LDA+U, energy and potential, why there is spin nondiagonal part and what is its form

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I. ELECTRON REPULSION AND DENSITY MATRIX

Let

$$W = \frac{1}{2}\sum_{i\neq j} w(i,j);\;\; w(i,j) = \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

is a two-electron repulsion and

$$\Psi = \mathcal{A}\{\psi_{i_1}(1), \psi_{i_2}(2)...\psi_{i_n}(n)\}$$

is a Slater determinant wave function. Then the expectation value of W in state Ψ is

$$\langle\Psi|W|\Psi\rangle = \frac{1}{2}\sum_{i,j}[\langle\psi_i(1)\psi_j(2)|w(1,2)|\psi_i(1)\psi_j(2)\rangle - \langle\psi_i(1)\psi_j(2)|w(1,2)|\psi_i(2)\psi_j(1)\rangle]. \tag{1}$$

The first and second term in this equation correspond to direct and exchange interaction, respectively.

In the solid state electron structure calculation the one-electron wave functions ψ_i are expressed as linear combinations of the basis set functions $\varphi_k(\vec{r})\chi_\sigma(\vec{s})$

$$\psi_i = \sum_{k=1}^{N}\sum_{\sigma=\downarrow,\uparrow} c^i_{k\sigma}\varphi_k(\vec{r})\chi_\sigma(\vec{s}). \tag{2}$$

Substitution of (2) in (1) leads to:

$$\langle\Psi|W|\Psi\rangle = \frac{1}{2}\sum_{kk'k''k'''}\sum_{\sigma\sigma'\sigma''\sigma'''}\rho^{\sigma\sigma''}_{kk''}\rho^{\sigma'\sigma'''}_{k'k'''} \tag{3}$$
$$[\langle\varphi_k(\vec{r}_1)\varphi_{k'}(\vec{r}_2)|w(\vec{r}_1,\vec{r}_2)|\varphi_{k''}(\vec{r}_1)\varphi_{k'''}(\vec{r}_2)\rangle\delta_{\sigma\sigma''}\delta_{\sigma'\sigma'''} - \langle\varphi_k(\vec{r}_1)\varphi_{k'}(\vec{r}_2)|w(\vec{r}_1,\vec{r}_2)|\varphi_{k''}(\vec{r}_2)\varphi_{k'''}(\vec{r}_1)\rangle\delta_{\sigma\sigma'''}\delta_{\sigma'\sigma''}],$$

where we used the fact that w is spin independent $w(1,2)\equiv w(\vec{r}_1,\vec{r}_2)$. The elements of the density matrix are:

$$\rho^{\sigma\sigma'}_{kk'} = \sum_{i\in occ} c^{i*}_{k\sigma}c^i_{k'\sigma'}. \tag{4}$$

Note that the summation is over occupied states only. Inspection of (3) reveals that the direct part contains only density matrix elements diagonal in spin, while the exchange part depends also on $\rho^{\sigma\sigma'}_{kk'}$; $\sigma\neq\sigma'$:

$$\langle\Psi|W|\Psi\rangle = \frac{1}{2}\sum_{kk'k''k'''}\sum_{\sigma\sigma'} \tag{5}$$
$$[\rho^{\sigma\sigma}_{kk''}\rho^{\sigma'\sigma'}_{k'k'''}\langle\varphi_k(\vec{r}_1)\varphi_{k'}(\vec{r}_2)|w(\vec{r}_1,\vec{r}_2)|\varphi_{k''}(\vec{r}_1)\varphi_{k'''}(\vec{r}_2)\rangle - \rho^{\sigma\sigma'}_{kk''}\rho^{\sigma'\sigma}_{k'k'''}\langle\varphi_k(\vec{r}_1)\varphi_{k'}(\vec{r}_2)|w(\vec{r}_1,\vec{r}_2)|\varphi_{k''}(\vec{r}_2)\varphi_{k'''}(\vec{r}_1)\rangle].$$

