Expression for total energy in LDA+U methods

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I. LDA TOTAL ENERGY

Total energy as given by Singh [1] eq. (2.1.3) is

$$E_0 = T_{S,0} + E_{ei} + E_H + E_{ii} + E_{XC} \tag{1}$$

where:
$T_{S,0}$ is the kinetic energy,
E_{ei} is Coulomb electron-nuclei interaction,
E_H is the Hartree energy

$$E_H = \frac{e^2}{2}\int d\vec{r}d\vec{r}\,'\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \tag{2}$$

E_{ii} is the nuclei-nuclei Coulomb interaction, and
E_{XC} is the exchange correlation energy

Corresponding Kohn-Sham equation is (Singh eqs. 2.1.6-2.1.9)

$$(T + V_{ei} + V_H + V_{XC})\varphi_i = \epsilon_i\varphi_i \tag{3}$$

with

$$V_H(\vec{r}) = e^2\int d\vec{r}\,'\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \tag{4}$$

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}}{\delta\rho} \tag{5}$$

and

$$\rho = \sum_{occ}\varphi_i^*\varphi_i \tag{6}$$

To express the kinetic energy $T_{S,0}$ in (1) using $\sum_{occ}\epsilon_i$, equation (3) is multiplied from left by φ_i^*, integrated over $\vec{r}$ and summed over occupied orbitals. The result is:

$$T_{S,0} = \sum_{occ}\epsilon_i - \int d\vec{r}\rho(\vec{r})[V_{ei} + V_H + V_{XC}] \tag{7}$$

This expression is then substituted to (1). Taking into account that

$$E_{ei} = \int d\vec{r}\rho(\vec{r})V_{ei};\quad E_H = \frac{1}{2}\int d\vec{r}\rho(\vec{r})V_H \tag{8}$$

$$\tilde{E}_0 = \sum_{occ}\epsilon_i + E_{ii} + E_{XC} - \int d\vec{r}\rho(\vec{r})[\frac{1}{2}V_H + V_{XC}] \tag{9}$$

which is the desired expression (Singh 2.2.2). The tilde upon E_0 means that $T_{S,0}$ was replaced by $\sum_{occ}\epsilon_i$. The above derivation assumes the non-spin polarized calculation, but the generalization for the spin-polarized problems is straightforward and obvious.

II. LDA+U TOTAL ENERGY

First we assume (general case will be treated afterwards) that:

- Density matrix is diagonal.
- U is the same for all Coulomb interaction ($U_{ij} \equiv U$) and J is the same for all exchange interaction ($J_{ij} \equiv J$).

In the LDA+U methods the total energy may be written as:

$$E = E_0 + E_{LDA+U} \tag{10}$$

A. LDA+U^{DFT}

In the AMF (Around Mean Field) method of Czyzyk and Sawatzky [2] which is also the method we prefer now and call LDA+U^{DFT}:

$$E_{LDA+U} = -\frac{U-J}{2}\sum_{iat}\sum_{m=-l}^{l}\sum_{\sigma=\uparrow,\downarrow}(n_{m,\sigma} - \bar{n}_\sigma)^2 \tag{11}$$

where the first sum is over atoms selected for the LDA+U correction , $n_{m,\sigma}$ is occupation of the $|l, m, \sigma\rangle$ orbital, and

$$\bar{n}_\sigma = \frac{1}{2l+1}\sum_{m=-l}^{l} n_{m,\sigma} \tag{12}$$

is the average number of electrons in orbital with spin σ.

The potential which corresponds to E_{LDA+U} may be written as

$$V_{LDA+U} = \sum_{iat}\sum_{m,\sigma}|m,\sigma\rangle v_{m,\sigma}\langle m,\sigma| \tag{13}$$

with

$$v_{m,\sigma} = \frac{\partial E_{LDA+U}}{\partial n_{m,\sigma}} = -(U-J)(n_{m,\sigma} - \bar{n}_\sigma). \tag{14}$$

Kohn-Sham equation is now:

$$(T + V_{ei} + V_H + V_{XC} + V_{LDA+U})\varphi_i = \epsilon_i\varphi_i. \tag{15}$$

The kinetic energy in presence of the LDA+U potential is:

$$T_S = T_{S,0} - \sum_{occ}\langle\varphi_i|V_{LDA+U}|\varphi_i\rangle. \tag{16}$$

Taking into account that V_{LDA+U} is nonzero only within the atomic spheres of selected atoms:

$$T_S = T_{S,0} - \sum_{m,\sigma} \sum_{occ} |\langle \varphi_i | m, \sigma \rangle|^2 v_{m,\sigma} = T_{S,0} - \sum_{m,\sigma} n_{m,\sigma} v_{m,\sigma} \tag{17}$$

The expression for the total energy is now:

$$\tilde{E} = \tilde{E}_0 + E_{LDA+U} - \sum_{m,\sigma} n_{m,\sigma} v_{m,\sigma} \tag{18}$$

