Phonon Transport in Nanostructures

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Abstract

Recent experiments aiming to produce TiO_2 nanostructures have been riddled with complications. It has been found that an undesired reaction occurs with the water used in the flaking process producing a sulphurous smell. This product suggests the production of TiO_xS_{2-x} in the layered crystal structure. This nanostructure has great potential benefits for the construction of semiconductor devices and novel electronic devices.

In this investigation computational methods were used to preform first-principles Density Functional Theory (DFT) calculations of the layered crystal structures graphene and Molybdenum Disulphide, MoS_2, as implemented with Quantum Espresso using the General Gradient Approximation (GGA). Unit crystal cells were built, and the DFT used to perform *ab inito* total energy calculations, bandstructure calculations, and to calculate the phonon frequencies at Γ and the K and M symmetry points. These were then used to ascertain the viability of the stability of a layered TiO_2 crystal structure.

It was found that for a two atom graphene nanostructure the total energy of the system is $-22.731\,\text{Ry}$. Moreover, the MoS_2 layered nanostructure was found to have a total energy of $-139.311\,\text{Ry}$ using a six basis atom unit cell. These values correspond to lattice constants of $2.54\,\text{Å}$ and $3.16\,\text{Å}$ for the two systems respectively.

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Quantum Espresso: a modular and open-source software project for quantum simulations of materials, P. Giannozzi *et al.*, Journal of Physics: Condensed Matter, **21**, 39 (2009).

1 Introduction & Theory

1.1 TiO_2 Nanostructure Production

There is currently a large volume of research on layered crystals, and their potential use as semiconductors and in novel electronic devices. Much of this research is in graphene, the single layer allotrope of Carbon, however this nanostructure is not suitable for the production of novel electronic devices as it is not a semiconductor, despite it's noted electrical properties and conductivity[1].

Recent efforts have looked elsewhere, such as the efforts of J. Coleman to produce nanostructure flakes of TiS_2. This is attempted using a pealing reaction with water. However, when the reaction is carried out it is noted that there is a strong sulphurous smell, suggestion that the reaction

$$\mathrm{TiS_2} + x\mathrm{H_2O} \rightarrow \mathrm{TiO}_x\mathrm{S}_{2-x} + x\mathrm{H_2S} \tag{1}$$

is occurring.

This reaction has huge potential, if it is indeed occurring. As the TiS_2 is known to form a layered crystal structure, the substitution of Sulphur atomic sites with Oxygen atoms producing a layered TiO_2 nanostructure would allow for tuning the electronic bandgap to produce novel electronic devices. Moreover, the electronic properties and applications of TiO_2 as a semiconductor are well documented.

In this study the graphene and MoS_2 systems are studied as a pedagogical exercise, with applications to study the doped TiO_xS_{2-x} layered crystal nanostructure. Graphene, a single atomic layer of graphite[2], and MoS_2, a layered structure[3, 5], are well studied systems.

1.2 Density Functional Theory

Density Functional Theory (DFT) in the Local Density Approximation (LDA) is an approximation method which may be used to solve the many-electron quantum mechanical equations for the electronic structure of solids. This replaces the many-electron problem with a single-particle in an effective potential[6, 7]. While this method improves upon those of the Hartree-Fock approximation, it again gives rise to problems with the calculation of the band gaps, in this instance giving results which are too small. However, DFT provides an excellent description of the ground-state properties and overall crystal energies of the system, and gives an accurate description of structural parameters. Hence total energy calculations computed using DFT are reliable.

1.3 The Quantum Espresso Suite

The DFT was implemented using the Quantum Espresso code[4]. This is a self-consistent iterative method, which works to minimise the energy of the system by filling up electron bands and relaxing the lattice constant in turn. In this way it solves the quantum mechanical Schrödinger equation. Thus these calculations use first-principle methods.

Ultrasoft Pseudopotentials are used to represent the interaction between the valance electrons and the inert ion cores. Moreover, Quantum Espresso itself is an open source code, allowing the researcher to see exactly how the code implements the DFT, in contrast to many commercially available electronic structure computational codes. The suite contains a series of pieces of code, each of which may be used to perform different electronic structure calculations.

