Computational study of point defects in crystal structures using *Python for Defect Energy Formation* 1.1.0

30th April 2016

Contents

Prologue

This document explains how to perform point defect computational analysis using *Python for Defect Energy Formation* 1.0.0 (PyDEF). In the first part, the basics of point defect formation computational analysis as developed by Zunger *et. al* are reviewed. The second part gives the computational parameters required in the Density Functional Theory software *Vienna Ab Initio Simulation Package*. Finally, the last section presents the different possibilities of PyDEF and explains how to use it to plot defect formation energies, transition levels and density of states.

1. Defect formation energy model

1.1 General concept

The formation of a point defect in a semiconductor or an insulator material can be viewed as an exchange of atoms and electrons between a host cell (*i.e.* a reference cell without defect) and atomic and electronic reservoirs. The required energy to create a point defect D in charge state q is hence [4, 9, 7]:

$$E_{for}^{D,q}\left(\Delta E_F\right) = E_{tot}^{D,q} - E_{tot}^{host} + \sum_i n_i \mu_i + q \underbrace{\left(E_V^{host} + \Delta E_F\right)}_{E_F} \qquad (1.1)$$

The two first terms represent the difference of energy between the defect cell (*i.e.* the cell containing the defect D) and the host cell: E_{tot}^{host} is the total electronic energy of the host cell which is obtained after optimising the positions and geometry of the host cell. $E_{tot}^{D,q}$ is the energy of the defect cell which is obtained by optimising only the position of the atoms using the same volume as the host cell in order to keep a same reference.

1.1.1 Atomic reservoir

The third term corresponds to the energy of the atomic reservoir: n_i is the number of atoms of species i added ($n_i < 0$) or removed ($n_i > 0$) from the host cell and μ_i is the chemical potential of species i in the synthesised compound. This later can be expressed as:

$$\mu_i = \mu_i^0 + \Delta \mu_i$$

where μ_i^0 is the chemical potential of species i in its stable configuration (*e.g.* O_2 for the oxygen of air, S_8 for solid sulphur) and $\Delta \mu_i$ corresponds to its variation which depends on the synthesis conditions and the material synthesised[1].

1.1.2 Electronic reservoir

The fourth and last term corresponds to the energy of the electrons in the electronic reservoir *i.e.* the Fermi energy E_F. Thereafter, for simplification, this latter is defined with respect to the valence band maximum (VBM) such as:

$$E_F = E_V^{host} + \Delta E_F \qquad (1.2)$$

where E_V^{host} is the energy of the VBM of the host cell and ΔE_F takes its values between $0\ eV$ and the value of the gap of the host cell.

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[1]The determination of this latter will not be discussed in this document.

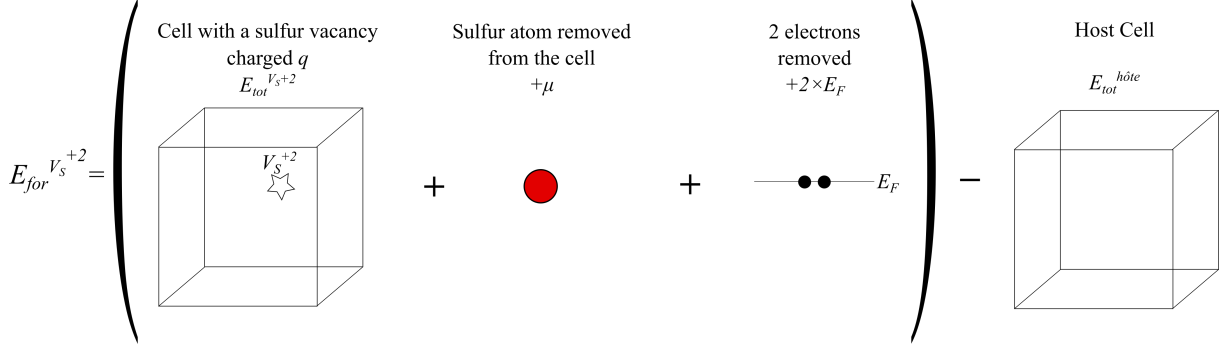Figure 1.1 schematically represents equation 1.1 in the case of a sulphur vacancy in charge state $q = +2$.

Figure 1.1: Schematic representation of the formation energy of a sulphur vacancy in charge state $+2$.

The use of computational methods such as the Density Functional Theory (DFT) for calculating the previous parameters leads to approximations that it is necessary to correct in order to obtain results closer to the reality.

1.2 Corrections of the defect formation energy

Two types of approximation arise from the use of DFT for calculating defect formation energy. The first one is linked to the error in the calculated electronic gap while the second is associated to the spurious effects induced by the use of small cells in the calculations.

1.2.1 Gap corrections

The use of precise methods such as hybrid functionals and the GW method yield excellent results regarding the electronic gap, however they may require large computation times (of the order of several weeks or months) in the case of defect cell calculation. At contrary, simple methods such as LDA and GGA have a small computation times but give an incorrect position of the VBM and the conduction band maximum (CBM) which begets an error on the calculated band-gap. The range of possible values of the Fermi level is then reduced compared to reality which can have important consequences on the interpretation of the results. It is then required to correct the gap when GGA and LDA functionals are used.

Various methods exist to correct the gap [8, 1, 7, 3]. An efficient one consists to compare the position of the band extrema of the host cell computed with a simple method A (*e.g.* LDA or GGA) and a method more precise B (*e.g.* hybrid or GW).

