

## Calculations of total energy in the density functional theory using FHI98MD code

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### Abstract

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*We have computed total energy for Al, Si, Ga, and As in the framework of density-functional theory within LDA approximation by using the Williams-Solar minimization scheme to iterate the wave functions. Different values for the electronic time step,  $\Delta t$ , an energy cutoff,  $E_{cut}$  and damping parameter,  $\gamma$  are used. The Monkhorst-Pack  $k$ -point mesh was taken as  $4 \times 4 \times 4$  with the initial  $k$ -point  $(0.5, 0.5, 0.5)$ .  $E_o$  is the well-converged value of the total energy approached. Each computation gives an optimal convergence for all the four elements.*

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### 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.

### 2.0 Total energy calculation:

The key variable in density functional theory (DTF) is the electron density  $n(r)$ , given as stated by the fundamental theorem of Hohenberg and Kohn [2] the ground state energy  $E_0(\{R_j\})$  of the system for given positions of the nuclei  $\{R_j\}$  is the minimum of the Kohn-Sham total-energy functional with respect to the electron density  $n$ . The total-energy functional,  $E[n]$  is given by

$$E[n] = T^s[n] + E^H[n] + E^{e-nuc} + E^{XC}[n] + E^{nuc-nuc} \quad (2.1)$$

Where  $T^s$  is the kinetic energy of non-interacting electrons,  $E^H$  is the Hartree energy, and  $E^{XC}$  is the exchange-correlation energy.

The energy of the electron-nuclei and nuclei-nuclei interaction  $E^{e-nuc}$  and  $E^{nuc-nuc}$  are

$$E^{e-nuc}[n] = \int d^3r V^{e-nuc}(r)n(r) \quad \text{and} \quad E^{nuc-nuc} = \frac{1}{2} \sum_{IJ, I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}, \quad (2.2)$$

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where  $Z_I$  and  $Z_J$  are the charges of the corresponding nuclei. As approximations to the exchange-correlation energy functional  $E^{XC}[n]$  we employ the local-density approximation (LDA),

$$E_{xc}^{LDA} \equiv \int \varepsilon_{xc}(n(r))n(r)dr, \quad (2.3)$$

where  $\varepsilon_{xc}(n)$  is the exchange – correlation energy of a uniform electron gas of density  $n$ . The exchange part is elementary and given, in atomic units, by Dirac [3]

$$\varepsilon_x(n) \equiv -\frac{0.458}{r_s}, \quad (2.4)$$

where  $r_s$  is the radius of a sphere containing one electron and given by  $(4\pi/3)r_s^3 = n^{-1}$ . The correlation part was first estimated by Wigner [4]

$$\varepsilon_c(n) = -\frac{0.44}{r_s + 7.8}, \quad (2.5)$$

and more recently with a high precision of about  $\pm 1\%$  by Ceperly [5] using Monte Carlo methods.

The pseudopotentials are represented in the fully separable form as proposed by Kleiman and Bylander [6].

$$\hat{V}_{I_s}^{e-nuc} = \hat{V}_{I_s, l_{loc}} + \sum_{\substack{i=0, \\ i \neq l_{loc}}}^{l_{max}} \sum_{m=-l}^l \frac{|\Delta V_{I_s, l}^{nl} \langle \psi_{I_s, l, m}^{ps} | \langle \psi_{I_s, l, m}^{ps} | \Delta V_{I_s, l}^{nl} | \psi_{I_s, l, m}^{ps} \rangle|}{\langle \psi_{I_s, l, m}^{ps} | \Delta V_{I_s, l}^{nl} | \psi_{I_s, l, m}^{ps} \rangle}, \quad (2.6)$$

where  $\Delta V_{I_s, l}^{nl}(r) = V_{I_s, l}(r) - V_{I_s, l_{loc}}(r)$ , and  $V_{I_s, l}(r)$  are the radial components of the semi-local pseudopotential and  $\psi_{I_s, l, m}^{ps}(r) = R_l^{ps}(r)Y_l^m(\theta, \phi)$  are the node-free atomic pseudo wave functions. In this form the pseudopotential is split into a local part  $\hat{V}_{I_s}^{ps, local}$  and a nonlocal but separable part  $\hat{V}_{I_s}^{ps, nl}$ .

