

Calculation of forces, Kohn-Sham energies,  
Isolated systems

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## Electronic forces

The forces on the electronic degrees of freedom

$$\frac{\delta E\{\Psi\}}{\delta \Psi_i^*} = \mathbf{H}\Psi_i = \Phi_i$$

where  $\mathbf{H}$  is defined by

$$\mathbf{H} = -\frac{1}{2}\nabla^2 + V_{PS}^L(r) + V_{PS}^{NL} + V_H(r) + V_{xc}(r)$$

are calculated in three steps.

The kinetic energy operator is diagonal in reciprocal space

$$-\frac{1}{2}\nabla^2 f_i \Psi_i = -f_i \sum_G G^2 c_{Gi} e^{iGr}$$

$V_{PS}^L(r)$ ,  $V_H(r)$ , and  $V_{xc}(r)$  are local potentials in real space.  $V_{PS}^L(r)$  and  $V_H(r)$  are calculated in reciprocal space and then transformed to real space and added to the exchange and correlation potential. The force coming from these potentials is calculated by first calculating  $\Psi_i$  on the real space mesh by using a fast Fourier transform then multiplied by the potential and transformed back to reciprocal space.

$$\begin{aligned} \Psi_i(G) &= c_{Gi} \xrightarrow{FFT} \Psi_i(R) \\ \Psi_i(R) * V(R) &\xrightarrow{FFT} \Phi_i(G) \end{aligned}$$

The nonlocal part of the pseudo potential force finally is calculated from (we assume again the fully separable Kleinman-Bylander form )

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

If we analyze the number of operations needed to calculate the different parts of the electronic force, we find (for N states and M plane waves)

Kinetic energy contribution :  $\mathcal{O}(N M)$   
 local potentials :  $\mathcal{O}(N M \log(M))$   
 non-local pseudo potential :  $\mathcal{O}(N^2 M)$ .

From this it is clear that eventually for big systems the nonlocal part will dominate the calculation of the forces. For this reason it was proposed to calculate the non-local parts also in real space.

- X. Gonze, J.P. Vigneron, and J.-P. Michenaud, *J. Phys. Condens. Matter* **1**, 525 (1989)
- R.D. King-Smith, M.C. Payne, and J.S. Lin, *Phys. Rev. B*, **44**, 13063 (1991)

By making use of the local character of the projector functions  $|\beta_L^I\rangle$  the number of operations needed reduces to  $\mathcal{O}(N^2)$ . As there is a big prefactor to this scaling law, the calculation of the non-local parts in real space becomes only favorable for rather large systems. This procedure needs special care as it can only approximate the integrals and their derivatives. Currently this scheme is not implemented in CPMD.

## Ionic forces

The forces on the ions are calculated using the Hellmann-Feynman theorem

$$\frac{\partial E_{tot}}{\partial R_I} = \langle \Psi | \frac{\partial \mathbf{H}}{\partial R_I} | \Psi \rangle$$

The terms in  $\mathbf{H}$  that depend on  $R_I$  are

- local pseudo potential
- non-local pseudo potential
- ion-ion interaction

## Ion-ion interaction

We have re-written this term because of divergences in the sum over full space. To get the exact derivative of the energy we have to derive the separate terms. The ion-ion interaction was split into  $E_{self}$ ,  $E_{ovrl}$  and two terms that were added to the Hartree energy  $E_H$  and the local pseudo potential energy

$E_{PS}^L$ . The self energy of the smeared charges does not contribute to the ionic force.

$$\frac{\partial E_{self}}{\partial R_I} = 0$$

The overlap Energy depends on inter-atomic distances and gives a contribution to the force

$$\begin{aligned} \frac{\partial E_{ovrl}}{\partial R_{I\alpha}} &= \sum_J \frac{\partial}{\partial R_{I\alpha}} \left\{ \frac{Z_I Z_J}{|R_I - R_J|} \operatorname{erfc} \left( \frac{|R_I - R_J|}{\sqrt{(R_I^c)^2 + (R_J^c)^2}} \right) \right\} \\ &= -Z_I Z_J \frac{(R_{I\alpha} - R_{J\alpha})}{|R_I - R_J|^2} \left[ \frac{\operatorname{erfc} \left( \frac{|R_I - R_J|}{\sqrt{(R_I^c)^2 + (R_J^c)^2}} \right)}{|R_I - R_J|} + \frac{2}{\sqrt{\pi}} \frac{\exp \left( \frac{-|R_I - R_J|^2}{(R_I^c)^2 + (R_J^c)^2} \right)}{\sqrt{(R_I^c)^2 + (R_J^c)^2}} \right] \end{aligned}$$