Let us note E_V^A $\left(E_V^B\right)$ and E_C^A $\left(E_C^B\right)$ the respective energies of the VBM and the CBM computed with method A (B). The corrections of the band extrema are then defined as:

$$\Delta E_V = E_V^{B,host} - E_V^{A,host} \tag{1.3}$$

$$\Delta E_C = E_C^{B,host} - E_C^{A,host} \tag{1.4}$$

The Figure 1.2 schematically represents this correction
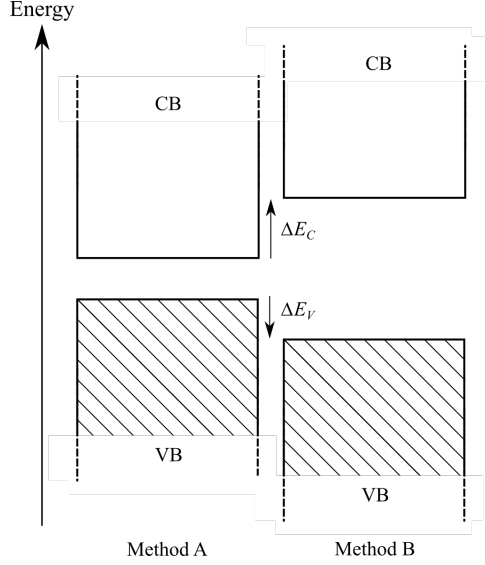
FIGURE 1.2: Schematic representation of the band diagram of the host cell computed with methods A and B. The conduction band (CB) is empty while the valence band (VB) is full.

Hereinafter, we will talk about "computation A corrected B" for formation energy computed with method A and which the gap has been corrected with method B.

Correction of the energy of the electronic reservoir

The correction of the VBM induce the correction of the energy of the electronic reservoir which becomes:

$$q\left(E_V^{host} + \Delta E_V + \Delta E_F\right) \tag{1.5}$$

where ΔE_F takes now its values between $0eV$ and the value of the gap computed with method B. The defect formation energy is hence corrected by [4] :

$$\boxed{\Delta E_{V,corr} = +q\Delta E_V} \tag{1.6}$$

Correction of the levels associated to the defects (alias PHS correction)

The introduction of defects in a cell can create localised states in the DOS called Defect Localised States (DLS) [3]. In the case where a DLS is located in the conduction (valence) band, the electrons (holes) which may occupy it will fall down to the CBM (VBM) level where they will occupy a new DLS called Perturbed Host State (PHS) [3, 4].

The correction of the electronic gap leads to the correction of the quasiparticles in these PHS:

$$\boxed{\Delta E_{PHS} = +z_e\Delta E_C - z_h\Delta E_V} \tag{1.7}$$

where z_e electrons are located in the conduction band and z_h holes are in the valence band.

1.2.2 Corrections of spurious effects from the cell size

Potential alignment

In DFT calculations, the "zero" of energy is determined from the average electrostatic energy in the cell. In the case of charged defect calculations, the electrostatic potential created by the defect modify the electrostatic energy of the closest atoms to the defect. Hence the zero-of-energy is not the same between the host cell and the defect cell. One of the simplest methods to correct this offset is to compute the difference of electrostatic energy of an atom located far away from the defect between the host cell and defect cell calculations:

$$\Delta V = V_{D,q}^r - V_{host}^r \tag{1.8}$$

where r is distance between the atom considered and the defect, $V_{D,q}^r$ is the mean electrostatic energy around the atom in the defect cell and V_{host}^r is the mean electrostatic energy of the atom in the host cell [7]. In order to increase the precision of this correction, a similar method as the ones explained by Kumagai and Fumiyasu in [2] and Lany and Zunger in [5] can be used: the average value $\overline{\Delta V \left(r > R \right)}$ of ΔV is computed for a set of atoms located at a minimum distance R from the defect and its images. To do that, we consider spheres of radius R around the defect and its images. Only the atoms located outside the spheres are considered for the calculation of the potential alignment. Figure 1.3 represent the process to obtain this correction:
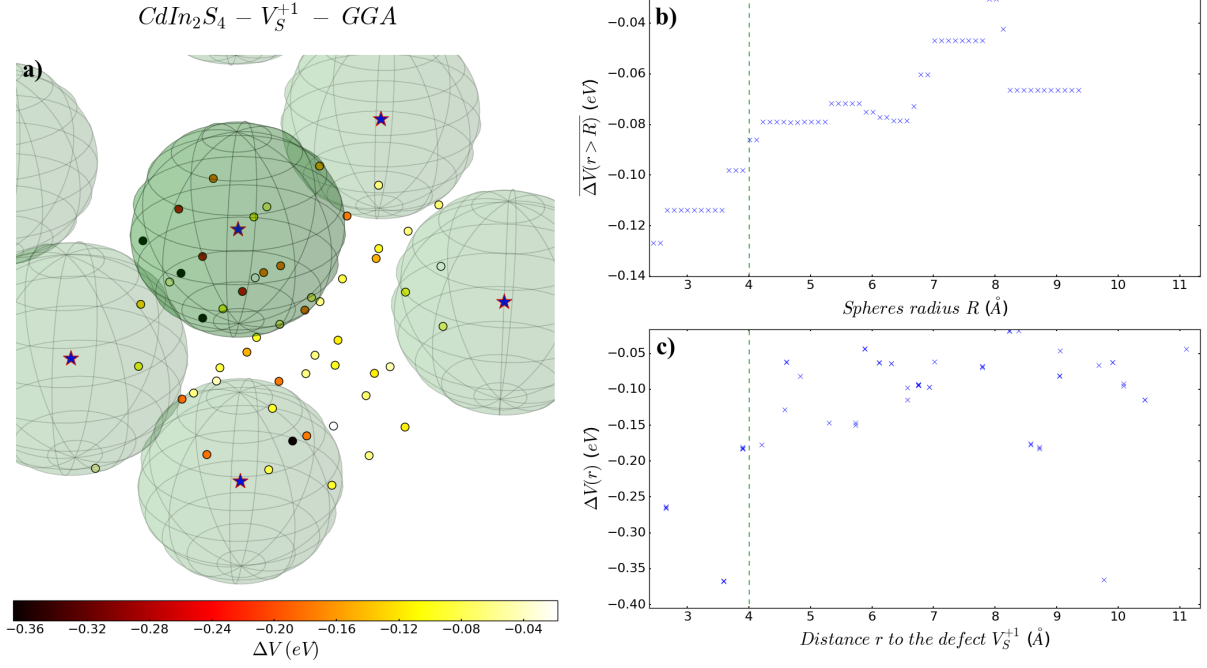
Figure 1.3: Calculation process of the potential alignment applied to a 56-atoms cell of CdIn$_2$S$_4$ with a sulphur vacancy charge +1. **a)** Representation of the cell (atoms are represented by the coloured dots) and of the spheres of radius 4 Å around the defect and its images (blue stars). **b)** Average difference of electrostatic energy $\overline{\Delta V\,(r > R)}$ outside the spheres in function of the radius R of the spheres. **c)** Difference of electrostatic energy for every atom in function of their closest distance to the defect or its images.

