HSE06 functional in siesta

Honghui Shang

FHI-Berlin

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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 based on this.

I. METHODS

A. HSE total energy

In a general fore, no matter what basis set you use or what interaction you use to describe the electron-nuclue interaction, we have

B. HSE force

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

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

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

The first term can be calculated in the orthogonalization force:

$$\sum_{\mu\nu}F_{\mu\nu}\frac{\partial P_{\mu\nu}}{\partial R_I} = -\sum_{\mu\nu}E_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial R_I} \tag{2}$$

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:

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

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

$$\times[(\frac{\chi^{\mathbf{0}}_{\mu}}{\partial\mathbf{R_I}}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\frac{\chi^{\mathbf{N}}_{\nu}}{\partial\mathbf{R_I}}|\chi^{\mathbf{G}}_{\lambda}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\frac{\chi^{\mathbf{G}}_{\lambda}}{\partial\mathbf{R_I}}\chi^{\mathbf{H}}_{\sigma}) + (\chi^{\mathbf{0}}_{\mu}\chi^{\mathbf{N}}_{\nu}|\chi^{\mathbf{G}}_{\lambda}\frac{\chi^{\mathbf{H}}_{\sigma}}{\partial\mathbf{R_I}})] \tag{3}$$

II. CONCLUSIONS

ACKNOWLEDGMENTS

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

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

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