Correspondingly the potential  $\hat{V}^{e-nuc}$  and the energy  $E^{e-nuc}$  are expressed as

$$\hat{V}^{e-nuc} = \hat{V}^{ps, local} + \hat{V}^{ps, nl} \quad \text{and} \quad E^{e-nuc} = E^{ps, local} + E^{ps, nl}. \quad (2.7)$$

Also, the effect of the core electron density on the exchange-correlation energy is described by a pseudo core density  $\rho_s^{core}(r)$ , which is the superposition of the smoothed core densities  $\rho_s^{core}(r - \tau_{I_s, l_a} - R)$  constructed together with the pseudopotentials. The exchange-correlation functionals  $E^{XC}[n]$  and  $V^{XC}[n]$  are then replaced by  $E^{XC}[n + \rho_s^{core}]$  and  $V^{XC}[n + \rho_s^{core}]$ .

In the past few years iterative techniques have become the method of choice to solve the Kohn-Sham equations and enable first-principles studies even for large systems. The key idea is to minimize the total energy with respect to the wave function  $|\psi_{i,k}\rangle$  starting with a trial wave function  $|\psi_{i,k}^o\rangle$ . The energy minimization scheme is formulated in terms of an equation of motion (EOM) for the wave function  $|\phi_{i,k}^{(t)}\rangle$  in the fictitious time variable  $t$ .

The simplest scheme to iterate the wave functions is the steepest descent approach [11]. It can be derived from a first-order equation of motion,

$$\frac{d}{dt} |\psi_{i,k}^{(t)}\rangle = \left( \mathcal{E}_{i,k}^o - \hat{H}_{KS} \right) |\psi_{i,k}^{(t)}\rangle, \quad (2.8)$$

imposing the ortho-normality constraint  $\langle \psi_{i,k}^{(t)} | \psi_{j,i}^{(t)} \rangle = \delta_{i,j}$ , where  $\hat{H}_{KS}$  is the Kohn-Sham Hamiltonian and  $\mathcal{E}_{i,k}^0$  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,

$$\langle G+k | \psi_{i,k}^{(t-1)} \rangle = \langle G+k | \psi_{i,k}^{(t)} \rangle + \beta \langle G+k | \psi_{i,k}^{(t)} \rangle - \eta \langle G+k | \hat{H}_{KS} | \psi_{i,k}^{(t)} \rangle, \quad (2.9)$$

where  $\beta = \mathcal{E}_{i,k}^0 \delta t$  and  $\eta = \delta t$ . However, it turns out that this discretization scheme is not very efficient.

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

$$\frac{d^2}{dt^2} | \psi_{i,k}^{(t)} \rangle + 2\gamma \frac{d}{d\tau} | \psi_{i,k}^{(t)} \rangle = (\mathcal{E}_{i,k}^0 - \hat{H}_{KS}) | \psi_{i,k}^{(t)} \rangle, \quad (2.10)$$

where  $\gamma$  is a damping parameter. The equation of motion is integrated for a step length  $\delta\tau$  by the Joannopoulos approach [7], which iteratively improves the initial wave functions. In this algorithm the new wave functions  $| \psi_{i,k}^{(t-1)} \rangle$  is constructed from the wave functions of the last two iteration steps  $t$  and  $(t-1)$ ,

$$\langle G+k | \psi_{i,k}^{(t+1)} \rangle = \langle G+k | \psi_{i,k}^{(t)} \rangle + \beta_G \langle G+k | \psi_{i,k}^{(t)} \rangle - \gamma_G \langle G+k | \psi_{i,k}^{(t-1)} \rangle - \eta_G \langle G+k | \hat{H}_{KS} | \psi_{i,k}^{(t)} \rangle,$$

where the coefficients are

$$\beta_G = \frac{\mathcal{E}_{i,k}^0 (h_G(\delta t) - 1) - \langle G+k | \hat{H}_{KS} | G+k \rangle e^{-\gamma\delta t}}{\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle}, \quad (2.11)$$

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

$$\eta_G = \frac{(h_G(\delta t) - e^{-\gamma\delta t} - 1)}{\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle}, \quad (2.12)$$

with  $\mathcal{E}_{i,k}^0 = \langle \psi_{i,k}^t | \hat{H}_{KS} | \psi_{i,k}^t \rangle$ . The function  $h(\delta t)$  is defined by

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

with  $\omega_G^2 = \langle G+k | \hat{H}_{KS} | G+k \rangle - \mathcal{E}_{i,k}^0 - \frac{\gamma^2}{4}$ .