In the case of Figure 1.3, we can see that the most affected atoms are located in a radius of 4 Å around the defect and its images. The energy of the electronic reservoir is then:

$$q \cdot \left(E_V^{h\hat{o}te} + \Delta E_V + \overline{\Delta V\,(r > R)} + \Delta E_F \right) \tag{1.9}$$

Hence the potential alignment correction to the formation energy is:

$$\boxed{\Delta E_{PA} = +q \cdot \overline{\Delta V\,(r > R)}} \tag{1.10}$$

Moss-Burstein correction (alias Band-filling correction)

The utilisation of small cells for defect calculations lead to a high defect concentration (of the order of $10^{21} cm^{-3}$ for a 56 atoms cell), far from the dilute limit of $10^{18} cm^{-3}$. The ratio of the density of states of the conduction band to the DLS created by the defect is hence different from the reality (Figure 1.4).
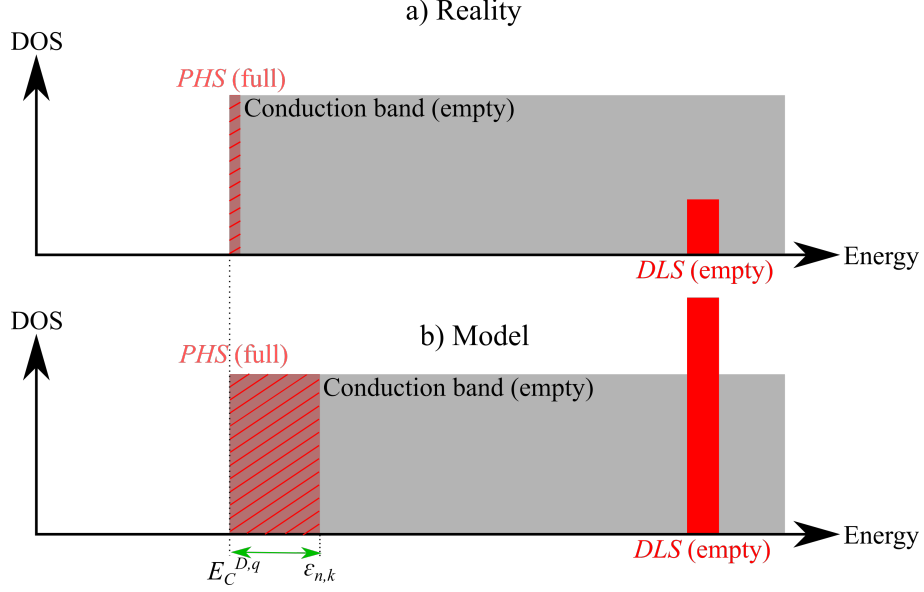
Figure 1.4: Schematic representation of the band-filling effect in the case of a DLS located in the CB. **a)** Dilute case (reality). The DOS of the CB is much larger than the DOS of the DLS. The electrons occupying the DLS go down to the bottom of the conduction band where they have all about the same energy $E_C^{D,q}$. **b)** Modelled case. The DOS of the DLS is comparable to the one of the CB. The electrons occupying the DLS go down to the bottom of the CB. However, because there are few available states, these electrons become delocalised and possess an overestimated energy compared to the reality.

Electrons and, less significantly, the holes located in the conduction and valence band respectively have their energy overestimated in the modelled case. The correction of the energy of the defect cell is hence, for electrons in the conduction band [4] :

$$\Delta E_{MB}^{\text{électrons}} = -\sum_{n,k} \omega_k \eta_{n,k} \left(\epsilon_{n,k} - \left[E_C^{h\hat{o}te} + \overline{\Delta V} \right] \right) \cdot \Theta \left(\epsilon_{n,k} - \left[E_C^{h\hat{o}te} + \overline{\Delta V} \right] \right) \qquad (1.11)$$

where ω_k is the weight of k-point k, $\eta_{n,k}$ of the occupation of band n for k-point k, $\epsilon_{n,k}$ is the energy of band n for k-point k and Θ is the Heaviside function. Similarly, for holes in the valence band

$$\Delta E_{MB}^{\text{trous}} = -\sum_{n,k} \omega_k (2 - \eta_{n,k}) \left(\left[E_V^{h\hat{o}te} + \overline{\Delta V} \right] - \epsilon_{n,k} \right) \cdot \Theta \left(\left[E_V^{h\hat{o}te} + \overline{\Delta V} \right] - \epsilon_{n,k} \right) \qquad (1.12)$$

Makov-Payne correction

As the volume of the modelled defect cell is small, a defect and its closest image see each other in term of electrostatic potential. This does not happen in the reality where defect concentrations are small and thus a defect and its closest neighbour are further apart such as depicted in Figure 1.5.
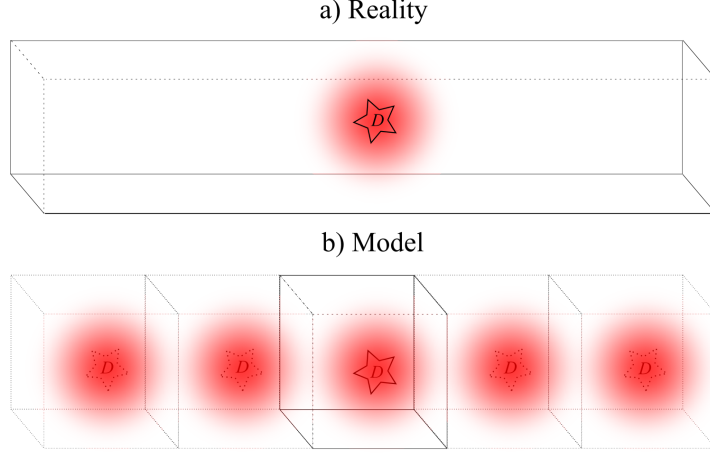
9