In this investigation the `pw.x`, `ph.x` and a collection of post-procession codes were used. The `pw.x` code may be used to preform total energy calculations, and to calculate the electronic bandstructure eigenvalues for a many-electron system. The `ph.x` code may be used to calculate the phonon frequencies of the crystal structure at any specified point in the Brillouin zone.

Finally, post-procession codes `bands.x`, `plotband.x`, `dos.x` and `projwfc.x` are used in extracting eigenvalues from the total energy data for the electronic bandstructure, to prepare the data in a format which may be plotted by programs such as `XMGrace`, to extract the density of states from the total energy data, and again to prepare the data in a format which may be plotted by `Gnuplot` respectively.

1.4 Points of High Symmetry

Due to the periodic nature of crystal structures, there exists many equivalent points in the reciprocal space of the crystal lattice. Thus the space may be divided into a Brillouin Zone, which contains representative points from the entire crystal. Within this Brillouin Zone, there are points of high symmetry which are equivalent, dependent of the type of crystal structure under investigation. For the graphene and MoS_2 crystal structure, these points are the Γ-point, the K-point and the M-point, given by

$$\Gamma = \frac{2\pi}{a}(0,0,0)\,, \quad K = \frac{2\pi}{a}\left(\frac{2}{3},0,0\right) \quad \text{and} \quad M = \frac{2\pi}{a}\left(0,\frac{1}{\sqrt{3}},0\right) \tag{2}$$

where a is the lattice constant.

2 Experimental Method

2.1 Installation of the Quantum Espresso Suite

The most recent version of the Quantum Espresso suite, version 4.3.1, was downloaded from the official website[8] as a `.tar` file, and saved on the machine `chuck` of the Trinity Centre for High Performance Computing (TCHPC). This was then extracted, and compiled using the the GCC compiler[9]. A series of tests of the code were run from the terminal to verify correct compilation.

2.2 Unit Cell Construction

The unit cell for the graphene Carbon allotrope was constructed[10]. The input file was specified as per the Input File Description for the `pw.x` code[11]. The atomic position were given as function of the primitive lattice vectors

$$\begin{aligned} \vec{v_1} &= \frac{1}{2}a\,\hat{x} - \frac{\sqrt{3}}{2}a\,\hat{y} + 0\,\hat{z} \\ \vec{v_2} &= \frac{1}{2}a\,\hat{x} + \frac{\sqrt{3}}{2}a\,\hat{y} + 0\,\hat{z} \\ \vec{v_3} &= 0\,\hat{x} + 0\,\hat{y} + 10a\,\hat{z} \end{aligned} \tag{3}$$

where a is the lattice constant to be specified in units of Bhor radii with

$$r_{Bhor} = 0.5292 \times 10^{-10} m$$

The atomic positions for the two basis Carbon atoms were then

$$\begin{aligned} \vec{b_1} &= \frac{1}{3}\,\vec{v_1} + \frac{2}{3}\,\vec{v_2} + 0\,\vec{v_3} \\ \vec{b_2} &= \frac{2}{3}\,\vec{v_1} + \frac{2}{3}\,\vec{v_2} + 0\,\vec{v_3} \end{aligned} \tag{4}$$

Moreover, for the MoS_2 crystal structure[12] the atomic positions were again given as a function of the primitive vectors, where here

$$\begin{aligned}\vec{v_1} &= \frac{1}{2}a\,\hat{x} - \frac{\sqrt{3}}{2}a\,\hat{y} + 0\,\hat{z}\\ \vec{v_2} &= \frac{1}{2}a\,\hat{x} + \frac{\sqrt{3}}{2}a\,\hat{y} + 0\,\hat{z}\\ \vec{v_3} &= 0\,\hat{x} + 0\,\hat{y} + 3.8892a\,\hat{z}\end{aligned} \tag{5}$$

with the basis vectors being

$$\begin{aligned}\vec{b_1} &= 1/3\,\vec{v_1} + 2/3\,\vec{v_2} + 1/4\,\vec{v_3}\\ \vec{b_2} &= 2/3\,\vec{v_1} + 1/3\,\vec{v_2} + 3/4\,\vec{v_3}\\ \vec{b_3} &= 1/3\,\vec{v_1} + 2/3\,\vec{v_2} + c\,\vec{v_3}\\ \vec{b_4} &= 2/3\,\vec{v_1} + 1/3\,\vec{v_2} + (1/2 + c)\ \vec{v_3}\\ \vec{b_5} &= 1/3\,\vec{v_1} + 2/3\,\vec{v_2} + (1/2 - c)\ \vec{v_3}\\ \vec{b_6} &= 2/3\,\vec{v_1} + 1/3\,\vec{v_2} - c\,\vec{v_3}\end{aligned} \tag{6}$$

where c is the atomic layer shift parameter.

