Total energy and SCF in PWSCF

Honghui Shang*

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

(Dated: November 15, 2013)

Abstract

The total energy and SCF equation using plane wave basis sett is written here. I have also compared PW basis set with AO basis set. So we can see the difference between 'near-free' electron approximation and tight-binding. 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 in PW basis set.

* Electronic address: shang@fhi-berlin.mpg.de

I. METHODS

A. Total energy expressions are the same in both basis set

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

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

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

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

B. crystal-orbital-SCF equations are the same in both basis set

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.

C. SCF equations are the same in both basis set

II. CONCLUSIONS

ACKNOWLEDGMENTS

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