Figure 1.5: Schematic representation of a cell containing a charged defect (full lines) and its images (dotted lines). The red gradient represents the electrostatic potential created by the defect D and its images. **a)** Reality: the defect concentration is such that a defect and its closest neighbour (*i.e.* image) are far apart. **b)** Model: the defect concentration is very high and the defect and its first neighbour are close to each other and see each other electrostatic potential.

The energy of the cell must then be corrected. In the case of a cubic cell of volume V, the correction is [6] :

$$\Delta E_{MP} = \frac{q^2 \alpha_M}{2\epsilon V^{1/3}} + \frac{2\pi q Q}{3\epsilon V} \tag{1.13}$$

where α_M is the Madelung constant of the cell and ϵ is the relative permittivity of the material. In the case where only the atoms around the defects are updated, the relative permittivity corresponds to the electronic relative permittivity ϵ_e. At contrary, if all the atoms positions are updated after the creation of the defect, the relative permittivity corresponds to the relative permittivity at $0\ eV$ [5].

The second term is the correction associated with the quadrupolar moment Q. Lany and Zunger have shown in 2009 [5] that this term could be expressed with the first one and thus the Makov-Payne correction can be simplified as:

$$\Delta E_{MP} = \left(1 + c_{sh}\left[1 - \epsilon^{-1}\right]\right)\frac{q^2 \alpha_M}{2\epsilon V^{1/3}} \tag{1.14}$$

where c_{sh} is a factor dependent on the geometry of the host cell. Its range of values is displayed in Table 1.1

Table 1.1: Values of the factor c_{sh}

Geometry	c_{sh}
SC	-0.369
FCC	-0.343
BCC	-0.342
HCP	-0.478

1.3 Corrected defect formation energy and transition levels

Finally, the corrected formation energy of a point defect D in charge state q is given by:

$$
\begin{aligned}
E_{for}^{D,q}\left(\Delta E_F\right) = {} & E_{tot}^{D,q} - E_{tot}^{host} + \sum_i n_i\left(\mu_i + \Delta\mu_i\right) + q\left(E_V^{host} + \Delta E_V + \overline{\Delta V} + \Delta E_F\right) \\
& + z_e\Delta E_C - z_h\Delta E_V + \left(1 + c_{sh}\left[1 - \epsilon^{-1}\right]\right)\frac{q^2\alpha_M}{2\epsilon V^{1/3}} \\
& - \sum_{n,k}\omega_k\eta_{n,k}\left(\epsilon_{n,k} - \left[E_C^{host} + \overline{\Delta V}\right]\right)\cdot\Theta\left(\epsilon_{n,k} - \left[E_C^{host} + \overline{\Delta V}\right]\right) \\
& - \sum_{n,k}\omega_k\left(2 - \eta_{n,k}\right)\left(\left[E_V^{host} + \overline{\Delta V}\right] - \epsilon_{n,k}\right)\cdot\Theta\left(\left[E_V^{host} + \overline{\Delta V}\right] - \epsilon_{n,k}\right)
\end{aligned}
\tag{1.15}
$$

Transition levels or transition energies are defined as the values of the Fermi energy for which the energy of two charge states are equal. Let us note $\epsilon\left(q/q'\right)$ the transition level for which the defect goes from a charge state q to a charge state $q' < q$, or in other words:

$$
E_{for}^{D,q}\left(\epsilon\left(q/q'\right)\right) = E_{for}^{D,q'}\left(\epsilon\left(q/q'\right)\right)
\tag{1.16}
$$

hence:

$$
\epsilon\left(q/q'\right) = \frac{E_{for}^{D,q'}\left(0\right) - E_{for}^{D,q}\left(0\right)}{q - q'}
\tag{1.17}
$$

For Fermi energy values lower than the transition level $\epsilon\left(q/q'\right)$, the charge state q is the most stable while for higher values, the charge state q' is more stable as illustrated in Figure 1.6.
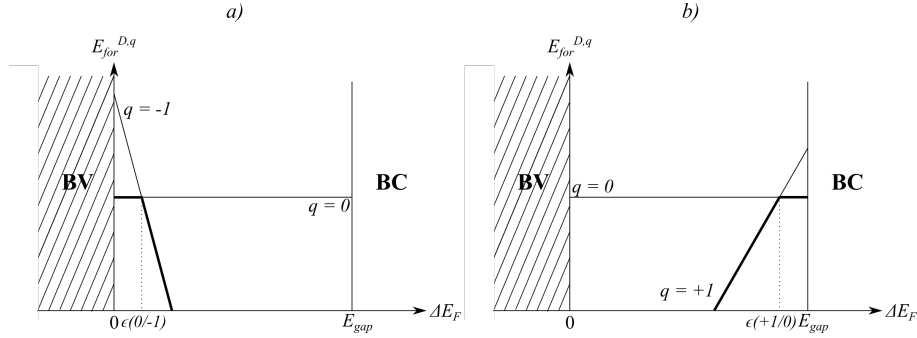

Figure 1.6: Schematic examples of formation energy diagrams. The lowest formation energy is highlighted in black and corresponds to the most stable charge state of the defect. **a)** Formation energy diagram of a defect which can be in charge state $q = 0$ and $q = -1$. A transition level $\epsilon\left(0/-1\right)$ between these states is located near the VBM. **b)** Formation energy diagram of a defect which can be in charge state $q = +1$ and $q = 0$. A transition level $\epsilon\left(+1/0\right)$ is located near the CBM.