II. APW-LIKE METHODS, OCCUPATION NUMBER MATRIX

In APW-like methods (APW, LAPW, APW+lo) space is divided in the interstitial region and atomic spheres and the index k of $\varphi_k(\vec{r})$ becomes wave vector $\vec{k}_n = \vec{k} + \vec{K}_n$. In the APW method the basis functions have the form:

$$\varphi_{\vec{k}_n}(\vec{r}) = \frac{1}{\sqrt{\omega}}e^{i\vec{k}_n\vec{r}} \qquad interstitial$$
$$\varphi_{\vec{k}_n}(\vec{r}) = \sum_{l=0}^{l_{max}}\sum_{m=-l}^{l} A^{\vec{k}_n}_{lm}u_l(r)Y_{lm}(\hat{r}) \qquad at.sphere \tag{6}$$

Using (4-6) we determine that the contribution $\langle\Psi|W|\Psi\rangle_l$ from the $2l+1$ states of selected atom sphere and selected orbital momentum l to $\langle\Psi|W|\Psi\rangle$ is:

$$\langle\Psi|W|\Psi\rangle_l = \frac{1}{2}\sum_{mm'm''m'''}\sum_{\sigma\sigma'}[n^{\sigma\sigma}_{mm''}n^{\sigma'\sigma'}_{m'm'''}\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle - n^{\sigma\sigma'}_{mm''}n^{\sigma'\sigma}_{m'm'''}\langle mm'|w(\vec{r}_1,\vec{r}_2)|m'''m''\rangle] \quad (7)$$

where the elements $n^{\sigma\sigma'}_{mm'}$ of the occupation number matrix are given by:

$$n^{\sigma\sigma'}_{mm'} = \sum_{i\in occ}\sum_{\vec{k}_n\vec{k}'_n}(c^i_{\vec{k}_n\sigma}A^{\vec{k}_n}_{lm})^*\, c^i_{\vec{k}'_n\sigma'}A^{\vec{k}'_n}_{lm'}. \quad (8)$$

and

$$\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle = \int_{r_1,r_2\le R_{MT}} d^3r_1 d^3r_2 \frac{|u_l(r_1)|^2|u_l(r_2)|^2}{|\vec{r}_1-\vec{r}_2|}Y^*_{lm}(\hat{r}_1)Y^*_{lm'}(\hat{r}_2)Y_{lm''}(\hat{r}_1)Y_{lm'''}(\hat{r}_2). \quad (9)$$

Neglecting that $u_l(r)$ is nonzero also for r larger than the atomic sphere radius R_{MT}, the above integrals can be expressed through the Slater integrals F_κ [1]:

$$\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle = \sum_{\kappa=0,2..}^{2l} a_\kappa(m,m',m'',m''')F_\kappa; \quad (10)$$

$$a_\kappa(m,m',m'',m'') = \frac{4\pi}{2\kappa+1}\sum_{q=-\kappa}^{\kappa}\int d\hat{r}\,Y^*_{lm}(\hat{r})Y_{\kappa q}(\hat{r})Y_{lm''}(\hat{r})\int d\hat{r}\,Y^*_{lm'}(\hat{r})Y^*_{\kappa q}(\hat{r})Y_{lm'''}(\hat{r}).$$

The value of F_0 is substantially reduced by screening; $F_0 = U$, where U is the Hubbard parameter. F_2, F_4, F_6 may be related to the exchange parameter J and their screening is weaker.