The Hartree energy depends explicitly on the ionic positions through the Gaussian charge distributions.

$$\begin{aligned} \frac{\partial E_H}{\partial R_{I\alpha}} &= \frac{\partial}{\partial R_{I\alpha}} \left( \frac{1}{2} \int \int dr dr' \frac{n(r)n(r')}{|r - r'|} \right) \\ &= \int V_H(r) \frac{\partial n(r)}{\partial R_{I\alpha}} dr \\ &= \int V_H(r) \frac{\partial n_I(r)}{\partial R_{I\alpha}} dr \\ &= \sum_{G \neq 0} \frac{4\pi}{G^2} n^*(G) \frac{\partial}{\partial R_{I\alpha}} n_I(G) e^{iGR_I} \end{aligned}$$

The derivative of the ionic charge distribution can be written in reciprocal space

$$\frac{\partial}{\partial R_{I\alpha}} n_I(G) e^{iGR_I} = n_I(G) \frac{\partial}{\partial R_{I\alpha}} e^{iGR_I} = iG_\alpha n_I(G) e^{iGR_I}$$

Making use of the symmetry of the G vectors we end up with the following working formula

$$\frac{\partial E_H}{\partial R_{I\alpha}} = 2\Omega \sum_{G \neq 0} \operatorname{Re} \left( iG_\alpha n_I(G) e^{iGR_I} \frac{4\pi}{G^2} n^*(G) \right)$$

## Local pseudo potential

In the local part of the pseudo potential energy only the pseudo potential depends on the ionic positions. As the contribution from the Hartree term we can easily calculate this term in G space.

$$\frac{\partial E_{PS}^L}{\partial R_{I\alpha}} = 2\Omega \sum_{G \neq 0} \text{Re} \left( e^{iGR_I} iG_\alpha \tilde{V}_I(G) n_e^*(G) \right)$$

## Non-local pseudo potential

By straightforward derivation of the formula for the non-local pseudo potential energy, we get

$$\frac{\partial E_{PS}^L}{\partial R_{I\alpha}} = 2 \sum_i f_i \sum_{l,m} W_{l,m}^I F_{i,l,m}^I \frac{\partial F_{i,l,m}^I}{\partial R_{I\alpha}}$$

where the derivative of F is calculated in reciprocal space.

$$\frac{\partial F_{i,l,m}^I}{\partial R_{I\alpha}} = \sum_G iG_\alpha c_{Gi}^* \beta_{l,m}^I(G) e^{iGR_I}$$

## Kohn-Sham energies

The Kohn-Sham (KS) equations can be expressed in matrix form for a given set of basis functions  $\{\chi_i\}$ .

$$\mathbf{H}_{KS}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{\Lambda}$$

$\mathbf{H}_{KS}$ ,  $\mathbf{C}$ ,  $\mathbf{\Lambda}$ , and  $\mathbf{S}$  are matrices of dimension  $M$ , the number of basis functions.  $\mathbf{H}_{KS}$  is the KS matrix,  $\mathbf{C}$  the matrix of orbital expansion coefficients

$$\Psi_i(r) = \sum_{k=1}^M c_{ki} \chi_k(r)$$

$\mathbf{S}$  the overlap matrix

$$\mathbf{S}_{ij} = \langle \chi_i | \chi_j \rangle$$

( $\mathbf{S}$  is the unit matrix for plane wave or other orthogonal basis sets, but not if Vanderbilt ultra-soft pseudo potentials are used), and  $\mathbf{\Lambda}$  the matrix of Lagrange multipliers.

The condition for stationary wavefunctions is, that  $\mathbf{\Lambda}$  has the following special structure

$$\mathbf{\Lambda} = \begin{pmatrix} \mathbf{\Lambda}_o & 0 \\ 0 & \mathbf{\Lambda}_u \end{pmatrix}$$

where  $\mathbf{\Lambda}_o$  is a  $N \times N$  matrix ( $N$ : number of occupied orbitals). From the stationarity conditions it can be derived that the KS equations are invariant to unitary transformations within the space of occupied and unoccupied orbitals respectively. The special set of orbitals that lead to a diagonal matrix  $\mathbf{\Lambda}$  are called canonical KS orbitals and the eigenvalues of  $\mathbf{\Lambda}$  are the KS eigenvalues.

