HSE06 functional in siesta

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Abstract

The total energy and force equations for HSE06 functional in siesta is written here. By this way, further extension (mp2, hessian) can be done in my coming work. Here we follow the Kohn-Sham approach [1] to derive our equations. The Kohn-Sham ansatz(A mathematical assumption, especially about the form of an unknown function, which is made in order to facilitate solution of an equation or other problem) is to replace the difficult interaction many-body system with this Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{i}\nabla_i^2 - \sum_{i}\sum_{I}\frac{Z_I}{|\mathbf{r_i} - \mathbf{R_I}|} + \frac{1}{2}\sum_{i}\sum_{j\neq i}\frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} + \frac{1}{2}\sum_{I}\sum_{J\neq I}\frac{Z_I Z_J}{|\mathbf{R_I} - \mathbf{R_J}|} \tag{1}$$

into a independent-particle problem. What they have been done is to define a ground state energy E_{KS}, and then derive a Kohn-Sham Schödinger-like equation using Lagrange multipliers or Rayleigh-Ritz principle. In this paper we will show the detailed formula derivation.

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I. METHODS

A. HSE total energy

Kohn-Sham wrote the total energy of a many-body system as:

$$E_{KS} = -\frac{1}{2}\sum_i < \phi_i|\nabla^2|\phi_i > - \int \rho(\mathbf{r}) \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} d\mathbf{r} +$$

$$\frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\sum_I\sum_J \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_{xc}(\rho) \tag{2}$$

$$= T + E_{ext} + E_{hartree} + E_{IJ} + E_{xc} \tag{3}$$

So all the many-body effect go to $E_{xc}(\rho)$ term. Using Lagrange multipliers, we have

$$\frac{\delta[E_{KS} - \sum_i \epsilon_i (< \phi_i|\phi_i > -1)]}{\delta\phi_i} = 0 = \tag{4}$$

$$\frac{\delta T}{\delta\phi_i} + [\frac{\delta E_{ext}}{\delta\rho(r)} + \frac{\delta E_{hartree}}{\delta\rho(r)} + \frac{\delta E_{xc}}{\delta\rho(r)}]\frac{\delta\rho(r)}{\delta\phi_i} - \epsilon_i\phi_i = \tag{5}$$

$$-\frac{1}{2}\nabla^2\phi_i + [V_{ext}(r) + V_{hartree} + V_{xc}]\phi_i - \epsilon_i\phi_i = 0 \tag{6}$$

So we get Kohn-Sham Schödinger-like equation in Eq. 6.

In siesta, using psedopotential, so the E_{KS} in siesta is written as Eq. 53 of siesta-2002 paper, again, it equals E_{KS} we get before:

$$E_{KS} = T + E_{ext} + E_{hartree} + E_{IJ} + E_{xc} \tag{7}$$

So for HSE total energy, we only addE_{HSE} to E_{xc} part. The expression for HSE06 is given by:

$$E_{xc}^{HSE} = \frac{1}{4}E_x^{SR-HF}(\omega) + \frac{3}{4}E_x^{SR-PBE}(\omega) + E_x^{LR-PBE}(\omega) + E_c^{PBE} \tag{8}$$

where ω =0.11$Bohr^{-1}$.

For un-spin-polarized systems (nspin=1), the Hartree-Fock exchange matrix element is defined as (here the 1/2 is coming from exchange interaction, when we use slater-determinant to get HF total energy):

$$[V^X]_{\mu\lambda}^{\mathbf{G}} = -\frac{1}{2}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P_{\nu\sigma}^{\mathbf{H}-\mathbf{N}}[(\chi_\mu^{\mathbf{0}}\chi_\nu^{\mathbf{N}}|\chi_\lambda^{\mathbf{G}}\chi_\sigma^{\mathbf{H}})] \tag{9}$$

where **G**, **N**, and **H** represent different unit cells.

So we can get Hartree-Fock exchange energy , here 1/4 is because exchange energy is always 1/2 of hartree energy (3rd term in Eq. 2), so $\frac{1}{2} * \frac{1}{2} = \frac{1}{4}$

$$E^{HFX} = -\frac{1}{4}\sum_{\mu\lambda}\sum_{\mathbf{G}} P^{\mathbf{G}}_{\mu\lambda}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}[(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})] \tag{10}$$

B. HSE total force

The PBE part force is calculate directly with siesta, we only write Hartree-Fock Exchange part for HSE force here.

For un-spin-polarized systems (nspin=1), the Gradient is divided into two terms:

$$\frac{\partial E_{HFX}}{\partial R_I} = -\frac{1}{2}\sum_{\mu\lambda}\sum_{\mathbf{G}} \frac{P^{\mathbf{G}}_{\mu\lambda}}{\partial R_I}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}[(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})] \tag{11}$$

$$-\frac{1}{4}\sum_{\mu\lambda}\sum_{\mathbf{G}} P^{\mathbf{G}}_{\mu\lambda}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}\frac{\partial(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})}{\partial \mathbf{R_I}}$$

The first term can be calculated in the orthogonalization force:

$$\sum_{\mu\nu} F_{\mu\nu}\frac{\partial P_{\mu\nu}}{\partial R_I} = -\sum_{\mu\nu} E_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial R_I} \tag{12}$$

where

$$E_{\mu\nu} = \sum_i c_{\mu i}c_{\nu i}n_i\varepsilon i$$

The second term need the gradient of ERIs. In the following, we will deal with this term:

$$F_{\mathbf{R_I}} = \frac{1}{4}\sum_{\mu\lambda}\sum_{\mathbf{G}} P^{\mathbf{G}}_{\mu\lambda}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}\frac{\partial(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})}{\partial \mathbf{R_I}}$$

$$= \frac{1}{4}\sum_{\mu\lambda}\sum_{\mathbf{G}} P^{\mathbf{G}}_{\mu\lambda}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}} P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}$$

$$\times[(\frac{\chi^{\mathbf{0}}_{\mu}}{\partial \mathbf{R_I}}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\frac{\chi^{\mathbf{N}}_{\nu}}{\partial \mathbf{R_I}}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\frac{\chi^{\mathbf{G}}_{\lambda}}{\partial \mathbf{R_I}}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\frac{\chi^{\mathbf{H}}_{\sigma}}{\partial \mathbf{R_I}})] \tag{13}$$

II. CONCLUSIONS

ACKNOWLEDGMENTS

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[2] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

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