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The effect of the parameter *ecuti* on the total energy convergence of bulk crystal using FHI98MD code.

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Abstract

We have presented the effect of total energy convergence for some bulk crystal in the framework of density-function theory within Local Density approximation (LDA) by using Williams-Solar and Joannopoulos minimization scheme. We have implemented these with a powerful code (FHI98MD). This was achieved by using different values for the parameter ecuti in Rydberg. It has been found that, the value of the parameter ecuti influences the speed and accuracy of the convergence.

1.0 Introduction

Total- energy calculation and molecular dynamics simulations employing density functional theory represent a reliable tool in condensed matter physics, material science, chemical physics and physical chemistry. A large variety of applications in system as different as molecules, bulk materials and surfaces have proven the power of these methods in analyzing as well as in predicting equilibrium and non – equilibrium properties. *Ab initio* molecular dynamics simulations enable the analysis of the atomic motion and allow the accurate calculation of thermodynamic properties such as the free energy, diffusion constant and melting temperatures of materials.

The package **fhi98md** is designed to investigate the material properties of large systems. The package **fhi98md** is based on a previous version **fhi96md** [1]. The new version, however, is based on FORTRAN90 and allows dynamic memory allocation. The package consists of the program **fhi98md** and a start utility **fhi98start**. The program **fhi98md** can be used to perform static total energy calculation or *ab initio* molecular dynamics simulations. The utility **fhi98start** assists in generating the input file required to run **fhi98md**, thereby ensuring the lowest possible memory demand for each individual run. Thus no recompilations are required; a full calculation can be performed by calling the two binary executables **fhi98start** and **fhi98md** in sequence.

In this work, the effect of the variable *ecuti*, on the convergence of total energy in bulk crystal is investigated. The minimisation schemes in the total energy calculations are outlined in section two.

2.0 Total energy minimization scheme:

2.1 Introduction

In an electronic structure calculation using a plane-wave basis, the Hilbert space is typically spanned by a huge number of basis functions (up to 10^5 plane waves). Therefore it would be unwise to attempt to diagonalize the Hamiltonian operator in this high-dimensional

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space directly. Instead, one uses algorithms which only imply vector operations on the wave function vector (in Hilbert space), rather than matrix operations. The wave functions are gradually improved in an iterative process, until they eventually converge towards the eigenvectors [2].

The goal is to minimize the total energy with respect to the wave function $\left|\psi_{i.k}\right\rangle$ starting with a trial wave function $\left|\psi_{i,k}^{o}\right\rangle$. The energy minimization scheme is formulated in terms of an equation of motion for the wave function $\left|\psi_{i,k}^{(t)}\right\rangle$ in the fictitious time variable t.

2.2 Steepest Descent:

The simplest scheme to iterate the wave functions is the steepest descent approach [3]. It can be derived from a first-order equation of motion,

$$\frac{d}{dt}\left|\psi_{i,k}^{(t)}\right\rangle = \left(\tilde{\in}_{i,k} - \hat{H}_{KS}\right)\left|\psi_{i,k}^{(t)}\right\rangle, \tag{2.1}$$

imposing the ortho-normality constraint $\left\langle\psi_{i,k}^{(t)}\middle|\psi_{j,i}^{(t)}\right\rangle = \delta_{i,j}$, where $\hat{H}_{KS}$ is the Kohn-Sham Hamiltonian and $\tilde{\in}_{i,k}$ are the Lagrange parameters introduced to account for the ortho-normality constraint. In the simplest possible discretization of this differential equation, only information from the last step is used,

$$\left\langle G+k\middle|\psi_{i,k}^{(t-1)}\right\rangle = \left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle + \beta\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle - \eta\left\langle G+k\middle|\hat{H}_{KS}\middle|\psi_{i,k}^{(t)}\right\rangle, \tag{2.2}$$

where $\beta = \tilde{\varepsilon}_{i,k}\delta t$ and $\eta = \delta t$. However, it turns out that this discretization scheme is not very efficient.

2.3 Damped Joannopoulos

A more efficient scheme based on a second order equation of motion might also be used

$$\frac{d^2}{dt^2}\left|\psi_{i,k}^{(t)}\right\rangle + 2\gamma\frac{d}{d\tau}\left|\psi_{i,k}^{(t)}\right\rangle = \left(\tilde{\in}_{i,k} - \hat{H}_{KS}\right)\left|\psi_{i,k}^{(t)}\right\rangle, \tag{2.3}$$

where γ is a damping parameter. The equation of motion is integrated for a step length δt by the Joannopoulos approach [4], which iteratively improves the initial wave functions. In this algorithm the new wave functions $\left|\psi_{i,k}^{(t-1)}\right\rangle$ is constructed from the wave functions of the last two iteration steps t and (*t* - 1),