In calculations with plane wave basis sets  $M \gg N$  and for efficiency reasons the energy functional  $E(\{\Psi_i\})$  is optimized directly. At the end of such an optimization the orbitals  $\Psi_i$  are not the canonical KS orbitals. It is easy to find the unitary transformation to get canonical KS orbitals and corresponding eigenvalues by diagonalizing the  $N \times N$  matrix  $\mathbf{\Lambda}_o$ . From the direct optimization of the energy it is not possible to get unoccupied orbitals. But as  $\mathbf{H}_{KS}$  is fully determined by the occupied orbitals, eigenvalues and eigenfunctions for unoccupied states can be calculated by diagonalizing  $\mathbf{H}_{KS}$ .

## The zero of energy

The total energy is a functional of  $\{\Psi_i\}$ , where  $\Psi_i$  fulfills

$$\mathbf{H}_{KS}\Psi_i = \epsilon_i\Psi_i$$

but also

$$(\mathbf{H}_{KS} + a\mathbf{1})\Psi_i = (\epsilon_i + a)\Psi_i.$$

The potential and the KS eigenvalues are only determined up to a constant value  $a$ . A reasonable (standard) choice for the potential is,

$$\begin{aligned} V(\infty) &= 0 && \text{for isolated systems} \\ V(G=0) &= 0 && \text{for periodic systems} \end{aligned}$$

This choice allows for the interpretation of the KS eigenvalues as ionization potentials.

**Warning:** In version 2.5 of CPMD the potential was chosen as  $V_H(G=0) = 0$ . From version 3.0 on we will use  $V_H(G=0) + V_{PS}(G=0) = 0$ . For isolated systems the reference potential is in all versions  $V(\infty) = 0$ .

## Davidson diagonalization

The huge size of the basis set in plane wave calculations prohibits the calculation and full diagonalization of the KS matrix. There exist several methods to calculate only some of the eigenvectors of big matrices. For these methods it is not necessary to calculate the matrix, only its action on an arbitrary vector has to be known.

$$\Phi_i = \mathbf{H}\Psi_i$$

The method implemented in CPMD was developed by E. Davidson in the context of configuration interaction calculations.

- E.R. Davidson, *J. Comput. Phys.* **17**, 87 (1975)
- B.N. Parlett, *The Symmetric Eigenvalue Problem*, Prentice-Hall, N.J. 1980
- P.-A. Malmquist, *Mathematical Tools in Quantum Chemistry*, in *Lecture Notes in Quantum Chemistry*, Ed. B.O. Roos, Springer-Verlag, Berlin 1992

We assume in the following that eigenvalues are numbered in increasing order.

$$\mathbf{H}x_i = \lambda_i x_i$$

We expand the eigenvectors in some set of orthonormal vectors  $b_i$  ( $i=1, \dots, k$ ).

$$\begin{aligned}\mathbf{B} &= (b_1, \dots, b_k) \\ x_i &= \mathbf{B}c_i \\ \mathbf{B}^\dagger \mathbf{H} \mathbf{B} c_i &= E_i c_i\end{aligned}$$

It is now strictly valid that

$$E_i \geq \lambda_i$$

and if we increase the size of  $\mathbf{B}$  by adding some new vectors

$$E_i^k \geq E_i^{k+l} \geq \lambda_i$$

### Structure of the diagonalization routine

1. Choose some initial set of vectors and form the matrices  $\mathbf{B}$  and  $\sigma = \mathbf{H} \mathbf{B}$ .
2. Calculate  $\mathbf{B}^\dagger \mathbf{H} \mathbf{B} = \mathbf{B}^\dagger \sigma$  (the Davidson matrix) and diagonalize to get  $E_i$ .
3. Calculate the residuals

$$r_i = (\mathbf{H} - E_i)x_i.$$

If  $|r_i| < \text{threshold}$ , this state and its eigenvalue are converged and kept fixed.

If  $|r_n| < \text{threshold}$ , where  $n$  is the number of required eigenvalues, stop the procedure.