Although the damped Joannopoulos 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 [9] is recommended whenever storage requirements do not permit to employ the damped Joannopoulos algorithm. The coefficients of this scheme are

$$\beta_G = \frac{\mathcal{E}_{i,k}^0 [e^{(\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle) \delta t - 1}]}{\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle},$$

$$\eta_G = \frac{e^{(\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle) \delta t - 1}}{\mathcal{E}_{i,k}^0 - \langle G+k | \hat{H}_{KS} | G+k \rangle},$$

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

### 3.0 Program structure:

The program uses two input files as an input for the start utility. The file `inp.mod` contains the control parameters for the run, like e.g. the time steps for the electronic and atomic minimizations scheme, the convergence criteria and maximum number of steps. The file `start.inp` describes the geometry of the super cell,

the configuration of the nuclei and parameters relevant for the structure optimization, and the calculation of the electron ground state.

The input file `inp.ini` is usually generated automatically by the start utility **fhi98start** from the files `inp.mod`, `start.inp` and `constraints.ini`. However, the program **fhi98md** also runs individually without the help of the start utility. This requires to provide the file `inp.ini` in addition to `inp.mod`, the pseudopotentials and possible restart file.

Finally, the program terminates when all the output files are written.

### 4.0 Procedure:

First, we compute the *celldm* parameters for each element which depends on the *ibrav* parameter of each structure in the `start.inp` files. Aluminium is a face centred cubic structure with *ibrav* = 2, lattice parameter  $a_{\text{lat}} = (7.5, 0.0, 0.0)$  of *celldm* (1..3) and scaling of the super cell of *celldm* (4..6) = (0,0,0). Silicon is a diamond structure with *ibrav* = 2, lattice parameter  $a_{\text{lat}} = (10.26, 0.0, 0.0)$  and scaling of the super cell of *celldm* (4..6) = (0,0,0). Gallium is a base centred orthorhombic structure with *ibrav* = 12, lattice parameter  $a_{\text{lat}} = (8.25, 8.21, 13.96)$  of *celldm* (1..3) and scaling of super cell of *celldm* (4..6) = (1.0, 1.0, 1.0). Arsenic is a rhombohedral structure with *ibrav* = 10, lattice parameter  $a_{\text{lat}} = (7.1, 2.67, 0.227)$  of *celldm* (1..3) and scaling of super cell of *celldm* (4..6) = (1.0, 1.0, 1.0). These values are put into the `start.inp` files with the atoms per unit cell and valence electron of each structure.

Secondly, in `inp.mod` files the most important parameters which are individually optimized are the electronic time step, *delt* damping parameter, *gamma*. The electronic time step, *delt* has a recommended value ranging from 1 to 40. The damping parameter *gamma* also has a recommended value ranging from 0 p  $\gamma$  p 1.

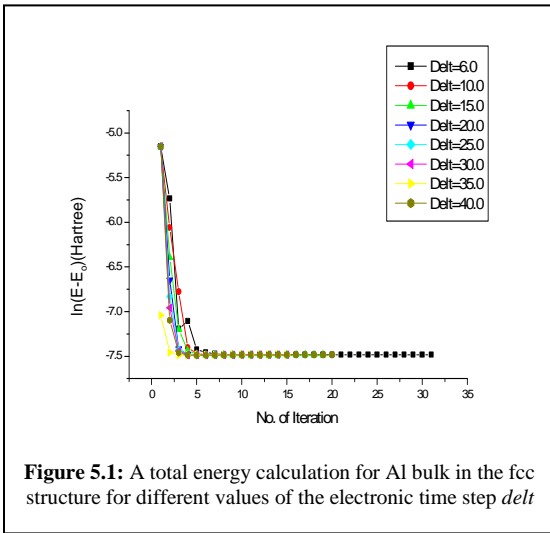
Thirdly, the `inp.mod` and `start.inp` are compile and run the start utility **fhi98start** to generate the input and parameters files for **fhi98md** and finally compile and run the program **fhi98md**. Pseudopotentials files *ga\_aa.cpi* for Gallium, *as\_aa.cpi* for Arsenic, *al\_aa.cpi* for Aluminium and *si\_aa.cpi* for Silicon are provided in the directory `pseudo` for the runs.