$\left\langle G+k\middle|\psi_{i,k}^{(t+1)}\right\rangle = \left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle + \beta_G\left\langle G+k\middle|\psi_{i,k}^{(t)}\right\rangle - \gamma_G\left\langle G+k\middle|\psi_{i,k}^{(t-1)}\right\rangle - \eta_G\left\langle G+k\middle|\hat{H}_{KS}\middle|\psi_{i,k}^{(t)}\right\rangle$, where the coefficients are

$$\beta_G = \frac{\tilde{\in}_{i,k}\,(h_G(\delta t)-1) - \left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle e^{-\gamma\delta t}}{\tilde{\in}_{i,k} - \left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle}, \tag{2.4}$$

$$\gamma_G = e^{-\gamma\delta t},$$

$$\eta_G = \frac{(h_G(\delta t) - e^{-\gamma\delta t} - 1}{\tilde{\in}_{i,k} - \left\langle G+k\middle|\hat{H}_{KS}\middle|G+k\right\rangle}, \tag{2.5}$$

with $\tilde{\epsilon}_{i,k} = \left\langle \psi_{i,k}^{t} \middle| \hat{H}_{KS} \middle| \psi_{i,k}^{t} \right\rangle$. The function $h(\delta t)$ is defined by

$$h_G(\delta t) = \begin{cases} 2e^{-\frac{\gamma}{2}\delta t} \cos(\omega_G \delta t) & if \quad \omega_G^2 \geq 0 \\ 2e^{-\frac{\gamma}{2}\delta t} \cosh\left(\sqrt{|\omega_G^2|}\delta t\right) & if \quad \omega_G^2 < 0 \end{cases}$$

with $\omega_G^2 = \left\langle G+k \middle| \hat{H}_{KS} \middle| G+k \right\rangle - \tilde{\varepsilon}_{i,k} - \frac{\gamma^2}{4}$.

2.4 Williams-Solar

Although the damped Jaonnopoulos algorithm is more efficient than the first order scheme, additional storage for the wave function $|\psi_{i,k}^{(t-1)}\rangle$ is needed. Therefore the William-Soler algorithm [5] is recommended whenever storage requirements do not permit to employ the damped Joannopoulos algorithm. The coefficients of this scheme are

$$\beta_G = \frac{\tilde{\epsilon}_{i,k}\,[e^{(\tilde{\epsilon}_{i,k} - \langle G+k|\hat{H}_{KS}|G+k\rangle)\delta t - 1}]}{\tilde{\epsilon}_{i,k} - \langle G+k|\hat{H}_{KS}|G+k\rangle},$$

$$\eta_G = \frac{e^{\tilde{\epsilon}_{i,k} - \langle G+k|\hat{H}_{KS}|G+k\rangle \delta t - 1}}{\tilde{\epsilon}_{i,k} - \langle G+k|\hat{H}_{KS}|G+k\rangle},$$

With $\gamma_G = 0$ Thus, damped Joannopoulos scheme contains the Williams-Solar scheme as a limiting case, when $\gamma \to \infty$. On the other hand, the Williams-Solar scheme itself approaches the steepest descent scheme, if δt is sufficiently small.

The choice of δt and γ depends on the atomic species and the configuration. The corresponding parameters in the *inp.mod* input file are *delt* and *gamma*. Typically *delt* lies between 1 and 40 and *gamma* is within the range $0 \prec \gamma \prec 1$.

If the improvement in the total energy per iteration is less than *eps_chg_delt* the parameters *delt2* and *gamma2* are used instead, in order to ensure the stability of convergence.

The Table 2.1 contains some values to the electronic time step *delt*, the damping parameter *gamma* and the minimization scheme used for bulk calculations. The labels J, WS and SD mean that either the damped Joannopoulos or Williams-Solar or Steepest Descent minimization scheme was adopted. The table provides a few numbers which should be used as a guide to have an optimal parameters for successful convergence.

Table 2.1: Electronic time step *delt*, damping parameter *gamma*, and minimization scheme [6].

Bulk				
Material	**Number of atoms**	**Scheme**	***delt***	***gamma***
Si	2	J	30	0.4
Ga	4	J	20	0.3
As	2	J	20	0.3
Al	1	WS	06	0.4
Al	1	SD	12	0.4

3.0 Procedure

The input file **inp.mod** has thirty four variables while the other input file, **starting** has thirty nine variables. These seventy three variables can be broadly classified into five categories based on what the specify. Thus, we have variables that specify the: (i) Lattice structure, e.g *ibrav*, *celldm* (ii) the atoms in the crystals, e.g number of atoms, number of valence electron, name of crystal, gauss radius, mass (iii) the type of run e.g continuation run, total energy run, energy band run, etc, and (iv) computational scheme employed. The fifth class is composed semi-empirical variables that have to be optimised on running the code. The *ecuti* is one of such variables.