4. Calculate new vectors  $b$  to be added to  $\mathbf{B}$ . If the size of  $\mathbf{B}$  becomes too large replace  $b_i$  by  $\mathbf{B}c_i$ , for  $i=1, \dots, n$ , and reinitialize  $\mathbf{H} \mathbf{b}_i$  with  $(\mathbf{H} \mathbf{B})c_i$ ,  $\mathbf{B}^\dagger \mathbf{H} \mathbf{B}$  by  $(\mathbf{B}c_j)^\dagger (\mathbf{H} \mathbf{B}c_i)$ . Go back to step 2.



### Calculation of new expansion vectors

There are several possibilities to generate new expansion vectors. The theoretical background of the different procedures is directly connected to the theory of optimization (conjugate gradient methods and quasi-Newton methods). The original Davidson method uses a preconditioner to get new vectors.

$$q_i = \mathbf{X}_i r_i$$

The preconditioner should be as close as possible to  $(\mathbf{H} - \lambda_i)^{-1}$ . This is conveniently approximated by the diagonal matrix

$$(\mathbf{H} - \lambda_i)^{-1} \approx \mathbf{X}_i = \frac{1}{\mathbf{H}_{ii} - E_i}$$

An even better approximation is used in CPMD

$$\begin{aligned} s_i &= \mathbf{X}_i r_i \\ A_i &= \frac{x_i^\dagger r_i}{x_i^\dagger s_i} \\ q_i &= \mathbf{X}_i (r_i - A_i x_i) \end{aligned}$$

Before adding the vectors  $q_i$  to  $\mathbf{B}$  they are orthogonalized with respect to all vectors in  $\mathbf{B}$  and with respect to each other.

**Homework:** The problem of finding the lowest eigenvalue and eigenvector of a matrix can be written as an optimization problem.

$$\text{Min} \left[ \frac{x^\dagger \mathbf{H} x}{x^\dagger x} \right]$$

Derive a quasi-Newton method to calculate  $x$  and its corresponding eigenvalue.

## Isolated systems

### References

- R.N. Barnett and U. Landman, Phys. Rev. B **48**, 2081 (1993).
- R.W. Hockney, Methods Comput. Phys. **9**, 136 (1970).
- J.W. Eastwood and D.R.K. Brownrigg, J. Comp. Phys. **32**, 24 (1979).

Plane wave based calculations imply periodic boundary conditions (PBC). This is appropriate for crystal calculations but very unnatural for molecule or slab calculations. For neutral system this problem is circumvented by use of the supercell method. Namely the molecule is periodically repeated but the distance between each molecule and its periodic images is so large that their interactions are negligible. This procedure is somewhat wasteful but can lead to satisfactory results. Handling charged molecular systems is however considerably more difficult, due to the long range Coulomb forces. A charged periodic system has infinite energy and the interaction between the images cannot really be completely eliminated. In order to circumvent this problem several solutions have been proposed. The simplest fix up is to add to the system a neutralizing background. This leads to finite energies but does not eliminate the interaction between the images and makes the calculation of absolute energies difficult.

The method implemented in CPMD is similar to the approach of Barnett and Landman and is based on the Poisson solver of Hockney.

If we analyze the individual terms in the expression for the total energy we see, that only the Coulomb like terms are of long range form. Only the Hartree energy and the local part of the pseudo potential energy have to be considered anew. In a first step we proceed like in the calculation of the Ewald sum and replace the ionic point charges by Gaussian charge distributions.  $E_{self}$  and  $E_{ovrl}$  have still the same form, with the sum in  $E_{ovrl}$  restricted to the finite system. The redefined local pseudo potential is now of short range form as the long range Coulombic  $1/r$  part is exactly canceled by the correction for the Gaussian charge distribution. The term left is the modified Hartree energy. The only part of the program that has to be changed is the solution of Poisson's equation to get the Hartree potential.

## Poisson solvers

For a one dimensional system we have to solve

$$\nabla^2 \Phi(x) = \rho(x)$$

or equivalent

$$\Phi(x) = \int \frac{\rho(y)}{|x-y|} dy$$

subject to the boundary conditions  $\Phi(x) = \Phi(x+L)$  for periodic systems and  $\Phi(\infty) = 0$  for isolated systems. For periodic systems  $\Phi(x)$  is calculated in reciprocal space

$$\Phi(G) = \frac{4\pi}{G^2} \rho(G).$$

For isolated systems we assume that the electron density is nonzero only on a short interval  $L$  and that we sample it on this interval at  $N$  equidistant points. The convolution can then be written