Finally, the outputs file **fort.6** are compile and the program terminate on reaching the CPU time. Then, the outputs were analyzed and graphs are plotted using `origin`.

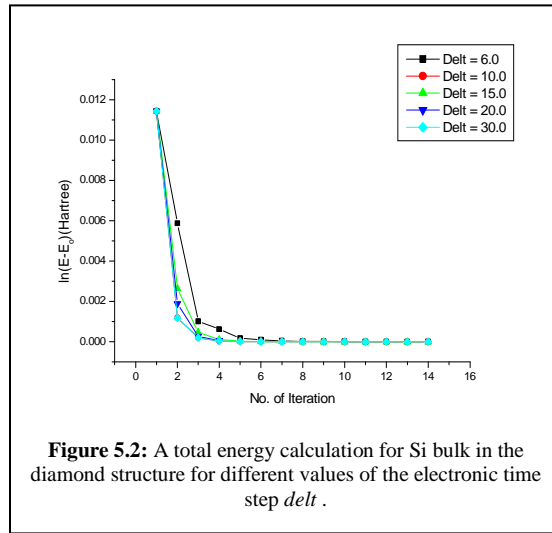
### 5.0 Results and discussion

Figures 5.1, 5.2, 5.3, and 5.4 are the total energy calculation for Al, Si, Ga, and As bulk in different structures within LDA approximation by using the Williams-Solar minimization scheme to iterate the wave functions. Different values for the electronic time step *delt* with an energy Cutoff of 8 Ry and damping parameter of 0.2 are used. The figures 5.5, 5.6, 5.7 and 5.8 are the different values of damping parameters *gamma* with the electronic time step *delt* in the range 1 to 40 and an energy cutoff of 8 Ry. Also, the figures 5.9, 5.10, 5.11, and 5.12 are the different values of an energy cutoff *Ecut* with the damping parameters *gamma* and electronic time step *delt*.

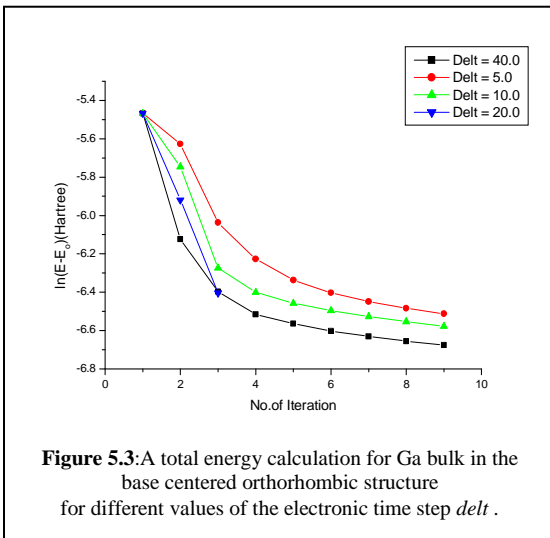
The total energy calculations for GaAs bulk in the zinc-blende structure within LDA approximation by using the Williams-Solar minimization scheme to iterate the wave functions agreed with our results [10].



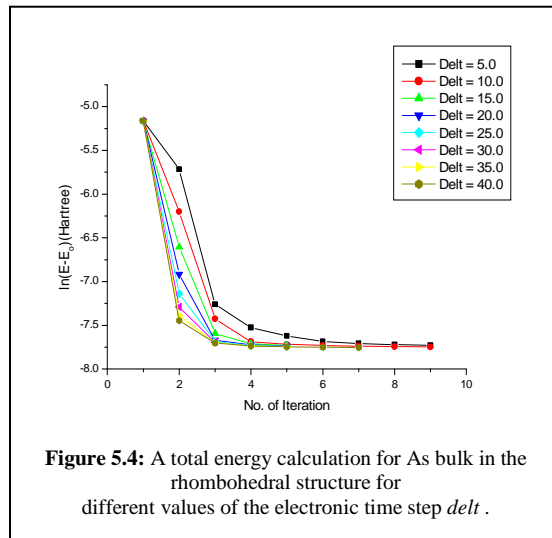
**Figure 5.1:** A total energy calculation for Al bulk in the fcc structure for different values of the electronic time step  $\delta t$



