

Total energy calculation with plane wave basis  
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## Total energy in density functional theory

### Literatur

- G.P. Srivastava and D. Weaire, *The theory of the cohesive energies of solids*, Advances in Physics, **36**, 463, (1987).
- G. Galli and M. Parrinello, *Ab-initio molecular dynamics: Principles and practical implementation*, in Computer Simulation in Materials Science, Eds. M. Meyer and V. Pontikis, Kluwer Acad. 1991.
- A. Dal Corso, *Density functional theory beyond the pseudopotential local density approach: A few cases studies*, PhD Thesis, SISSA, Trieste 1993.

The total energy of a system within the Kohn-Sham formulation of DFT is given by (assuming the Born-Oppenheimer approximation):

$$E_{tot} = E_k + E_{ext} + E_H + E_{xc} + E_i.$$

The Kohn-Sham orbitals  $\Psi_i$  are orthogonal

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

and with the occupation numbers  $f_i$  the electron density is defined as

$$n_e = \sum_i f_i |\Psi_i|^2.$$

$E_k$  is the kinetic energy

$$E_k = -\frac{1}{2} \sum_i f_i \langle \Psi_i | \nabla^2 | \Psi_i \rangle .$$

$E_{ext}$  is the interaction energy of the external potential  $V_{ext}$  (ionic cores and pseudo potentials) with the electrons

$$E_{ext} = \int V_{ext}(r) n_e(r) dr.$$

$E_H$  is the Hartree energy

$$E_H = \frac{1}{2} \int \int \frac{n_e(r_1) n_e(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

$E_{xc}$  is the exchange and correlation energy (we use the local approximation)

$$E_{xc} = \int \epsilon_{xc}(n_e(r), \nabla n_e(r)) n_e(r) dr.$$

$E_i$  is the ion-ion interaction

$$E_i = \sum_{I < J} \frac{Z_I Z_J}{|R_I - R_J|}$$

where  $Z_I$  is the charge and  $R_I$  is the position of ion I.

The Kohn-Sham equations derived from this energy expression are

$$\left[ -\frac{1}{2} \nabla^2 + V_H(r) + V_{xc}(r) + V_{ext}(r) \right] \Psi_i(r) = \epsilon_i \Psi_i(r)$$

where the Hartree potential is defined by

$$V_H(r) = \int \frac{n_e(r_1) n_e(r)}{|r_1 - r|} dr_1$$

and the exchange and correlation potential by

$$V_{xc}(r) = \frac{\delta E_{xc}(n_e(r))}{\delta n_e(r)}$$

## Periodic boundary conditions

Direct lattice vectors

$$\vec{a}_1, \vec{a}_2, \vec{a}_3$$

are calculated from the type of Bravais lattice and the input parameters

$$a, \frac{b}{a}, \frac{c}{a}, \cos(\alpha), \cos(\beta), \cos(\gamma).$$

The reciprocal lattice vectors

$$\vec{b}_1, \vec{b}_2, \vec{b}_3$$

are calculated in units of  $\frac{2\pi}{a}$ , where  $a$  is the lattice constant.

**Warning:** For fcc and bcc is the lattice constant one half of the input parameter  $a$ .

The potential is periodic, so the Bloch theorem applies for the wavefunctions

$$\Psi_i(r) = e^{ikr} \Phi_i(k, r)$$

where  $k$  is a vector inside the first Brillouin zone of the reciprocal lattice. In CPMD  $k$  is always  $(0,0,0)$ , the  $\Gamma$  point.

$$\Psi_i(r) = \Phi_i(0, r)$$

## Plane wave basis set

We expand

$$\Psi_i(r) = \frac{1}{\Omega^{1/2}} \sum_G c_{Gi} e^{iGr}.$$

Orthogonality condition on wavefunctions

$$\begin{aligned} \langle \Psi_i | \Psi_j \rangle &= \frac{1}{\Omega} \sum_G c_{Gi}^* \sum_{G'} c_{G'j} \int_{\Omega} e^{-iGr} e^{iG'r} dr \\ &= \frac{1}{\Omega} \sum_G c_{Gi}^* \sum_{G'} c_{G'j} \Omega \delta_{GG'} \\ &= \sum_G c_{Gi}^* c_{Gj} = \delta_{ij} \end{aligned}$$