Thermodynamic and optical transition levels Depending on the transition speed, two types of transition level are distinguished. If the transition between the charge states is slow, (by applying an electric field for example), then the atoms of the system can relax and find new equilibrium positions. The transition level is then called thermodynamic transition level and these levels can be experimentally observed by deep-level transient spectroscopy (DLTS). On the contrary, if the transition is fast (by exciting an electron for example), then the atoms do not

11

have time to relax and these levels are called optical transition levels.

Deep and shallow transition levels In function of the position of transition levels in the gap, these latter can be sorted in two categories: either levels are located deep in the gap and we speak about *deep level*s, either they are located near the band edges and they are called *shallow level*s. The transition levels given as an example in Figure 1.6, are represented in a similar way in Figure 1.7.
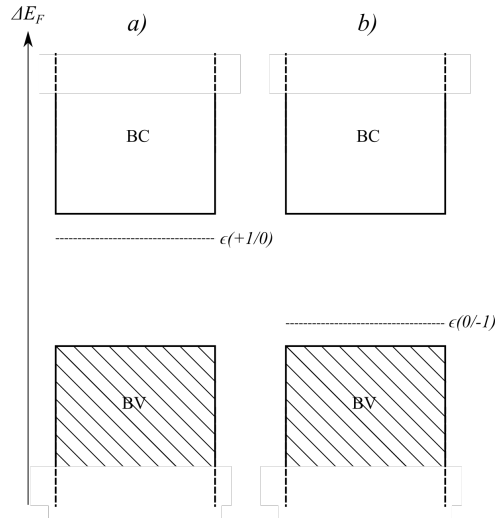

Figure 1.7: Position of the transition levels of Figure 1.6 with respect to the valence and conduction bands. The transition level $\epsilon\left(+1/0\right)$ is a shallow donor while the transition level $\epsilon\left(0/-1\right)$ is a shallow acceptor.

Doping induced by defects In order to contribute to the doping of the material, a defect must be stable in a non neutral charge state such that the charge induce the introduction of charge carriers in the material. Hence a n-type doping defect must be stable in a positive charge state while a p-type doping defect must be stable in a negative charge state. Of course, as the Fermi level varies between the VBM and the CBM, it is not possible to establish in which state a defect is at growth temperature. Hence a way to determine if a defect dope a material is to look at its transition levels. If a defect presents a CBM-shallow transition level $\epsilon\left(q/q'\right)$ between two positive or neutral charge states such that $q > q'$, it means that, for any value of the Fermi energy in the gap, away from the band edge, the defect will be in a positive charge state and thus will participate to the n-type doping of the material. In this case this transition level is called *shallow donor transition level*. At contrary, if a defect has a VBM-shallow transition level $\epsilon\left(q/q'\right)$ between two negative or neutral charge states such that $q > q'$, then this defect will participate to the p-type doping of the material. In this case the transition level is called *shallow acceptor transition level*. For example, the two transition levels displayed in Figure 1.7 are respectively a shallow donor level (a) and a shallow acceptor level (b).

Negative formation energy In the case where a defect has a negative formation energy, the creation of this defect in the material is then an endothermic process. In this case, the

defect concentration is such that the material is not thermodynamically stable and can not be synthesised for the corresponding values of the Fermi level.

2. Defect cell DFT calculations with *Vienna Ab Initio Simulation Package*

In this section, defect analysis using the software *Vienna Ab Initio Simulation Package* (VASP) is explored.

As a reminder, VASP requires 4 different files to operate:

- The INCAR file which contains the parameters of the calculations such as the cut-off energy;

- The POSCAR file which contains the crystallographic parameters of the cell and the atoms positions;

- The KPOINTS file which contains the position of the k-points;

- The POTCAR file which contains the pseudo-potentials of the atomic species in the system studied.

Particularly, the parameters required for an analysis of the results with *Python for Defect Energy Formation* will be outlined in this section.

2.1 Calculations parameters

In this subsection, the different parameters required for geometry optimisation and DOS calculations are reviewed.

For both types of calculations, there no restrictions of any kinds on the POSCAR and KPOINTS files. However the INCAR must follow a few rules. Tags in blue are recommended while the red ones are required for post-process analysis with PyDEF.

2.1.1 Geometry optimisation

When optimising the geometry of the cell, the following tags values are recommended

- `ISMEAR = 0`: Gaussian smearing

- `ISIF =`

    - `6` for optimisation of the volume and the crystallographic parameters of the cell;

    - `2` for optimisation of the positions of the atoms in the cell;

    - `3` for optimisation of both the volume of the cell and the positions of the atoms.

All others tags can be set at will.

2.1.2 DOS calculation

The tags for DOS calculations are:

- `PREC = ACCURATE`: accurate precision for better results;

- `ISIF = 0` or `IBRION = 0`: for calculating only the total energy of the system;

- `ISMEAR = -4`: tetrahedron method without Blöchl corrections. Although Bloch corrected smearing might seem better, this type of smearing creates negative occupation of energy levels which may cause problems with the use of the Moss-Burstein correction.

- `LORBIT = 11` if you want to plot the projected DOS on atoms or `LORBIT = 0` if you only want the total DOS.

The following tags values can be safely used if you plan to use PyDEF to process the calculations outputs.

- `NEDOS`: number of points in the DOS

- `EMIN`: lower value of the energy for the DOS

- `EMAX`: higher value of the energy for the DOS

- `EDIFF`: convergence energy

- `ENCUT`: cut-off energy

Other flags should be left at their default value if you plan to use PyDEF to analyse the results[1].

2.1.3 Band diagram calculation

Band diagram can be calculated using the method presented here: https://cms.mpi.univie.ac.at/wiki/index.php/

2.1.4 Functionals and methods of DFT

Local Density Approximation (LDA) The utilisation of the LDA functional in VASP is automatic when the corresponding pseudo-potentials are used.