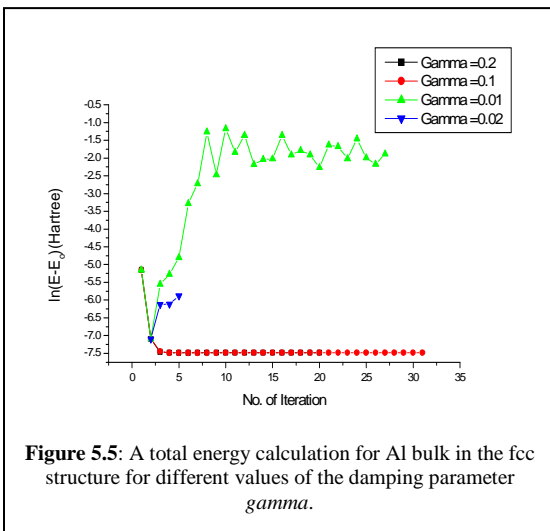
**Figure 5.2:** A total energy calculation for Si bulk in the diamond structure for different values of the electronic time step  $\delta t$ .



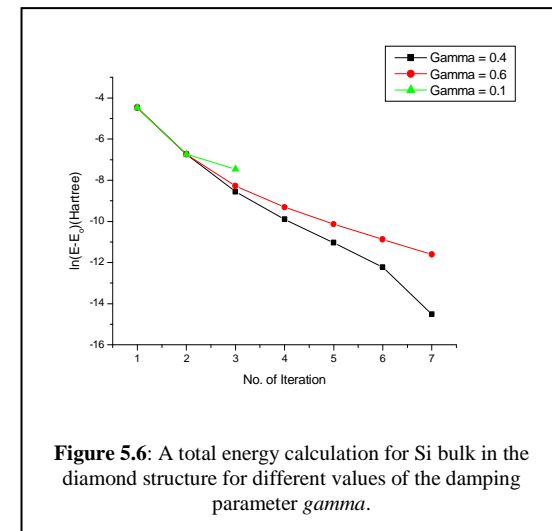
**Figure 5.3:** A total energy calculation for Ga bulk in the base centered orthorhombic structure for different values of the electronic time step  $\delta t$ .



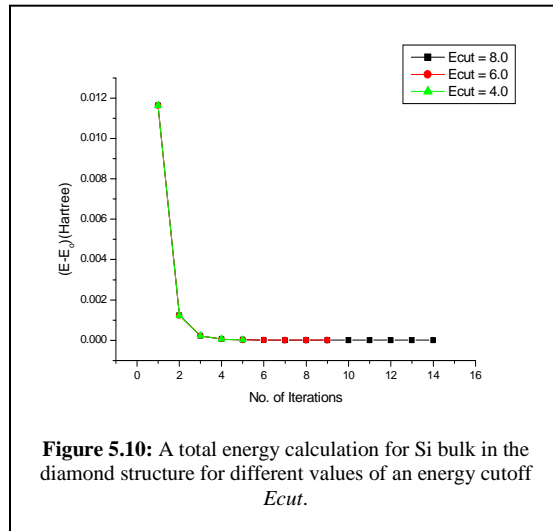
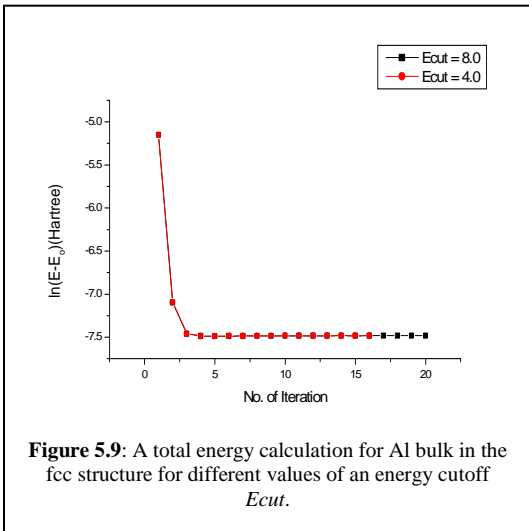
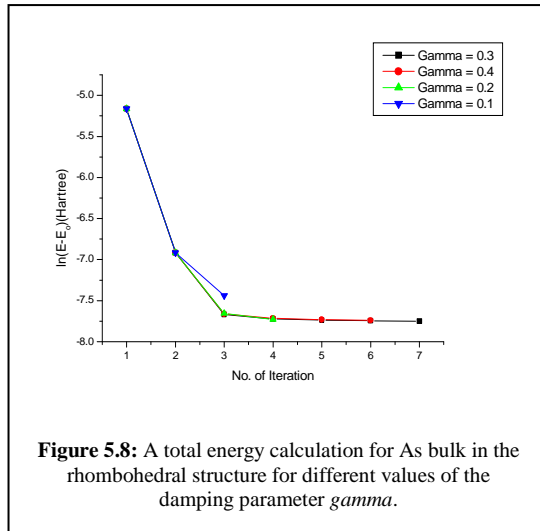
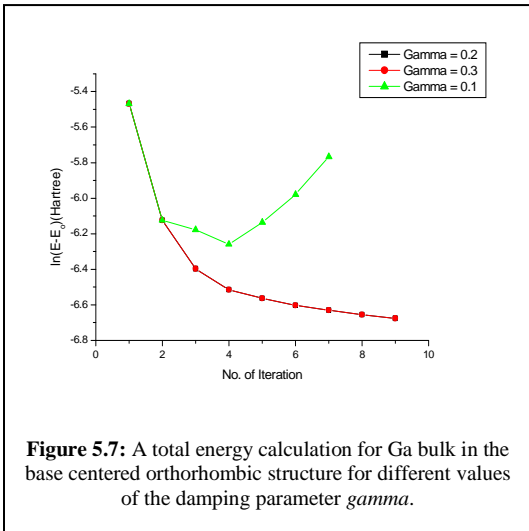
**Figure 5.4:** A total energy calculation for As bulk in the rhombohedral structure for different values of the electronic time step  $\delta t$ .