III. LDA+U ENERGY AND POTENTIAL

In the LDA+U method the additional term added to the LSDA total energy is

$$E_{LDA+U} = \langle\Psi|W|\Psi\rangle_l - E_{dc}. \quad (11)$$

The 'double counting' part E_{dc} is diagonal in spin and it is given by:

$$E_{dc} = \frac{U}{2}n(n-\eta) - \frac{J}{2}\sum_{\sigma=\downarrow,\uparrow}n^\sigma(n^\sigma-\eta_\sigma); \quad (12)$$

$$n^\sigma = \sum_{m=-l}^{l}n^{\sigma\sigma}_{mm};\ n = n^\uparrow + n^\downarrow;\ \eta = (\eta_\uparrow+\eta_\downarrow)/2 \quad (13)$$

where $\eta_\sigma = 1$ and $\eta_\sigma = \langle n_\sigma\rangle$ in the 'Fully localized limit' [2] and 'Around the mean field' [3] version of the double summation, respectively.

The matrix elements of the LDA+U potential $\hat{v}$, added to $\hat{V}_{LSDA}$ are given by:

$$v^{\sigma\sigma'}_{mm'} = \frac{\partial E_{LDA+U}}{\partial n^{\sigma\sigma'}_{mm'}}. \quad (14)$$

Using (7, 11-13), this leads to:

$$v^{\uparrow\uparrow}_{mm''} = \sum_{m'm'''}[(n^{\uparrow\uparrow}_{m,m''}+n^{\downarrow\downarrow}_{m,m''})\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle - n^{\uparrow\uparrow}_{m,m''}\langle mm'|w(\vec{r}_1,\vec{r}_2)|m'''m''\rangle] - \quad (15)$$

$$-\delta_{mm''}[U(n-\eta/2) - J(n^\uparrow-\eta^\uparrow/2)]$$

$$v^{\downarrow\downarrow}_{mm''} = \sum_{m'm'''}[(n^{\uparrow\uparrow}_{m,m''}+n^{\downarrow\downarrow}_{m,m''})\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle - n^{\downarrow\downarrow}_{m,m''}\langle mm'|w(\vec{r}_1,\vec{r}_2)|m'''m''\rangle] - \quad (16)$$

$$-\delta_{mm''}[U(n-\eta/2) - J(n^\downarrow-\eta^\downarrow/2)]$$

$$v^{\downarrow\uparrow}_{mm''} = -\sum_{m'm'''} n^{\uparrow\downarrow}_{m,m''}\langle mm'|w(\vec{r}_1,\vec{r}_2)|m'''m''\rangle \tag{17}$$

The analysis become simple if we assume that only diagonal matrix elements are nonzero, independent of m, m' and equal to U:

$$\langle mm'|w(\vec{r}_1,\vec{r}_2)|m''m'''\rangle = \delta_{mm''}\delta_{m'm'''}U \tag{18}$$

After simple algebra we get:

$$E_{LDA+U} = \frac{U}{2}(\eta n - \sum_{mm'}\sum_{\sigma\sigma'} n^{\sigma\sigma'}_{mm'} n^{\sigma'\sigma}_{m'm} \tag{19}$$

which leads to the potential

$$v^{\sigma\sigma}_{mm} = U(\frac{\eta}{2} - n^{\sigma\sigma}_{mm} \tag{20}$$

$$v^{\sigma\sigma'}_{mm'} = -Un^{\sigma'\sigma}_{m'm} \tag{21}$$

IV. PU ATOM

As a simple example we consider Pu atom. To calculate it we enlarged the lattice constant of fcc Pu to 20 a.u. and run starting atomic program (LSTART) with small spin polarization $n^{\uparrow} - n^{\downarrow} = 0.2$. In an isolated atom the $5f$ levels are split by spin-orbit interaction to manifolds with $j = 5/2$ and $j = 7/2$. The lowest state in an exchange field of $j = 5/2$ is:

$$\Psi = u_{5f}(r)[\sqrt{\frac{6}{7}}Y_{3,-3}(\hat{r})\uparrow - \sqrt{\frac{1}{7}}Y_{3,-2}(\hat{r})\downarrow] \tag{22}$$

which gives

$$n^{\uparrow\uparrow}_{-3,-3} = 0.8571,\ n^{\downarrow\downarrow}_{-2,-2} = 0.1429;\ n^{\uparrow\downarrow}_{-3,-2} = -0.3499. \tag{23}$$