2.3 Total Energy Calculations

Referring to the input file description for `pw.x`[11] the input files for the total energy calculations were created.

For the graphene calculation, the calculation type was specified to “`scf`” to give a self-consistent calculation. The crystal lattice structure was set to “`free`”, to allow the use of the unit cells constructed previously. In this instance the code was told to use hexagonal symmetries of the system to accelerate the calculation time.

The number of basis atoms was set to two, and the number of types of atoms set to one using the “`nat`” and “`ntyp`” flags respectively. The cutoff-energy of the calculation was set to 18.0 Ry using the “`ecutwfc`” flag. To diagonalise the system of equations the Davidson method was chosen. The default Carbon Perdew-Burke-Ernzerhof (PBE) pseudopotential `C.pbe-rrkjus.UPF` was used to provide the electronic interactions. Finally, an automatic Γ-centred k-point mesh was generated with 10, 10 and 1 k-points in the x-, y- and z-directions respectively.

In addition, the input file for the MoS_2 calculation was generated in a similar manor. In contrast to above, the number of atoms was set to six, and the number of types of atoms was set to two. Again, a cutoff-energy of 18 Ry and Davidson diagonalisation was used. Plane Wave Pseudopotentials for Mo and S were downloaded from the Quantum Espresso Download Page[13], `Mo.pw91-n-van.UPF` and `S.pw91-van_ak.UPF` respectively, and the code instructed to used these to represent the electronic interactions. The same automatically generated Γ-centred k-point mesh was used as that of the graphene calculation.

2.4 Structure Relaxation Calculations

The total energy calculation for the graphene system was repeated for a range of values of the lattice constant a, where a is specified in the input file through the “`celldm(1)`” flag. A graph of the total energy versus the lattice parameter was then plotted.

2.5 Bandstructure Calculations

A bandstructure total energy calculation was run using the `pw.x` code by setting the “`calculation`” flag to “`bands`”. The number of bands to be calculated was set to 20 using the “`nbnd`” flag. An automatic line of k-points was generated between the k-points of high symmetry in the order $K \rightarrow \Gamma \rightarrow M \rightarrow K$ using the “`tpiba_b`” flag.

The `bands.x`[14] code was then used to extract the relevant data from the output, and the `plotband.x` code to prepare it in a format to be read by `XMGrace`. A graph of the electronic bandstructure of graphene was then plotted.

The process was repeated to make a plot of the electronic bandstructure of MoS_2. The same number of bands and line of k-points was used.

In addition a non-self-consistent calculation was run using the `pw.x` to code by setting the “`calculation`” flag to “`nscf`”. The `dos.x`[15] and `projwfc.x`[16] codes were then used to extract the relevant data from the output and to prepare it in a format to be read by `Gnuplot`. A plot of the density of states of graphene was then made.

2.6 Phonon Frequency Calculations

The `ph.x`[17] code was run to calculate the phonon mode frequencies of graphene at the Γ-point.

The input file was then edited to allow the calculation of phonon mode frequencies away from the Γ-point by adding the flag "`lnscf=.true.`", to tell the code to preform a non-self-consistent calculation at the specified point. The `ph.x` code was then used to calculate the phonon frequencies of graphene at both the K- and M- k-points of high symmetry.

3 Results & Analysis

3.1 Installation of the Quantum Espresso Suite

On compiling the quantum espresso suite and running the tests it was found the the code had been correctly compiled.

3.2 Unit Cell Construction

The unit cells constructed were found to give the correct crystal structure for the systems being investigated.

3.3 Total Energy Calculations

For the graphene nanostructure, using a lattice constant of $a = 4.80\,\mathrm{r}_{Bhor}$, or 2.54 Å, the total energy calculation was found to converge. The total forces acting on the atoms was calculated to be $0.0001\,\mathrm{Ry\,au^{-1}}$, corresponding to an acceptably relaxed system. This resulted in the total energy of the system being $-22.731\,\mathrm{Ry}$.

