HSE06 functional in siesta

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(Dated: November 9, 2013)

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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TABLE I. Possion solver under PBC

problem	solution
(1) $V_{static-electric}$ in unit-cell of neutral system	Ewald-1921
(2)unit cell total energy of nuclei-nuclei interaction	Ewald-Coldwell-Horsfall 1960
(3) $V_{uc}(r) = \int \frac{\rho(r')}{\|r-r'\|} dr'$, equispaced grids	FFT poisson solver
(4) $V_{uc}(r) = \int \frac{\rho(r')}{\|r-r'\|} dr'$, atom-center grids	MP-poisson solver + Ewald

I. METHODS

A. possion solver under PBC

B. HSE total energy

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

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

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

$$= T + E_{ext} + E_{hartree} + E_{IJ} + E_{xc} \quad (3)$$

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

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

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

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

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:

$$E_{KS} = T + E_{ext} + E_{hartree} + E_{IJ} + E_{xc} \quad (7)$$

Here I gave a derivation of siesta's Eq(53):

$$E_{KS-siesta} = -\frac{1}{2}\sum_i < \phi_i|\nabla^2|\phi_i > + \sum_i < \phi_i|V^{KB}|\phi_i > + \int \rho^{pseudo}(\mathbf{r}) \sum_I V_I^{local}(r) d\mathbf{r} +$$

$$\frac{1}{2}\int\int \frac{\rho^{pseudo}(\mathbf{r})\rho^{pseudo}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\sum_I\sum_J \frac{Z_I^{pseudo}Z_J^{pseudo}}{|\mathbf{R}_I-\mathbf{R}_J|} + E_{xc}(\rho) \tag{8}$$

here all the $\rho^{pseudo}(r)$ and Z_I^{pseudo} and valence contribution, because we have already used pseudo-potential, in which way we only see valence electrons in system. $V_I^{local}(r)$ looks like $-Z_I^{pseudo}/|r-R_I|$ in far distance, but do not diverge near nuclear position.

$$V_I^{local}(r) \approx -Z_I^{pseudo}/|r-R_I| \tag{9}$$

$$U_{IJ}^{local}(R) = \int V_I^{local}(r)\rho_J^{local}(r-R)dr \tag{10}$$

$$\frac{1}{2}\sum_I\sum_{J\neq I}\frac{Z_I^{pseudo}Z_J^{pseudo}}{|\mathbf{R}_I-\mathbf{R}_J|} = \frac{1}{2}\sum_I\sum_J U_{IJ}^{local}(R_{IJ}) - \frac{1}{2}\sum_I U_{II}^{local}(0) + \frac{1}{2}\sum_I\sum_{J\neq I}\delta U_{IJ}^{local}(R_{IJ}) \tag{11}$$

$$\frac{1}{2}\int\int \frac{\rho^{pseudo}(\mathbf{r})\rho^{pseudo}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' = \frac{1}{2}\int\int \frac{[\rho^{atom}(r)+\delta\rho(r)][\rho^{atom}(r)+\delta\rho(r)]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \tag{12}$$

$$V^{NA}(r) = V^{local}(r) + V^{atom}(r) \tag{13}$$

So Eq.(8) can be written as:

$$E_{KS-siesta} =$$

$$-\frac{1}{2}\sum_i <\phi_i|\nabla^2|\phi_i> + \sum_i <\phi_i|V^{KB}|\phi_i> + \int [\rho^{atom}(r)+\delta\rho(r)]V^{local}(r)d\mathbf{r} + E_{xc}(\rho)$$

$$+\frac{1}{2}\int\int \frac{[\rho^{atom}(r)+\delta\rho(r)][\rho^{atom}(r)+\delta\rho(r)]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$+\frac{1}{2}\sum_I\sum_J U_{IJ}^{local}(R_{IJ}) - \frac{1}{2}\sum_I U_{II}^{local}(0) + \frac{1}{2}\sum_I\sum_{J\neq I}\delta U_{IJ}^{local}(R_{IJ})$$

$$= -\frac{1}{2}\sum_i <\phi_i|\nabla^2|\phi_i> + \sum_i <\phi_i|V^{KB}|\phi_i> + E_{xc}(\rho) + \frac{1}{2}\int\int \frac{\delta\rho(r')\delta\rho(r)}{|r-r'|}dr'dr$$

$$-\frac{1}{2}\sum_I U_{II}^{local}(0) + \frac{1}{2}\sum_I\sum_{J\neq I}\delta U_{IJ}^{local}(R_{IJ})$$

$$+\int [V^{local}(r)+V^{atom}(r)]\delta\rho(r)dr ==> \int V^{NA}(r)\delta\rho(r)dr$$

$$+\frac{1}{2}\sum_I\sum_J\int[V^{local}(r)+V^{atom}(r)][\rho^{local}+\rho^{atom}]dr ==> \frac{1}{2}\sum_I\sum_J U_{IJ}(R_{IJ}) \tag{14}$$

So it is the same as Eq(53) in siesta's paper. Here the idea is the same as Ewald method, because here ρ^{local} is just like Gaussian charge in Ewald, and then the V^{NA} is short ranged and calculated in real space and $\delta V(r)$ is calculated in moment space.

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

$$E_{xc}^{HSE}=\frac{1}{4}E_x^{SR-HF}(\omega)+\frac{3}{4}E_x^{SR-PBE}(\omega)+E_x^{LR-PBE}(\omega)+E_c^{PBE} \tag{15}$$

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):

$$[V^X]^{\mathbf{G}}_{\mu\lambda}=-\frac{1}{2}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}}P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}[(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})] \tag{16}$$

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 $\frac{1}{2}*\frac{1}{2}=\frac{1}{4}$

$$E^{HFX}=-\frac{1}{4}\sum_{\mu\lambda}\sum_{\mathbf{G}}P^{\mathbf{G}}_{\mu\lambda}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}}P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}[(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})] \tag{17}$$

C. 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:

$$\frac{\partial E_{HFX}}{\partial R_I}=-\frac{1}{2}\sum_{\mu\lambda}\sum_{\mathbf{G}}\frac{P^{\mathbf{G}}_{\mu\lambda}}{\partial R_I}\sum_{\nu\sigma}\sum_{\mathbf{N},\mathbf{H}}P^{\mathbf{H}-\mathbf{N}}_{\nu\sigma}[(\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma})] \tag{18}$$

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

The first term can be calculated in the orthogonalization force:

$$\sum_{\mu\nu}F_{\mu\nu}\frac{\partial P_{\mu\nu}}{\partial R_I}=-\sum_{\mu\nu}E_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial R_I} \tag{19}$$

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:

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

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

$$\times[(\frac{\chi^{\mathbf{0}}_{\mu}}{\partial \mathbf{R_I}}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\frac{\chi^{\mathbf{N}}_{\nu}}{\partial \mathbf{R_I}}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\frac{\chi^{\mathbf{G}}_{\lambda}}{\partial \mathbf{R_I}}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\frac{\chi^{\mathbf{H}}_{\sigma}}{\partial \mathbf{R_I}})] \qquad (20)$$

II. CONCLUSIONS

ACKNOWLEDGMENTS

[1] W. Kohn and L. Sham, Phys. Rev. **140**, 1133 (1965).

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

[3] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York,1989)