Finally, inserting (11),(14) in (18) we get

$$\tilde{E} = \tilde{E}_0 + \frac{U-J}{2} \sum_{m,\sigma} (n_{m,\sigma}^2 - \bar{n}_\sigma^2) \tag{19}$$

which is the same as:

$$\tilde{E} = \tilde{E}_0 + \frac{U-J}{2} \sum_{m,\sigma} (n_{m,\sigma} - \bar{n}_\sigma)^2 \tag{20}$$

Note that the results is an analog of the double correction term for the Hartree energy (compare eqs. 3, 8). This is not surprising, as it is a consequence of the fact that Hartree energy is quadratic function of density and E_{LDA+U} is quadratic in occupation numbers.

B. LDA+U^{SIC}

In the method we call LDA+U^{SIC} (Anisimov et al. [3], Solovyev et al. [4], Liechtenstein et al. [5], Shick et al. [6], also 'atomic limit' version of Czyzyk and Sawatzky [2]):

$$E_{LDA+U} = E^{ee} - E^{dc} \tag{21}$$

where E_{ee} is the mean field approximation to the electron-electron interaction in the spherically symmetrical atom, E^{dc} is the double counting correction. Using the same approximations as in preceeding subsection:

$$E^{ee} = \frac{U}{2} N^2 - \frac{J}{2} \sum_\sigma N_\sigma^2 - \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 \tag{22}$$

where N is the total number of electrons, N_σ is the total number of electrons with spin σ:

$$N_\sigma = \sum_m n_{m,\sigma}; \quad N = N_\uparrow + N_\downarrow. \tag{23}$$

The double summation term is:

$$E^{dc} = \frac{U}{2} N(N-1) - \frac{J}{2} \sum_\sigma N_\sigma (N_\sigma - 1) \tag{24}$$

and

$$E_{LDA+U} = \frac{U-J}{2} (N - \sum_{m,\sigma} n_{m,\sigma}^2). \tag{25}$$

additional potential, which corresponds to this energy is given by (13) with:

$$v_{m,\sigma} = \frac{U-J}{2} (1 - 2n_{m,\sigma}) \tag{26}$$

Proceeding as in the above subsection we get:

$$\tilde{E} = \tilde{E}_0 + \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 \tag{27}$$

If $U_{ij} \equiv U$, $J_{ij} \equiv J$ and $n_{i,j,\sigma} \equiv n_{i,\sigma} \delta_{i,j}$ is substituted in eq. 23 of Shick et al. [6], identical result is obtained.

C. LDA+U^{DFT} - general case

To simplify the equations we introduce the notation:

$$\tilde{n}_{m,m',\sigma} = n_{m,m',\sigma} - \bar{n}_{m,m,\sigma} \delta_{m,m'} \tag{28}$$

where $n_{m,m',\sigma}$ is (m,m') element of the occupation number matrix with spin σ. E_{LDA+U} is then

$$E_{LDA+U} = \frac{1}{2} \sum_{m_1,m_2,m_3,m_4}^{\sigma,\sigma'} \tilde{n}_{m_1,m_2,\sigma} \tilde{n}_{m_3,m_4,\sigma'} \{ \langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle - \langle m_1, m_3 | V_{ee} | m_4, m_2 \rangle \delta_{\sigma,\sigma'} \} \tag{29}$$

with

$$\langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle = \sum_k a_k(m_1, m_2, m_3, m_4) F_k;$$

$$a_k(m_1, m_2, m_3, m_4) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm_1 | Y_{kq} | lm_2 \rangle \langle lm_3 | Y_{kq}^* | lm_4 \rangle \tag{30}$$

The potential (14) now becomes a matrix with its (m,m') element:

$$v_{m_1,m_2,\sigma} = \sum_{m_3,m_4,\sigma'} \tilde{n}_{m_3,m_4,\sigma'} \{ \langle m_1, m_3 | V_{ee} | m_2, m_4 \rangle - \langle m_1, m_3 | V_{ee} | m_4, m_2 \rangle \delta_{\sigma,\sigma'} \} \tag{31}$$

The expression for the kinetic energy is:

$$T_S = T_{S,0} - \sum_{m_1,m_2,\sigma} v_{m_1,m_2,\sigma} \sum_{occ} \langle \varphi_i | m_1, \sigma \rangle \langle m_2, \sigma | \varphi_i \rangle \tag{32}$$

Noting that

$$\sum_{occ} \langle \varphi_i | m_1, \sigma \rangle \langle m_2, \sigma | \varphi_i \rangle = n_{m_2,m_1,\sigma} \tag{33}$$

the total energy, in which kinetic energy was replaced by the sum over eigenvalues, is rewritten as:

$$\tilde{E} = \tilde{E}_0 + E_{LDA+U} - \sum_\sigma Tr\{ n_\sigma v_\sigma \} \tag{34}$$

which is the final result to be used to calculate the total energy in the rotationally invariant LDA+U^{DFT} scheme.