In addition, for the MoS_2 crystal structure, using a lattice constant of $a = 5.9735\,\mathrm{r}_{Bhor}$, or 3.16 Å, and an atomic layer shift parameter of $c = 0.08$ the calculation was again found to converge. In this case the total forces acting on the atoms was calculated to be $0.8960\,\mathrm{Ry\,au^{-1}}$, similarly corresponding to an acceptably relaxed system. This resulted in the total energy of the system being $-139.311\,\mathrm{Ry}$.

3.4 Structure Relaxation Calculations

The following data was obtained for the total energy of the graphene system for a range of values of lattice constant and the resulting graph plotted

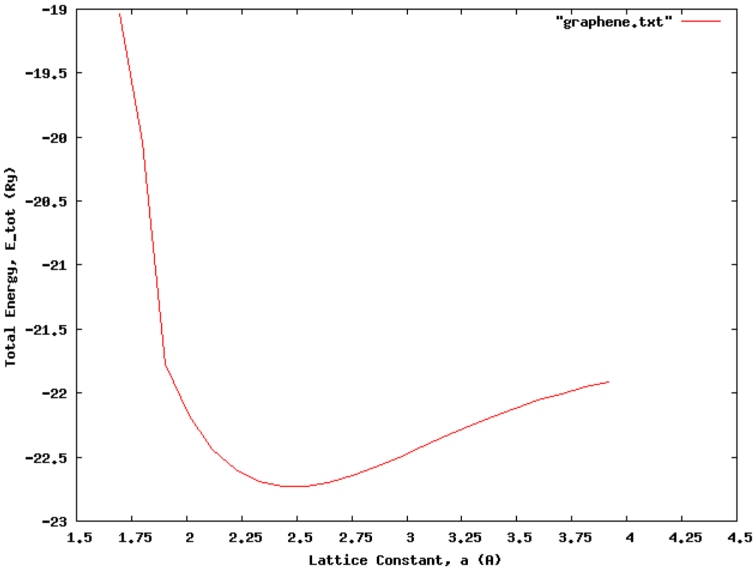

Figure 1: Total energy versus Lattice Constant

3.5 Bandstructure Calculations

The electronic bandstructure and density of states of graphene were calculated and plotted