$$\begin{aligned} \Phi(x_p) &= \frac{L}{N} \sum_{p'=-\infty}^{\infty} G(x_p - x_{p'}) \rho(x_{p'}) \\ &= \frac{L}{N} \sum_{p'=0}^N G(x_p - x_{p'}) \rho(x_{p'}) \end{aligned}$$

for  $p = 0, 1, 2, \dots, N$ , where  $G(x_p - x_{p'})$  is the Green's function. In Hockney's algorithm this equation is replaced by the cyclic convolution

$$\tilde{\Phi}(x_p) = \frac{L}{N} \sum_{p'=0}^{2N+1} \tilde{G}(x_p - x_{p'}) \tilde{\rho}(x_{p'})$$

where  $p = 0, 1, 2, \dots, 2N+1$ ,

$$\begin{aligned} \tilde{\rho}(x_p) &= \begin{cases} \rho(x_p) & 0 \leq p \leq N \\ 0 & N \leq p \leq 2N+1 \end{cases} \\ \tilde{G}(x_p) &= G(x_p) \quad -(N+1) \leq p \leq N \\ \tilde{\rho}(x_p) &= \tilde{\rho}(x_p + 2L) \\ \tilde{G}(x_p) &= \tilde{G}(x_p + 2L) \end{aligned}$$

The solution  $\tilde{\Phi}(x_p)$  can be obtained by a series of FFT and has the desired property

$$\tilde{\Phi}(x_p) = \Phi(x_p) \quad \text{for } 0 \leq p \leq N.$$

To remove the singularity of the Green's function at  $x = 0$  we modify  $G(x_p)$  for small  $x$  and correct for the difference by using the analytic form of the error.

$$G(x) = \frac{1}{x} \operatorname{erf}\left(\frac{r}{r_c}\right) + \frac{1}{x} \left(1 - \operatorname{erf}\left(\frac{r}{r_c}\right)\right),$$

where  $r_c$  is chosen to be  $\frac{L}{2N}$ . In an optimized implementation Hockney's method requires the double amount of memory and two FFT on the box of double size. In big electronic structure calculations the memory requirements are dominated by the orbitals and orthogonalization of the orbitals is the most time consuming step. Thus, the overhead introduced by Hockney's method is negligible for both cases.

## Practical implementation

Calculation of the influence functions (Fourier transforms of the Green's functions).

We have to calculate the influence function  $\Phi(G)$  on the double grid and the correction influence function  $\Phi_z$  on the normal grid. The correction is only of short range character and can be handled in the same way as the modified local pseudo potential.

$$\Phi_z(G) = \frac{4\pi}{\Omega} \int_0^\infty r^2 \left[ \frac{\operatorname{erfc}\left(\frac{r}{r_c}\right)}{r} \right] j_0(rG) dr$$

and the influence function  $\Phi(G)$  on the double grid

$$G = \frac{2\pi}{A} (i, j, k) (b_1, b_2, b_3)$$

where  $i, j, k = 0, \dots, 2N$ .

$$\Phi(G) = \int \frac{\operatorname{erf}\left(\frac{r}{r_c}\right)}{r} e^{iGr} dr$$

These two functions are computed at the beginning of a calculation and stored for later usage.

The calculation of the Hartree potential is done in three steps.

1. Calculate the total density  $n(\mathbf{r})$  on the regular grid. Initialize additional grid points with zero values. Transform the new function in the double box to reciprocal space. Make use of the sparsity of the density.
2. Multiply the transformed density by the influence function to get the potential on the double grid.
3. Transform the potential back to real space. Make use of fact that we only have to know the potential on the regular grid.

Finally we add  $V_H(G)$  to the correction term

$$V_Z(G) = \Phi_Z(G) * n(G)$$

### Energies

$$\begin{aligned} E_{H1} &= \frac{\Omega}{2N_R} \sum_R V_H(R) * n_e(R) \\ E_{H2} &= \Omega \sum_I \sum_{G>0} V_H^*(G) n_I(G) e^{iGR_I} \\ E_Z &= \Omega \sum_G \Phi_Z(G) * \text{Re}(n(G))^2 \end{aligned}$$

### Forces on the ions

$$\frac{\partial E_H}{\partial R_{I\alpha}} = 2\Omega \text{Re} \left[ \sum_{G>0} iG_\alpha (V_Z^*(G) + V_H^*(G)) n_I(G) e^{iGR_I} \right]$$