U method. (But the construction of a DC term is still not unique)

For such a calculation two schemes are used: (1) Originally the value of U^I was chosen based on a constrained LSDA calculation[7] and (2) A newer method is the linear response approach, which leads to smaller values of U^I compared to constrained LSDA [8].

The LSDA+ U method has proved to be able to reproduce the correct band structure for the Mott insulators [7]. These materials have a partially filled d (or f) shell, and a $d-d$ (or $f-f$) band gap. The gap is caused by a large on-site Coulomb repulsion which splits the d (or f) bands in a lower (occupied) and upper (unoccupied) Hubbard band. This mechanism is captured by the LSDA+ U method. Bands with mainly d (or f) character are shifted down in energy if $n_{mm}^{I\sigma} > 0.5$ and shifted up if $n_{mm}^{I\sigma} < 0.5$. The magnitude of the energy shift is proportional to the value of U . By increasing the Coulomb repulsion the d (or f) states around the Fermi level are shifted either up or down and a gap opens. This can be seen in Fig. (1) for the four TMOs, which are prototypical Mott insulators.

Not only ground state properties like the gap, magnetic moment or charge distribution are effected by the U , also excitations like magnons or phonons change [9]. In Fig. (1) the magnon spectrum for three TMOs is shown. The magnon energies are suppressed with increasing U , which is due to enhanced charge localization around the transition metal atoms [10].

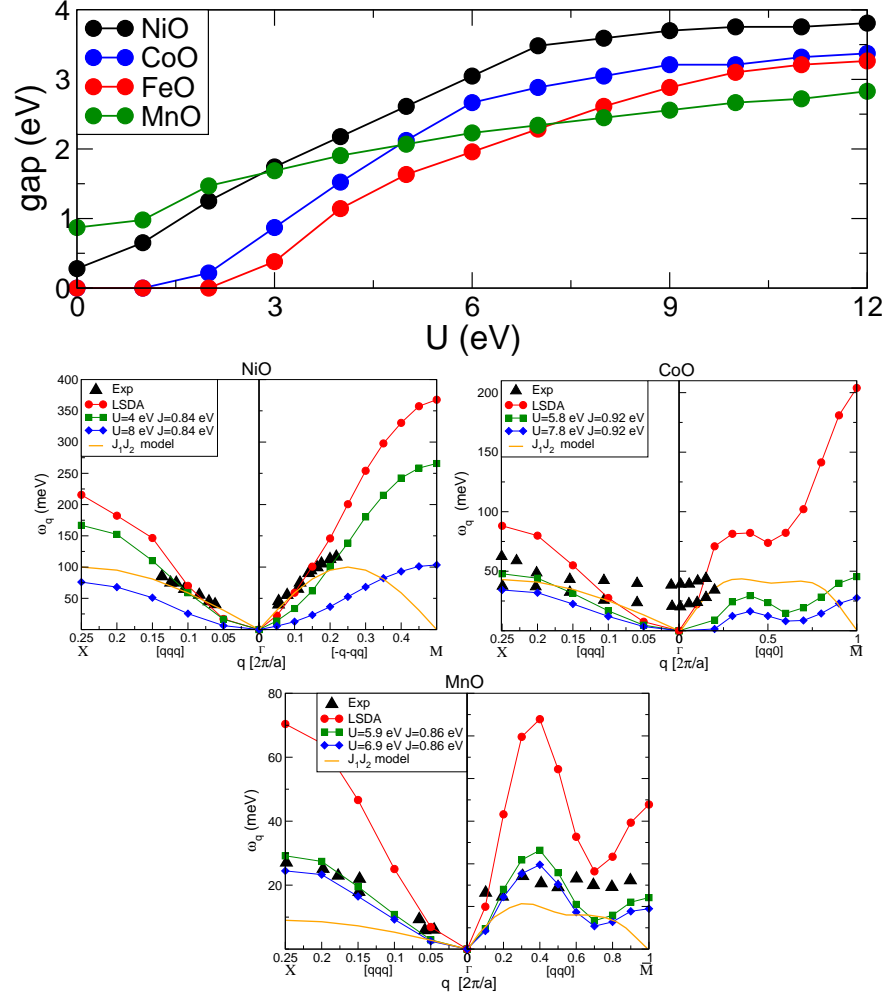


Figure 1: (Top) Opening of a gap due to on-site Coulomb repulsion in the TMOs. (Bottom) Magnon spectrum for NiO, CoO and MnO. LSDA results are shown with red circles, the two different values of U with green squares and blue diamonds, experiment [11–13] with black triangles and the J_1J_2 results [14] with orange line.

-
- [1] P. Mori-Sanchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **100**, 146401 (2008).
 - [2] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993).
 - [3] C. Rödl, F. Fuchs, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **79**, 235114 (2009).
 - [4] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
 - [5] F. Bultmark, F. Cricchio, O. Grånäs, and L. Nordström, Phys. Rev. B **80**, 035121 (2009).
 - [6] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B **42**, 5459

(1990).

- [7] V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Phys. Rev. B* **44**, 943 (1991).
- [8] M. Cococcioni and S. de Gironcoli, *Phys. Rev. B* **71**, 035105 (2005).
- [9] A. Floris, S. de Gironcoli, E. K. U. Gross, and M. Cococcioni, *Phys. Rev. B* **84**, 161102 (2011).
- [10] F. Essenberger, S. Sharma, J. K. Dewhurst, C. Bersier, F. Cricchio, L. Nordström, and E. K. U. Gross, *Phys. Rev. B* accepted (2011).
- [11] M. T. Hutchings and E. J. Samuelsen, *Phys. Rev. B* **6**, 3447 (1972).
- [12] S. Tomizasu, K. Itoh, *JPSJ* **75**, 084708 (2006).
- [13] G. Pepy, *J. Phys. Chem. Solids* **35**, 433 (1973).
- [14] G. Fischer, M. Däne, A. Ernst, P. Bruno, M. Lüders, Z. Szotek, W. Temmerman, and W. Herger, arXiv:0905.0391 (2009).