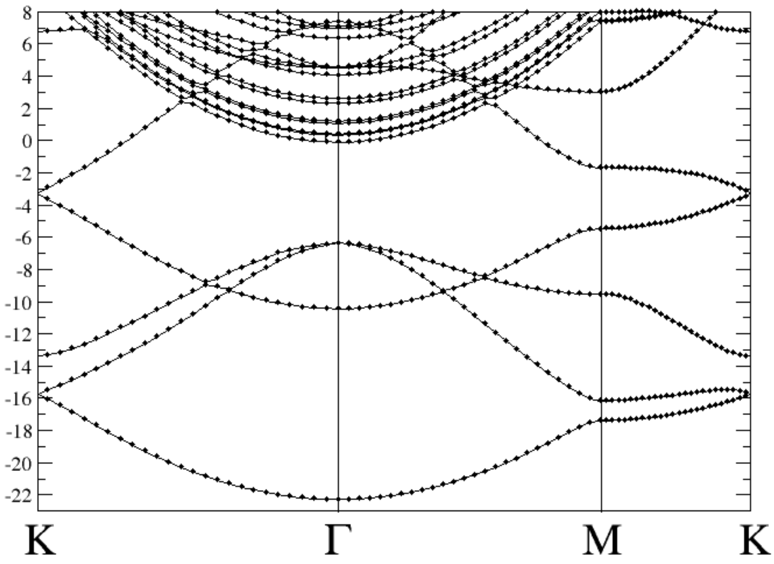

Figure 2: The Electronic Bandstructure of Graphene

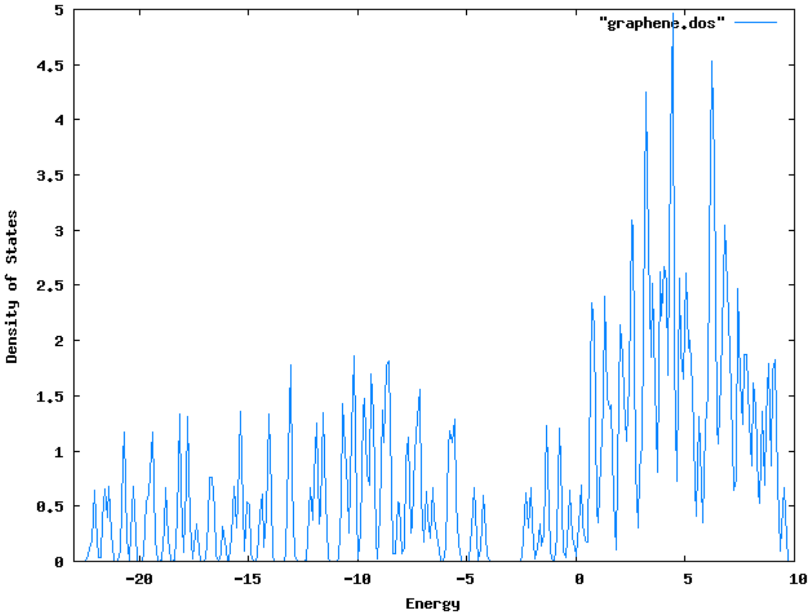

Figure 3: The Density of States of Graphene

Moreover, the electronic bandstructure of MoS_2 was calculated and a graph was plotted

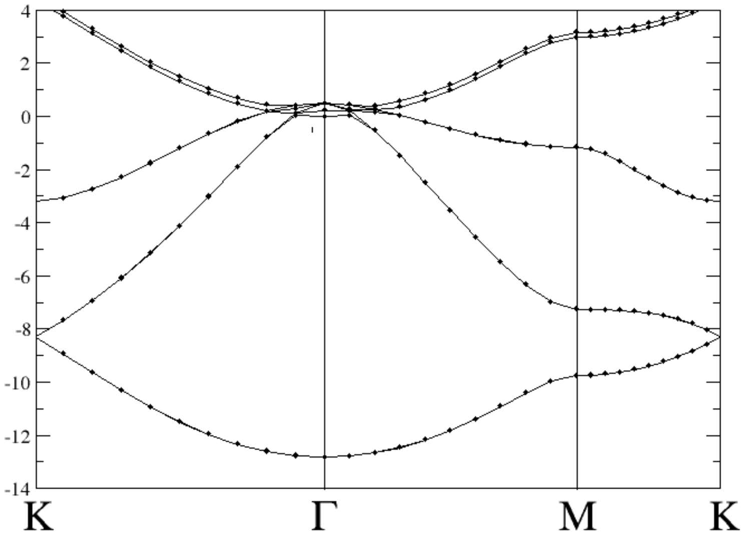

Figure 4: The Electronic Bandstructure of MoS_2

3.6 Phonon Frequency Calculations

The following table of phonon mode frequencies were calculated for graphene at the Γ-, K- and M- k-points of high symmetry

Table 1: Phonon mode frequencies for Graphene

Γ-Point		K-point		M-point	
mode	frequency cm^{-1}	mode	frequency cm^{-1}	mode	frequency cm^{-1}
ω_1	-85	ω_1	543	ω_1	469
ω_2	102	ω_2	558	ω_2	605
ω_3	102	ω_3	977	ω_3	627
ω_4	821	ω_4	1233	ω_4	1310
ω_5	1562	ω_5	1240	ω_5	1365
ω_6	1562	ω_6	1349	ω_6	1425

4 Conclusions

It was found that the Quantum Espresso suite may effectively be used to preform electronic structure calculations of crystal nanostructures. Moreover, as it is an open source code, it can easily be obtained and compiled without any errors, to allow any researcher to enter the area of computational materials simulation.

The Quantum Espresso suit allows for the input of a systems's structure in a range of different ways, and has tools to identify the symmetries of a given system in order to accelerate the calculation time. Furthermore, using the on-line database, as compiled by the U.S. Naval Research Laboratory, which contains a large amount of crystal structure information for a wide range of different systems, the difficulty in the construction of crystal unit cells was greatly decreased.

Total energy calculations computed using Quantum Espresso are dependent on a great range of input parameters. The exact specification of any given calculation's input parameters is essential to allow for the direct comparison of calculations performed by different researchers or institutions.