A bulk crystal e.g Silicon is selected and the variables specifying it and its lattice structure, computational scheme and type of run (Total energy in this case) are evaluated and entered into the input files appropriately. An initial value of 2.0 Rydberg for the *ecuti* is chosen and the programme is executed. This is repeated for other values of *ecuti*.

The above procedure is repeated for Aluminium, Gallium and Arsenic. The data generated from the output files are analysed and the graphs showing the effect of the value of *ecuti* on convergence of total energy are plotted.

4.0 Results and discussion

Figure 4.1 shows the variation of the total energy as a function of the number of electronic iterations for different values of *ecuti* for bulk *Al* (in the fcc structure) within Local Density approximation by using the Williams-Solar minimization scheme to iterate the wave functions. Figure 4.2 shows the variation of the total energy as a function of the number of electronic iterations for different values of *ecuti* for bulk *Si* (in the diamond structure) within Local Density approximation by using the Joannopoulos minimization scheme to iterate the wave functions. Figure 4.3 shows the variation of the total energy as a function of the number of electronic iterations for different values of *ecuti* for bulk *Ga* (in the base centered orthorhombic structure) within Local Density approximation by using the Joannopoulos minimization scheme to iterate the wave functions. Figure 4.4 shows the variation of the total energy as a function of the number of electronic iterations for different values of *ecuti* for bulk As (in the rhombohedral structure) within Local Density approximation by using the Joannopoulos minimization scheme to iterate the wave functions.

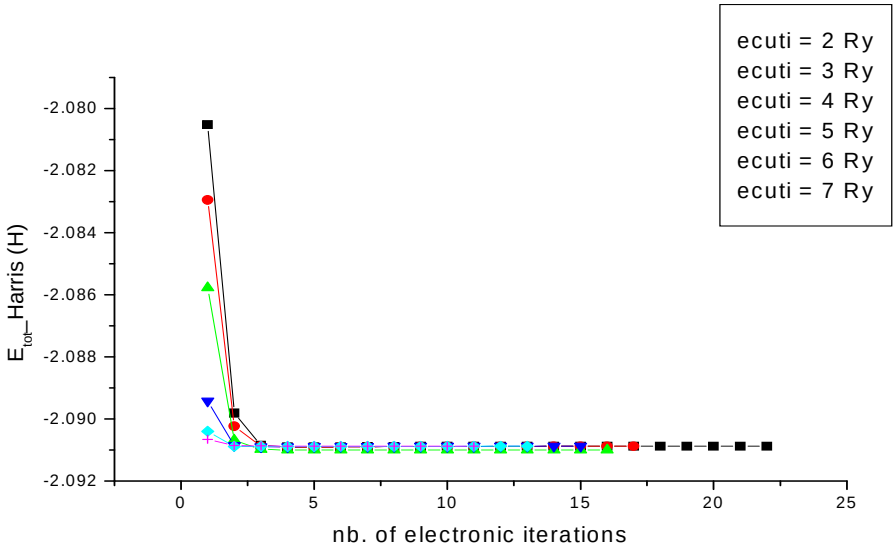

Figure 4.1: Effect of total energy convergence for *Al* bulk in the fcc structure for different values of the electronic iterations *ecuti*.

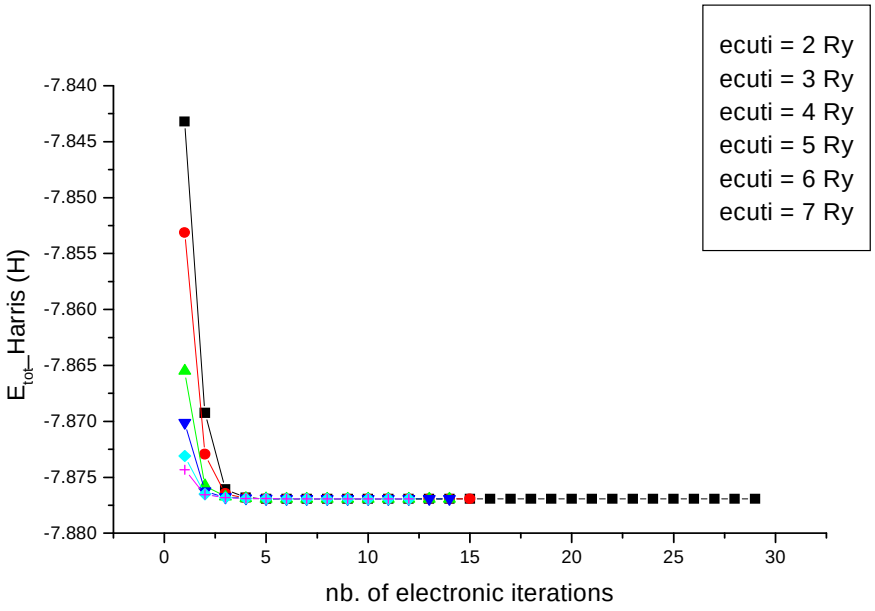

Figure 4.2: Effect of total energy convergence for Si bulk in the diamond structure for different values of the electronic iterations *ecuti*.