Generalised Gradient Approximation (GGA) The utilisation of the GGA functionals in VASP is automatic when the corresponding pseudo-potentials are used.

HSE06 and PBE0 functionals HSE06 and PBE0 functionals can be used through the GGA PBE pseudo-potentials and by setting the following tags in the INCAR file[2]:

- `LHFCALC = TRUE`: specify that Hartree-Fock type calculations are performed;

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[1]Next main version of PyDEF will support more complex calculations such as spin polarised calculation.

[2]Refer to http://cms.mpi.univie.ac.at/wiki/index.php/Specific_hybrid_functionals for more informations on the use of hybrid functionals in VASP.

- **HFSCREEN**: electrons screening. `0.2` for HSE06 calculations and `0.0` for PBE0 calculations.

- **AEXX = 0.25**: percentage of the Hartree part in the exchange-correlation functional;

- **ALGO = ALL** or **ALGO = DAMPED**: the second one will give less precise results but in a shorter time

- **PRECFOCK = NORMAL** or **PRECFOCK = FAST**: FFT grid of the exact exchange, the second one will give less precise results but in a shorter time.

GW0 correction on non-hybrid DFT calculations This method consist to correct the Kohn-Sham levels of a non-hybrid DFT calculation[3]:

1. Perform a simple DFT DOS calculation with a low convergence energy (`EDIFF` tag)

2. Starting from the previous calculation, run another DOS calculation after adding these tags to the INCAR file

   (a) `NELM = 1`: only one electronic step since the calculation is already converged from step 1;

   (b) `LOPTICS = TRUE` : write the WAVEDER file which contains the derivates of the orbitals;

   (c) `ALGO = Exact` : exact diagonalisation of the Hamiltonien;

   (d) `NBANDS = N` where N must be higher than the number of bands in the simple DFT calculation.

3. Starting from the previous calculation, run a last DOS calculation after removing the previous tags and adding the following tags:

   (a) `ALGO = GW0`: set the GW_0 calculation;

   (b) `NOMEGA = 50`: number of frequency grid points.

   (c) `NELM = M` where M is the number of time the Green operator is applied.

2.2   VASP calculations for defect formation analysis

In order to perform a defect analysis, the formation energy of few charged defects must be computed. The first step is to optimise and compute the energy of the host cell. Then the energy of the cells containing the defect with different charge states must be computed.

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[3]Refer to http://cms.mpi.univie.ac.at/wiki/index.php/GW_recipes for more informations on GW calculations.

2.2.1 Host cell

For better results, the following scheme is recommended for the host cell:

- Optimisation of the volume and crystallographic parameters of the cell (`ISIF = 6` tag);

- Optimisation of the positions of the atoms in the cell (`ISIF = 2` tag);

- Optimisation of both the volume of the cell and the positions of the atoms (`ISIF = 3` tag);

- DOS calculation.

Note: It is important that the host cell is well optimised before studying the defect cells.

2.2.2 Defect cell

The first step to study a defect is to add it to the POSCAR file. To do that, take the optimised geometry of the host cell and modify it according to the defect you want to study. For example, for a vacancy of an atomic species C, remove the position of one of the C atoms and remove it also from the breakdown at the beginning of the file such as displayed in Figure 2.1.

Figure 2.1: Creation of a sulphur vacancy in the POSCAR file. Left: Optimised geometry of the host cell. Right: Geometry of the defect cell before optimisation. The position of the sulphur atom removed is framed in red.

The next step depends on if you want to compute thermodynamic of optical transition levels. For thermodynamic transition levels, the position of the atoms in the cell must be first optimised (`ISIF = 2` tag) and then the DOS can be computed using the optimised geometry. For optical transition levels, the geometry does not need to be optimised and the DOS can be directly computed.

For charged defect cells, the number of electrons in the cell must be set using the `NELECT` tag such that there are more or less electrons in the cell with respect to the valence electrons of the atomic species in the cell. Let us assume that the host cell has 496 valence electrons. After removing a C atom (6 valence electrons), this number goes down to $496 - 6 = 490$. This is the value of NELECT when the C vacancy charge is zero. In order to model a positively charged $+1$ defect, it is required to remove one electron from the cell which means that the NELECT tag must be set to $490 - 1 = 489$. Following this logic, the Table gives the number of electrons of the system and the associated charge of the defect.

Table 2.1: Number of electrons and associated charge of a C vacancy

Cell	NELECT	Charge
Host cell	496	/
	488	$+2$
	489	$+1$
Defect cell	490	0
	491	-1
	492	-2

2.2.3 Calculation of the relative permittivity

The relative permittivity that is used in the Makov-Payne correction can be easily calculated using VASP. The electronic contribution can be computed from a simple DOS calculation by setting the tag `LEPSILON = TRUE` for non-hybrid functionals or `LOPTICS = TRUE` for hybrid functionals. The lattice part can be computed from a GGA DOS calculation by setting the tags `LEPSILON = TRUE` and `IBRION = 8`.

2.2.4 Calculation of the Makov-Payne ratio

The following method allows to easily get the value of the ratio $\frac{\alpha_M}{2\epsilon_0 V^{1/3}}$.