On completion of the calculation a detailed output file of the calculation process was created, which allowed for verification of successful convergence, as indicated by the total forces acting on the atoms of the system. For a system in equilibrium these forces should be zero, to within experimental error. For the graphene and MoS_2 nanostructures studied, the forces acting on the atoms were found to be $0.0001\,\mathrm{Ry\,au}^{-1}$ and

$0.8960\,\mathrm{Ry\,au^{-1}}$ respectively, corresponding to relaxed structures, within the limits of experimental error. The corresponding total energies of the nanostructures were found to be $-22.731\,\mathrm{Ry}$ and $-139.311\,\mathrm{Ry}$, and these were calculated using lattice constants of $4.80\,\mathrm{r}_{Bhor}$ and $5.9735\,\mathrm{r}_{Bhor}$ for the two nanostructures respectively.

From the total energy calculations which were preformed for the given range of lattice constants it was seen that the graphs obtained from the resulting data have the expected Lennard-Jones shape, with the minimum in energy corresponding to the physical lattice constant assumed by the nanostructure when in equilibrium. These graphs verify that the total energy calculations preformed converged successfully.

Furthermore, the electronic bandstructure plotted for graphene was of the expected shape, and the graph of the density of states showed high densities at the correct energies for the bandstructure plot.

Finally, it was noted that calculated phonon mode frequencies for graphene were in the expected range.

4.1 Future Work

From the results generated in this study and the methods used therein, the investigation of the layered $\mathrm{TiO}_x\mathrm{S}_{2-x}$ may follow directly. To construct a unit cell for this system would require constructing a cell with many times more atoms, as there is realistically a doping concentration of the order of only 1×10^{-6}, or even less. Thus a unit cell in which the number of atoms is at absolute least of the order of 1×10^{3} is needed to obtain even an approximate calculation.

Moreover, the method of implementing the DFT with Quantum Espresso will directly follow from that used above. It must be noted however that the computational expense goes as N^3, where N is the number of atoms in the unit cell, and so a total energy calculation of the doped $\mathrm{TiO}_x\mathrm{S}_{2-x}$ system will be very computationally expensive if an accurate investigation is to be carried out.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, Nature, **438**, 197 (2005).

[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science, **306**, 5696 (2004).

[3] A. Molina-Sánchez, L. Wirtz, Phys. Rev. B, **84**, 155413 (2011).

[4] P. Giannozzi *et al.*, Journal of Physics: Condensed Matter, **21**, 39 (2009)

[5] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, American Chemical Society Nano **4**, 5 (2010).

[6] P. Honenberg, W. Kohn, Phys. Rev. **136**, B864 (1964).

[7] W. Kohn, L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[8] Quantum Espresso Download Page, (29/06/2011), <http://www.quantum-espresso.org/download.php/>, (visited 29/10/2011).

[9] User's Guide for Quantum Espresso, (17/07/2011), <http://www.quantum-espresso.org/user_guide/user_guide.html>, (visited 29/10/2011).

[10] L. A. Falkovsky, Journal of Experimental and Theoretical Physics **105**, 2 (2007).

[11] Input File Description: pw.x, (25/05/2011), <http://www.quantum-espresso.org/input-syntax/INPUT_PW.html>, (visited 15/11/2011).

[12] The MoS_2 Crystal Structure, (21/10/2004), <http://cst-www.nrl.navy.mil/lattice/struk/c7.html>, (visited 20/11/2011).

[13] Quantum Espresso Pseudopotentials, (29/06/2011), <http://www.quantum-espresso.org/pseudo.php/>, (visited 15/11/2011).

[14] Input File Description: bands.x, (25/05/2011), <http://www.quantum-espresso.org/input-syntax/INPUT_BANDS.html>, (visited 03/12/2011).

[15] Input File Description: dos.x, (25/05/2011), <http://www.quantum-espresso.org/input-syntax/INPUT_DOS.html>, (visited 05/01/2012).

[16] Input File Description: projwfc.x, (25/05/2011), <http://www.quantum-espresso.org/input-syntax/INPUT_PROJWFC.html>, (visited 05/01/2012).

[17] Input File Description: ph.x, (25/05/2011), <http://www.quantum-espresso.org/input-syntax/INPUT_PH.html>, (visited 30/12/2011).