D. LDA+U^{SIC} - general case

Expression (34) should be correct whatever is the form of the potential v_σ. As the trace is invariant with respect to the unitary transformation, the representation in which $n_{m,m',\sigma}$ is diagonal may be used, without lost of generality. Otherwise we follow Shick et al. [6] (SLP in what follows), as only in this paper the expression for $\tilde{E}$ is given. To make connection with above sections we denote:

$$\begin{aligned} U_{mm'} &= U + u_{mm'}; \\ J_{mm'} &= J + j_{mm'}, m \neq j, \\ J_{mm'} &= U + j_{mm}, m = j,\ j_{mm} = u_{mm} \end{aligned} \tag{35}$$

The energy E^{ee} (eq. 22, SLP eq. 2) is then

$$E^{ee} = \frac{1}{2} \sum_{m,m'}^{\sigma,\sigma'} \{U_{mm'} - J_{mm'}\delta_{\sigma,\sigma'}\} n_{m,\sigma} n_{m',\sigma'} \tag{36}$$

Using (35) this becomes

$$E^{ee} = \frac{U}{2} N^2 - \frac{J}{2} \sum_\sigma N_\sigma^2 - \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 + e \tag{37}$$

where e is given by (e=0, if $u_{m,m'} = j_{m,m'} = 0$)

$$e = \frac{1}{2} \sum_{m,m'}^{\sigma,\sigma'} \{u_{mm'} - j_{mm'}\delta_{\sigma,\sigma'}\} n_{m,\sigma} n_{m',\sigma'} \tag{38}$$

Double counting energy is still given by (24) so that

$$E^{ee} - E^{dc} = \frac{N}{2}(U-J) - \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 + e \tag{39}$$

According to eqs. (23-24) of SLP the energy $\tilde{E}$ is:

$$\tilde{E} = \tilde{E}_0 - E^{ee} + E^{dc} + \frac{1}{2}(U-J)N \tag{40}$$

inserting (39) we get

$$\tilde{E} = \tilde{E}_0 + \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 - e \tag{41}$$

Now we come to our derivation. The potential (SLP eq. 16) is:

$$\begin{aligned} v_{m,\sigma} = \sum_{m',\sigma'} & (U_{m,m'} - J_{m,m'}\delta_{\sigma,\sigma'}) n_{m',\sigma'} \\ & -U(N - \frac{1}{2}) + J(N_\sigma - \frac{1}{2}) \end{aligned} \tag{42}$$

Using the same notation as above

$$v_{m,\sigma} = (U-J)(\frac{1}{2} - n_{m,\sigma}) + w_{m,\sigma} \tag{43}$$

where

$$w_{m,\sigma} = \sum_{m',\sigma'} (u_{m,m'} - j_{m,m'}\delta_{\sigma,\sigma'}) n_{m',\sigma'} \tag{44}$$

trace of $(v_\sigma n_\sigma)$ is

$$Tr(v_\sigma n_\sigma) = (U-J)(\frac{1}{2} N_\sigma - \sum_m n_{m,\sigma}^2) + Tr(w_\sigma n_\sigma) \tag{45}$$

So that using (34) we get the result

$$\begin{aligned} \tilde{E} = \tilde{E}_0 &+ \frac{N}{2}(U-J) \\ &- \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 + e \\ -\frac{N}{2}(U-J) &+ (U-J) \sum_{m,\sigma} n_{m,\sigma}^2 \\ &- \sum_\sigma Tr(w_\sigma n_\sigma) \end{aligned} \tag{46}$$

which reduces to

$$\tilde{E} = \tilde{E}_0 + \frac{U-J}{2} \sum_{m,\sigma} n_{m,\sigma}^2 + e - \sum_\sigma Tr(w_\sigma n_\sigma) \tag{47}$$

Noting that

$$e = 2 \sum_\sigma Tr(w_\sigma n_\sigma) \tag{48}$$

we get the same result as SLP (see eq. 41, SLP eq. 23-24).

III. CONCLUSION

To calculate the total energy in the LDA+U method, in case the sum over eigenvalues is used instead of the kinetic energy, we recomend to use the equation:

$$\tilde{E} = \tilde{E}_0 + E_{LDA+U} - \sum_\sigma Tr\{n_\sigma v_\sigma\} \tag{49}$$

This formula holds for any LDA+U potential which may be written in the form

$$V_{LDA+U} = \sum_{iat} \sum_{m,m'\sigma} |m,\sigma\rangle v_{m,m',\sigma} \langle m',\sigma|, \tag{50}$$

in particular for both 'DFT' and 'SIC' methods. Moreover, it is rotationally invariant and may be easily implemented.

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