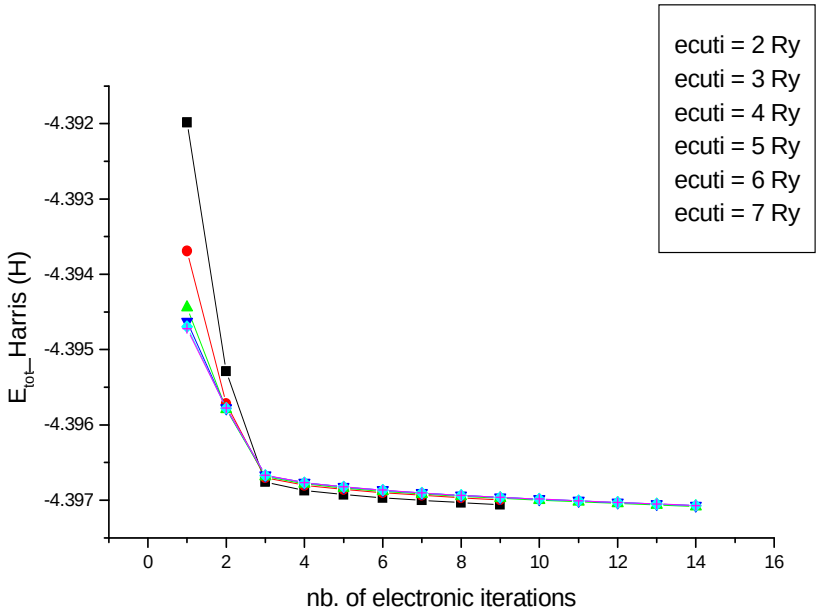

Figure 4.3: Effect of total energy convergence for Ga bulk in the base centered orthorhombic structure for different values of the electronic iterations *ecuti*.

As can be seen from the plots, convergence of total energy has been achieved for Al, Si, and As. However, in the case of Gallium the convergence is not as good as in the other crystals. In general, increasing the value of ecuti decreases the number of iteration required for convergence.

The slight non-convergence in Gallium is attributed for the use of an inaccurate variable not very obvious to the authors

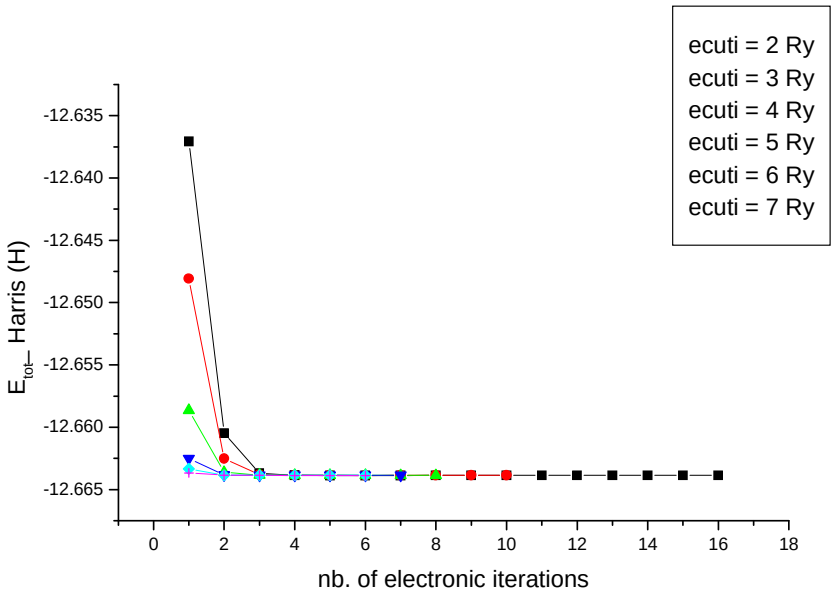

Figure 4.4: Effect of total energy convergence for as bulk in the rhombohedral structure for different values of the electronic iterations *ecuti* .

5.0 Conclusion

Electronic structural convergence depend on a set of parameters which have to be optimized for each system. In this paper, we have optimized the input parameter *ecuti* within the Local density approximation (LDA) by using Williams-Solar and Joannopoulos minimization scheme. It is obvious from the graphs that a higher value of *ecuti* results in a better start value for the main cycle. So less iterations are needed to get the converged eigenvalues.

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Reference:

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