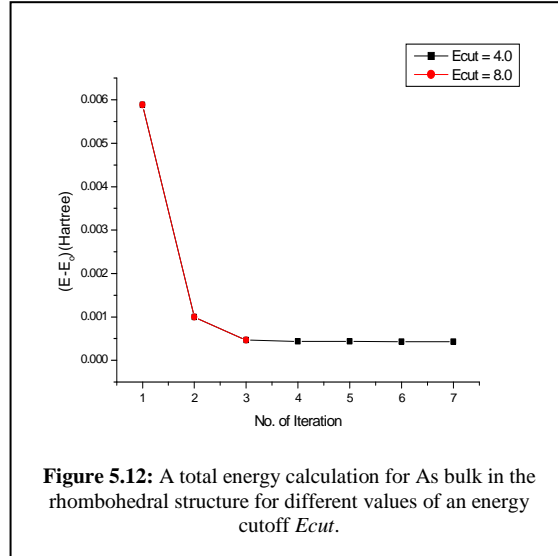
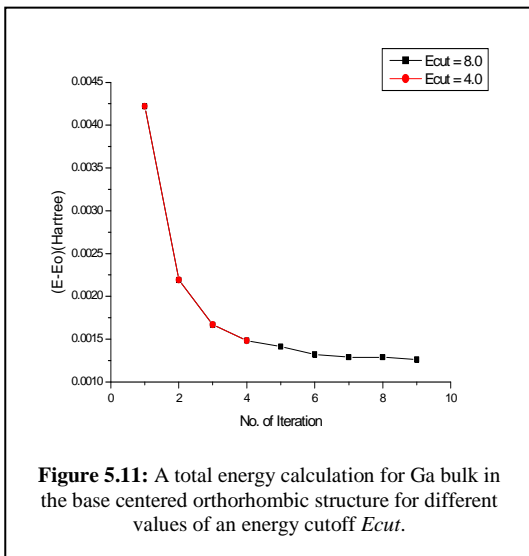


**Figure 5.5:** A total energy calculation for Al bulk in the fcc structure for different values of the damping parameter  $\gamma$ .



**Figure 5.6:** A total energy calculation for Si bulk in the diamond structure for different values of the damping parameter  $\gamma$ .





## 6.0 Conclusion

In conclusion, we have optimized some input parameters within the Local density approximation (LDA) along the k-point of Monkhorst-Pack scheme for different values of electronic time step, an energy cutoff and damping parameters. We observe that, a stable convergence of all the elements were achieved. Also, the corresponding parameters in the inp.mod input file,  $delt2$  and  $gamma2$  had to be smaller than that ones for  $delt$  and  $gamma$ , so as to have a stable convergence.

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