1. Take the POSCAR file of the optimised host cell and remove all of the atoms;

2. Add an hydrogen atom in the middle of the cell and change the POTCAR file accordingly;

3. Perform a regular DOS calculation (the functional used does not matter) with the following tags: `NELM = 1` and `NELECT = 0`;

4. The value of the ratio $\frac{\alpha_M}{2\epsilon_0 V^{1/3}}$ corresponds to the Ewald energy of the first electronic step (Figure 2.2).

```
---------------------------------------- Iteration   1(  1) ----------------------------------------


     POTLOK:  cpu time   1.42: real time   1.42
     SETDIJ:  cpu time   0.02: real time   0.02
     EDDAV:  cpu time   1.12: real time   1.23
   BZINTS: Fermi energy: -1.579655;  1.000000 electrons
       Band energy:  -2.061855;  BLOECHL correction: -0.204468
     DOS:  cpu time   0.00: real time   0.00
   --------------------------------------------
     LOOP:  cpu time   2.55: real time   2.67

   eigenvalue-minimisations  :    32
   total energy-change (2. order) : 0.4409235E+01  (-0.6450858E+01)
   number of electron      1.0000000 magnetization
   augmentation part       1.0000000 magnetization

   Free energy of the ion-electron system (eV)
   ---------------------------------------------------
   alpha Z        PSCENC =        0.00181922
   Ewald energy    TEWEN  =       -1.85334644
   -Hartree energ DENC   =       -6.04544665
   -exchange      EXHF   =        0.00000000
   -V(xc)+E(xc)   XCENC  =        1.88895321
   PAW double counting   =        2.13402744       -2.14290522
   entropy T*S    EENTRO =        0.00000000
   eigenvalues    EBANDS =       -2.06185495
   atomic energy  EATOM  =       12.48798843
   ---------------------------------------------------
   free energy    TOTEN  =        4.40923503 eV

   energy without entropy =        4.40923503  energy(sigma->0) =       4.40923503


   -----------------------------------------------------------------------------------------------------
```

Figure 2.2: Location of the Ewald enrgy in the OUTCAR file

3. Defect analysis using *Python for Defect Energy Formation* 1.1.0 (PyDEF)

Python for Defect Energy Formation 1.1.0 (PyDEF) is a software that enables simple and quick analysis of point defects. It is based on the fact that every information required to compute the defect formation energy can be retrieved from the OUTCAR output file of the VASP calculations.

In this section, it will be explained how to use PyDEF in order to obtain defect formation energy and transition levels for any defect in any material.

New features (1.1.0)

- Faster plotting of the DOS;

- Now able to plot spin calculations DOS (important note: PyDEF is not yet able to perform defect formation energy using spin projected calculations);

- New options for the plot of the DOS;

- Now able to consider f orbitals;

- Now able to plot band diagram;

- Various bugs corrections.

3.1 Main window

The main window of PyDEF (Figure 3.1) is composed of 6 buttons (from left to right and top to bottom):

1. *VASP calculations importation tool*: for importing VASP calculations and plotting DOS;

2. *Defect label tool*: for creating defect labels;

3. *Defect studies tool*: for plotting defect formation energy and transition levels of a defect;

4. *Material studies tool*: for plotting defect formation energy and transition levels of multiple defects in a same material;

5. *Chemical potential tool*: for computing the variations of the chemical potentials;

6. *Defect concentration tool*: for computing defects and charge carriers concentrations.
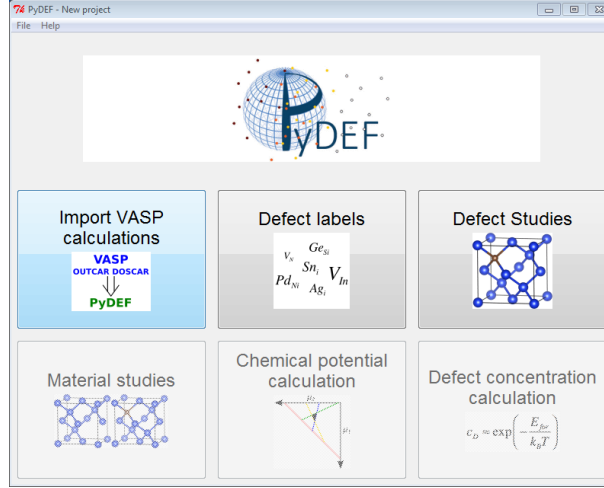
Figure 3.1: Screen capture of PyDEF main window

In his first version, PyDEF is able to compute the formation energy and transition levels of any defect (hence only the 3 first tools are available). Material studies, chemical potential and defect concentration tools will be available in a next version.

In order to plot the defect formation energy and transition levels, the user need to:

1. Provide the VASP output files for each cell of the calculations (host cell & defect cells);

2. Provide the chemical potential and the position associated to the defect (this latter being optional);

3. Give few informations on the material studied such as its relative permittivity and the different corrections applied to the defect formation energy.

3.2   VASP calculations importation tool

The VASP calculations importation tool (Figure 3.2) allows to import outputs of VASP calculations into PyDEF using the OUTCAR and DOSCAR files.
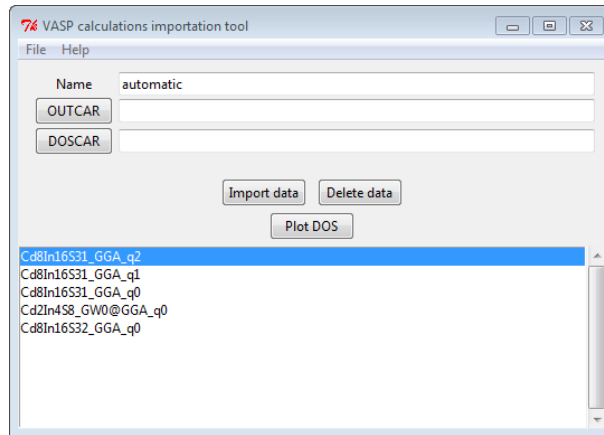
Figure 3.2: VASP calculations importation tool window

In this window, three input fields are displayed:

- the *Name* field corresponds to the name of the calculation once imported into PyDEF. If this field is empty or set to 'automatic', the name will automatically be generated from the OUTCAR file with the following pattern:

$$composition + method\ used + charge\ of\ the\ cell$$

- The *OUTCAR* field corresponds to the location of the OUTCAR file. This file is always required when importing a calculation.

- The *DOSCAR* field corresponds to the location of the DOSCAR file. This field is only required if you want to plot the DOS and is not necessary for defect formation energy calculation.

Once the informations provided, the files can be read using the *import data* button.

Note: If the imported calculation has the same name as another one previously imported, a message will pop-up to ask if the newly imported calculation may overwrite this latter.