Taking U=1, $J = 0$, it follows $v^{\uparrow\downarrow}_{-2,-3} = -n^{\uparrow\downarrow}_{-3,-2} = 0.3499$. Below are results from WIEN_2k, orb program that show fair agreement with these analytical results.

```
Calculation of orbital potential for spin block: dnup
 Type of potential:            LDA+U
 Vorb applied to atom   1 orbit. numbers   3
  Approx. SIC method
        Atom  1 L=  3 U=  1.000 J=  0.000 Ry
 Atom 1  density matrix UPDN block, L= 3
  Real part
    0.00000   -0.31527    0.00000    0.00000    0.00000    0.00027    0.00000
    0.00000    0.00000   -0.41667    0.00000    0.00000    0.00000   -0.00002
    0.00000    0.00000    0.00000   -0.46895    0.00000    0.00000    0.00000
   -0.00078    0.00000    0.00000    0.00000   -0.48174    0.00000    0.00000
    0.00000    0.00074    0.00000    0.00000    0.00000   -0.45235    0.00000
    0.00000    0.00000    0.00047    0.00000    0.00000    0.00000   -0.36161
    0.00000    0.00000    0.00000   -0.00083    0.00000    0.00000    0.00000
  DNUP block of orbital potential
 Slater integrals F0, F2, F4, F(6)   1.000   0.000   0.000   0.000 Ry
  Atom 1  spin dnup potential real part (Ry)
        M= -3   0.00000   0.00000   0.00000   0.00078   0.00000   0.00000   0.00000
        M= -2   0.31527   0.00000   0.00000   0.00000  -0.00074   0.00000   0.00000
        M= -1   0.00000   0.41667   0.00000   0.00000   0.00000  -0.00047   0.00000
        M=  0   0.00000   0.00000   0.46895   0.00000   0.00000   0.00000   0.00083
        M=  1   0.00000   0.00000   0.00000   0.48174   0.00000   0.00000   0.00000
        M=  2  -0.00027   0.00000   0.00000   0.00000   0.45235   0.00000   0.00000
        M=  3   0.00000   0.00002   0.00000   0.00000   0.00000   0.36161   0.00000
```

V. CONCLUDING REMARKS

For simplicity the above analysis was given for the APW function and assuming that the basis functions φ are spin independent. Both these restrictions are easily removed, in particular (15-17) is still applicable.

It might be argued that for magnetization along the symmetry direction $v^{\downarrow\uparrow}_{mm''} \equiv 0$ because its presence requires the presence of the perpendicular exchange-correlation field which would contradict the symmetry, i.e. with the spin quantization axis $z \parallel C_n$, $\hat{v}$ still contains $\hat{s}_x, \hat{s}_y$. This argument is incorrect, however, as $\hat{s}_x, \hat{s}_y$ occur in combination with the orbital operators making $\hat{v}$ invariant (similarly as in spin-orbit coupling). Note that $v^{\downarrow\uparrow}_{mm''}$ is nonzero if and only if $n^{\uparrow\downarrow}_{m,m''} \neq 0$. The occupation matrix $\hat{n}$ is symmetrized in WIEN code, as a consequence also $\hat{v}$ should possess correct symmetry.

From (10, 17) follows that $v^{\downarrow,\uparrow}_{mm''}$ contains terms proportional to U and could be thus quite large once $n^{\uparrow\downarrow}_{m,m''} \neq 0$. This could cause problems when converging the scf procedure. In particular this might be the source of troubles when spin-nondiagonal term was included for fcc Ce and wrong scf solution was obtained [4]. Once the scf is started without the nondiagonal term and this is included only after the convergency is achieved, correct solution is retained. Note also that the nondiagonal spin potential tends to decrease the spin. Thus if there are more than one scf solutions its inclusion will result in reaching the one with smaller spin.

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