At the  $\Gamma$  point,  $\Psi_i(r)$  can be chosen to be real

$$\begin{aligned} \Psi_i(r) &= \Psi_i^*(r) \\ \sum_G c_{Gi} e^{iGr} &= \sum_G c_{Gi}^* e^{-iGr} \\ c_{Gi} &= c_{-Gi}^* \end{aligned}$$

There is a symmetry relation between  $G$  and  $-G$  vectors. We only have to store half of the  $G$  vectors! This makes  $G = 0$  to a special vector and  $c_{0i}$  becomes a real quantity.

Whenever there is a operation on  $G$  vectors, the symmetry has to be taken into account.

Example: Orthogonality

$$\sum_G c_{Gi}^* c_{Gj} = \delta_{ij}$$

$$\sum_{G>0} (c_{Gi}^* c_{Gj} + c_{Gi} c_{Gj}^*) + c_{0i} c_{0j} = \delta_{ij}$$

with  $c_{Gi} = a_{Gi} + ib_{Gi}$  we get

$$\sum_{G>0} 2(a_{Gi} a_{Gj} + b_{Gi} b_{Gj}) + a_{0i} a_{0j} = \delta_{ij}$$

### CPMD GOLDEN RULE 4 :

Complex arithmetics should be avoided whenever possible. Due to the symmetry of the wavefunctions many results of complex operations are real quantities. Making use of this saves half of the operations.

### Plane wave cutoff

The maximum  $|G|$  value included in the basis set is controlled by the kinetic energy of the plane waves.

$$T_G = \langle G | -\frac{1}{2} \nabla^2 | G \rangle = \frac{1}{2} G^2 < E_{cut}$$

This is a spherical cutoff. All vectors

$$\vec{G} = \frac{2\pi}{a} (i\vec{b}_1 + j\vec{b}_2 + k\vec{b}_3)$$

with  $|G| < G_{max}$  are included in the calculation. Symmetry is taken into account by restricting the Miller indices (i,j,k) to

$$\begin{aligned} i = 0; \quad j = 0; \quad k \geq 0 \\ i = 0; \quad j > 0; \quad k > < 0 \\ i > 0; \quad j > < 0; \quad k > < 0 \end{aligned}$$

G vectors are stored in units of  $\frac{2\pi}{a}$  and ordered by increasing absolute value. There is a index array providing the relation between the G vectors in ordered storage form and in Miller index form.

$$\begin{aligned}\text{NZH}(\mathbf{G}) &= i \otimes j \otimes k \\ \text{INDZ}(\mathbf{G}) &= -i \otimes j \otimes k\end{aligned}$$

The product  $i \otimes j \otimes k$  refers to storage locations in a 3-dimensional array with positive indices. This gives the following pattern for the G vectors in the computational box.

**Figure:** Projection of the G vectors onto the xy plane. Diamonds and stars represent G vectors stored and not stored below the wavefunction cutoff. Squares and crosses represent G vectors stored and not stored below the density cutoff.

Example form the code: Prepare a wavefunction for Fourier transform

```
DO IG=1,NGW
  PSI(NZH(IG))=CO(IG,I)
  PSI(INDZ(IG))=DCONJG(CO(IG,I))
ENDDO
```

The number of G vectors depends on the shape of the unit cell and the cutoff. An estimate is

$$N_G \approx \frac{4\pi}{3\Omega} E_{cut}^{\frac{3}{2}}$$

The number of stored G vectors is

$$\text{NGW} = \frac{N_G}{2} \approx \frac{2\pi}{3\Omega} E_{cut}^{\frac{3}{2}}$$

