

Orbital-resolved total energy in OpenMX

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Orbital-resolved total energy in localized orbital methods

The total energy can be decomposed into each contribution resolved to atomic site and localized orbital.

$$\begin{aligned} E_{\text{tot}} &= \sum_{\sigma=\alpha,\beta} \sum_{\nu} f_{\nu} \langle \varphi_{\nu}^{\sigma} | \hat{T} | \varphi_{\nu}^{\sigma} \rangle + \sum_{\sigma\sigma'} \int w_{\sigma\sigma'} n_{\sigma'\sigma} + \frac{1}{2} \int \int \frac{n'(\mathbf{r})n'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dv dv' + E_{\text{xc}} \{n_{\sigma\sigma'}\} + E_{\text{cc}}, \\ &= E_{\text{band}} - \frac{1}{2} \int n' V_{\text{H}} dv - \int \text{Tr}(V_{\text{xc}} n) dv + E_{\text{xc}} + E_{\text{cc}}, \\ &= \text{Tr} \{ \rho F \} = \sum_{i\alpha} \left[\sum_{j\beta, \sigma\sigma'} \rho_{i\alpha, j\beta}^{\sigma\sigma'} F_{j\beta, i\alpha}^{\sigma'\sigma} \right] + \sum_{i\alpha j\beta} E_{\text{cc}}^{(i\alpha j\beta)}, \\ &= \sum_{i\alpha} E_{i\alpha}. \end{aligned}$$

where the matrix F is given by the sum of the KS effective potential plus double counting correction potentials.

$$F_{i\alpha, j\beta}^{\sigma\sigma'} = \langle i\alpha | v_{\text{eff}}^{\sigma\sigma'} + v_{\text{dc}}^{\sigma\sigma'} | j\beta \rangle$$

For even plane-wave codes, one may be able to perform the same analysis using Wannier functions.

Close look at each term #1

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{na}} + E_{\text{NL}} + E_{\delta\text{ee}} + E_{\text{xc}} + E_{\text{scc}}$$

The first three terms can be easily decomposed as follows:

$$E_{\text{kin}} = \sum_{\sigma} \sum_{i\alpha} \left(\sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{kin}}^{(R_n)} \right) \rightarrow E_{\text{kin}}^{(\sigma,i\alpha)} = \sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{kin}}^{(R_n)}$$

$$E_{\text{na}} = \sum_{\sigma} \sum_{i\alpha} \left(\sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{na}}^{(R_n)} \right) \rightarrow E_{\text{na}}^{(\sigma,i\alpha)} = \sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{na}}^{(R_n)}$$

$$E_{\text{NL}} = \sum_{\sigma} \sum_{i\alpha} \left(\sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{NL}}^{(R_n)} \right) \rightarrow E_{\text{NL}}^{(\sigma,i\alpha)} = \sum_n \sum_{i\alpha} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,\text{NL}}^{(R_n)}$$

Close look at each term #2

$$E_{\delta ee} = \frac{1}{2} \int dr \delta n(r) \delta V_H(r)$$

By noting the following definitions.

$$\delta n(r) = n(r) - \sum_i n_i^{(a)}(r) \quad n(r) = \sum_{\sigma} \sum_n \sum_{i\alpha j\beta} \rho_{\sigma, i\alpha j\beta}^{(R_n)} \phi_{i\alpha}(r - \tau_i) \phi_{j\beta}(r - \tau_j)$$

We can rewrite the energy term as follows:

$$E_{\delta ee} = \frac{1}{2} \sum_{\sigma} \sum_{i\alpha} \left(\sum_n \sum_{j\beta} \rho_{\sigma, i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta, \delta V_H}^{(R_n)} \right) - \frac{1}{2} \sum_{\sigma} \sum_{i\alpha} \left(\int dr \frac{1}{2N_i} n_i^{(a)}(r) \delta V_H(r) \right)$$

where N_i is the number of basis orbital on atom i .

Then, one can regard the resolved energy term as

$$E_{\delta ee}^{(\sigma, i\alpha)} = \frac{1}{2} \sum_n \sum_{j\beta} \rho_{\sigma, i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta, \delta V_H}^{(R_n)} - \frac{1}{2} \int dr \frac{1}{2N_i} n_i^{(a)}(r) \delta V_H(r)$$

Close look at each term #3

E_{xc} is also decomposed as follows:

$$\begin{aligned} E_{xc} &= \int dr \left(n(r) + n_{pcc}(r) \right) \varepsilon_{xc}(r) \\ &= \sum_{\sigma} \int dr \left(n_{\sigma}(r) + \frac{1}{2} n_{pcc}(r) \right) \varepsilon_{xc}(r) \\ &= \sum_{\sigma} \sum_{i\alpha} \left(\sum_n \sum_{j\beta} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,xc}^{(R_n)} \right) + \sum_{\sigma} \sum_{i\alpha} \left(\int dr \frac{1}{2N_i} n_{pcc,i}(r) \varepsilon_{xc}(r) \right) \end{aligned}$$

Then, one can regard the resolved energy term as

$$E_{xc}^{(\sigma,i\alpha)} = \sum_n \sum_{j\beta} \rho_{\sigma,i\alpha j\beta}^{(R_n)} h_{i\alpha j\beta,xc}^{(R_n)} + \int dr \frac{1}{2N_i} n_{pcc,i}(r) \varepsilon_{xc}(r)$$

Close look at each term #4

The screened core-core Coulomb energy is decomposed as

$$E_{\text{scc}} = \frac{1}{2} \sum_{ij} \left(\frac{Z_i Z_j}{|\tau_i - \tau_j|} - \int dr n_i^{(a)}(r) V_{\text{H},j}^{(a)}(r) \right)$$
$$= \sum_{\sigma} \sum_{i\alpha} \left(\sum_j \frac{1}{2N_i} \left[\frac{Z_i Z_j}{|\tau_i - \tau_j|} - \int dr n_i^{(a)}(r) V_{\text{H},j}^{(a)}(r) \right] \right)$$

Then, one can regard the resolved energy term as

$$E_{\text{scc}}^{(\sigma, i\alpha)} = \frac{1}{2N_i} \sum_j \left[\frac{Z_i Z_j}{|\tau_i - \tau_j|} - \int dr n_i^{(a)}(r) V_{\text{H},j}^{(a)}(r) \right]$$

An example: Methane

The energy decomposition can be performed by a keyword:

Energy.Decomposition on

One can find the decomposed energy in *.out.

```
*****  
*****  
Decomposed energies in Hartree unit  
*****  
*****
```

Total energy (Hartree) = -8.211879033365392

Decomposed energies (Hartree) with respect to atom

		Utot	Ukin	Una	Unl	UHl	Uxc	Ucore+UH0
1	C	-6.242767483919	4.35525	-3.60696	-0.46890	0.04426	-2.07025	-4.49616
2	H	-0.492277889157	0.55513	-0.65049	0.07550	0.00195	-0.32318	-0.15119
3	H	-0.4922778885800	0.55513	-0.65049	0.07550	0.00195	-0.32318	-0.15119
4	H	-0.492277885616	0.55513	-0.65049	0.07550	0.00195	-0.32318	-0.15119
5	H	-0.492277888873	0.55513	-0.65049	0.07550	0.00195	-0.32318	-0.15119

Decomposed energies (Hartree) with respect to atomic orbital

1	C	multiple	Utot	Ukin	Una	Unl	UHl	Uxc	Ucore+UH0	Ue
s		0	-0.99023	0.42235	-0.86043	0.25887	0.02991	-0.49506	-0.34586	0.
s		1	-0.35136	0.07199	-0.05751	0.01544	-0.00793	-0.02750	-0.34586	0.
px		0	-0.66723	1.12768	-0.81128	-0.20349	0.02765	-0.46193	-0.34586	0.
py		0	-0.66724	1.12776	-0.81135	-0.20350	0.02766	-0.46195	-0.34586	0.
pz		0	-0.66723	1.12768	-0.81128	-0.20349	0.02765	-0.46193	-0.34586	0.
px		1	-0.35263	0.13914	-0.06432	-0.04677	-0.00847	-0.02636	-0.34586	0.
py		1	-0.35264	0.13909	-0.06438	-0.04679	-0.00847	-0.02636	-0.34586	0.

It is confirmed that the sum of decomposed energy is exactly the same as the total energy.

$$-6.242767483919 - 0.492277889157 - 0.4922778885800 - 0.492277885616 - 0.492277888873 = -8.211879033365$$

Energy_Decomposition_flag==1

The decomposition for all the energy terms is performed in `Total_Energy()`. Those terms are listed below:

Kinetic energy:

Neutral atom potential energy:

Non-local pseudopotential energy:

Core-core repulsion energy:

Exchange correlation energy:

Delta Hartree energy:

Hubbard energy:

vdW energy:

By searching with “`Energy_Decomposition==1`” in the `Total_Energy.c`, one can easily confirm the places where the energy decompositions are performed.

Summary

- To analyze effects of distortion, defects, and impurities to the total energy, the orbital resolved total energy method might be useful.
- The formulation is quite simple, and easy to implement.
- Even for plane-wave codes, a similar analysis may be possible by employing Wannier functions.
- Only a single file “Total_Energy.c” has been modified, leading to easy trace of the implementation.
- The method will be also useful for analysis of magnetic anisotropy energy of magnetic systems.