### Density cutoff

$$\begin{aligned}n(r) &= \frac{1}{\Omega} \sum_i f_i \sum_{G,G'} c_{Gi} c_{G'i} e^{i(G+G')r} \\ &= \frac{1}{\Omega} \sum_G n_G e^{iGr}\end{aligned}$$

From this it is clear, that if we want to expand the density correctly in plane waves, we have to go to  $G$  vectors with maximal length  $2G_{max}$  or kinetic energy cutoff  $4E_{cut}$ . Reducing the cutoff for the density to a smaller value introduces a inconsistency between wavefunctions and density into the calculation. The cutoff of the density is controlled in CPMD by the keyword **DUAL**.

### Translation of a function in real space

$$\begin{aligned} F(r + R_I) &= \sum_G v_G e^{iG(r+R_I)} \\ &= \sum_G v_G e^{iGr} e^{iGR_I} \\ &= \sum_G \left( v_G e^{iGR_I} \right) e^{iGr} \end{aligned}$$

### Fourier Transforms

Inverse FT

$$F(R) = \sum_G F(G) e^{iGr}$$

Forward FT

$$F(G) = \frac{1}{N_R} \sum_R F(R) e^{iGR}$$

where  $N_R$  is the number of grid points in real space. In the code these operations are performed using Fast Fourier Transforms.

### Calculation of the density

$$n(R) = \frac{1}{\Omega} \sum_i f_i \sum_{G,G'} c_{G_i} c_{G'_i} e^{i(G+G')R}$$

Direct calculation of the density with this formula requires  $\mathcal{O}(N_S N_{PW}^2)$  operations ( $N_S$  number of occupied states). We use instead

$$n(R) = \sum_i f_i (\Psi_i(R))^2$$

where  $\Psi_i(R)$  is calculated by a Fast Fourier Transform. This only requires  $\mathcal{O}(N_S N_{PW} \log(N_{PW}^{\frac{1}{3}}))$  operations.

## The LDA energy for a plane wave expansion

$$E_{tot} = E_K + E_{xc} + E_H + E_{PS}^L + E_{PS}^{NL} + E_i$$

where we write now  $E_{ext}$  as a sum of local and non-local pseudo potential energies.

### Kinetic energy

$$\begin{aligned} E_K &= \frac{1}{2} \sum_{i,G} f_i G^2 c_{Gi}^* c_{Gi} \\ &= \frac{1}{2} \sum_i f_i \sum_{G>0} G^2 2 (a_{Gi}^2 b_{Gi}^2) \\ &= \sum_i f_i \sum_{G>0} G^2 (a_{Gi}^2 + b_{Gi}^2) \end{aligned}$$

### Exchange and correlation energy

$$\begin{aligned} E_{xc} &= \int_{\Omega} \epsilon_{xc}(r) n_e(r) dr \\ &\approx \frac{\Omega}{N_R} \sum_R \epsilon_{xc}(R) n_e(R) \end{aligned}$$

### Non-local pseudo potential energy

(for norm-conserving pseudo potentials in separable form (Kleinman - Bylander type)).

$$\begin{aligned} E_{PS}^{KB} &= \sum_i f_i \sum_I \sum_{l,m} W_{l,m}^I F_{i,l,m}^I F_{i,l,m}^I \\ F_{i,L}^I &= \langle \Psi_i | \beta_L^I \rangle \quad \text{where } L = l, m \end{aligned}$$

The  $F_{i,L}^I$  are overlap integrals between wavefunctions and atom centered projectors. The projectors are stored as functions in reciprocal space for an atom at the origin.

$$F_{i,L}^I = \sum_G c_{Gi}^* \beta_L^I(G) e^{iGR_i}$$



## Ion-ion interaction energy

The ion-ion interaction energy, the Hartree and the local pseudo potential energy are diverging due to the presence of slowly decaying Coulomb forces. As these diverging terms cancel each other, it is convenient to look at the sum

$$E_H + E_{PS}^L + E_i.$$

First we replace the ionic point charges by Gaussian charge distributions.

$$n_I(r - R_I) = -\frac{Z_I}{(R_I^c)^3} \pi^{-3/2} \exp\left(-\frac{|r - R_I|^2}{(R_I^c)^2}\right)$$

The energy  $E_i$  can now be written as

$$E_i = \sum_{I>J} \frac{Z_I Z_J}{|R_I - R_J|^2} = \sum_{I>J} \int dr dr' \frac{n_I(r - R_I) n_J(r - R_J)}{r - r'} - E_{self} - E_{ovrl}$$

The self energy  $E_{self}$  and nearest neighbor energy  $E_{ovrl}$  can be calculated analytically (this is the **HOMEWORK**).

$$E_{self} = \frac{1}{\sqrt{2\pi}} \sum_I \frac{Z_I^2}{R_I^c}$$

$$E_{ovrl} = \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} \operatorname{erfc}\left(\frac{|R_I - R_J|}{\sqrt{(R_I^c)^2 + (R_J^c)^2}}\right)$$

The energy  $E_{self}$  is constant during the calculation and the sum in  $E_{ovrl}$  converges rapidly. A inspection of the formula for  $E_{ovrl}$  shows that the overlap terms are smaller than  $10^{-10}$  Hartree if the distance between two ions is  $\approx 4(R_I^c + R_J^c)$ .

$R_j^c$  is in CPMD called **RAGGIO**.

To calculate the first, Hartree-like term efficiently, it is necessary to expand the Gaussian charges in the plane wave basis. To see if this can be done for a certain cutoff, we have to transform the charge distribution into reciprocal space.

$$n_I(G) = -\frac{Z_I}{\Omega(R_I^c)^2} \exp\left(-\frac{1}{4}G^2(R_I^c)^2\right)$$

$R_I^c$  has to be chosen so that  $n_I(\mathbf{G})$  is converged for the density cutoff. The Hartree-like term is not calculated independently but together with  $E_H$  and  $E_{PS}^L$ .

## Hartree energy

We define a total charge density

$$n(r) = n_e(r) + \sum_I n_I(r - R_I),$$

and the corresponding Hartree energy

$$E_H = \frac{1}{2} \int \int \frac{n(r_1)n(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

This energy includes not only the electron-electron and ion-ion interaction but also an interaction electron-ions. This term is compensated by another term included into  $E_{PS}^L$ . In the program  $E_H$  is calculated from the formula

$$\begin{aligned} E_H &= \frac{1}{2} \int V_H(r)n(r)dr \\ &= \Omega \sum_{G>0} \frac{4\pi}{G^2} n(G)n(G)^* \end{aligned}$$

where  $V_H$  in reciprocal space is defined by the solution of Poisson's equation for periodic boundary conditions.

The total charge  $n$  is conveniently calculated in  $\mathbf{G}$  space.

$$n(G) = n_e(G) + \sum_I n_I(G)e^{iGR_I}$$

## Local pseudo potential energy

$$E_{PS}^L = \int n_e(r) \sum_I \left\{ V_I(r - R_I) + \frac{Z_I}{r - R_I} \operatorname{erf} \left( \frac{r - R_I}{R_I^c} \right) \right\} dr$$

Where the second term in the potential is for the compensation of the electron-ion interaction in the Hartree term. This integral is again calculated in reciprocal space.

$$E_{PS}^L = \Omega \sum_G \left\{ \sum_I \check{V}_I(G) \right\} n_e(G)$$

This sum can be restricted to  $G \geq 0$  by taken the symmetry into account.  $\tilde{V}_I(G)$  is calculated by using Fourier interpolation

$$\tilde{V}_I(G) = \tilde{v}_{loc}(G)e^{iGR_I}$$

and where  $\tilde{v}_{loc}(G)$  is calculated during the initialization of the calculation by a Fourier transformation of

$$\tilde{v}_{loc}(r) = v_{loc}(r) - \frac{Z_I}{r} \operatorname{erf}\left(\frac{r}{R_I^c}\right)$$