The *plot DOS* button allows to plot the DOS of the calculation (if the DOSCAR file is provided).

Double-clicking on a calculation in the list will open a new window containing various informations about it (first panel, Figure 3.3) and parameters for the plot of the DOS (second panel, Figure 3.4).

3.2.1 System properties and calculation results
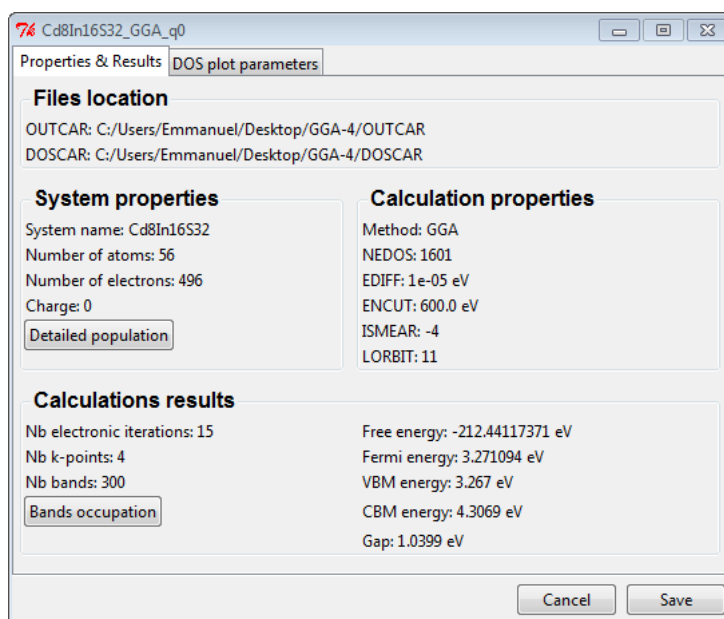
Figure 3.3: Calculation properties window

This first panel provide general informations on the parameters of the calculation and its results.

System properties

- *System name*: name of the system with the total population of each atomic populations;

- *Number of atoms*: overall number of atoms in the system;

- *Number of electrons*: overall number of electrons in the system;

- *Charge*: net charge of the system;

- *Detailed population*: open a new window with detailed informations on the atomic population of the system.

Calculation properties

- *Method*: Method or functional used for the calculation;

- *NEDOS*: number of points in the DOS;

- *EDIFF*: break energy for the self-consistent loop;

- *ENCUT*: cut-off energy used;

- *ISMEAR*: `ISMEAR` tag value;

- *LORBIT*: `LORBIT` tag value.

Calculation results

- *Nb electronic iterations*: number of electronic steps;

- *Nb k-points*: number of k-points calculated (considering the symmetry used);

- *Nb bands*: number of bands for any k-points;

- *Bands occupation*: open a new window containing the band occupation and energy for each k-point;

- *Free energy*: total electronic energy of the system;

- *Fermi energy*: Fermi energy of the system;

- *VBM energy*: energy of the valence band maximum;

- *CBM energy*: energy of the conduction band minimum;

- *Gap*: electronic gap value.

Note: For defect cell calculations, the position of the VBM and CBM (and thus, the gap value) may not be correct and should not be used.

3.2.2 DOS plot parameters

The plot parameters window of the DOS is displayed in Figure 3.4.
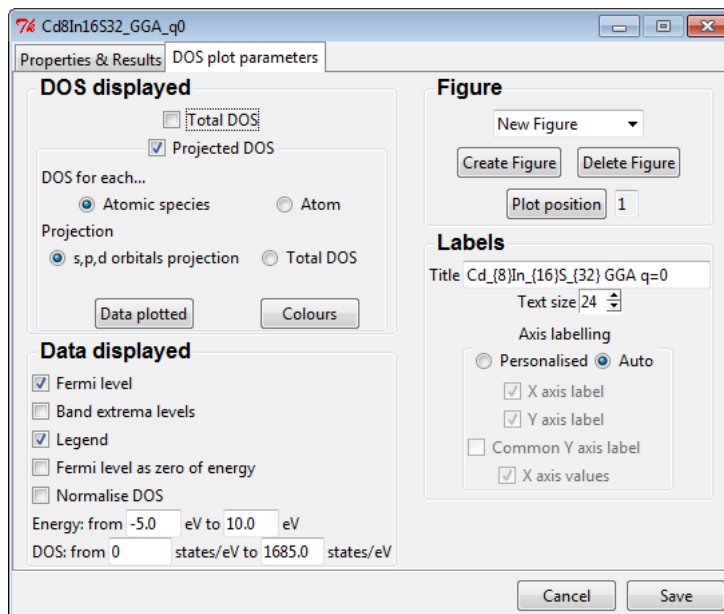
Figure 3.4: Parameters of the plot of the DOS

DOS displayed

- *Total DOS*: If checked, the total DOS is plotted

- *Projected DOS*: if checked, the projected DOS is plotted, according to the parameters below. This option is not available if the VASP tag LORBIT was not set to 11.

  - *DOS for each...*: you can plot the projected DOS on each atom or on each atomic species.
  - *Projection*: you can plot the s, p, d projected DOS or the total projected DOS.
  - *Projected DOS type*: choose between *stacked areas* and *non-stacked lines*.
  - *Data plotted*: allows you to select which elements (atoms or atomic species) are plotted.
  - *Colours*: allows you to choose the colours of the elements plotted.

Data displayed

- *Fermi level*: if checked, display the Fermi level;

- *Band extrema levels*: if checked, display the band extrema;

- *Legend*: if checked, display the legend of the plot;

- *Fermi level as zero of energy*: if checked, set the Fermi level as the zero-energy;

- *Normalise DOS*: if checked, normalise the DOS;

- *Energy range*: energy range displayed. By default the whole energy range is displayed;

- *DOS range*: DOS (y-axis) range displayed. By default the whole DOS range is displayed.

Figure   By default, any new imported calculation's DOS (thereafter *plot*) is plotted in a new window thereafter called *figure*.
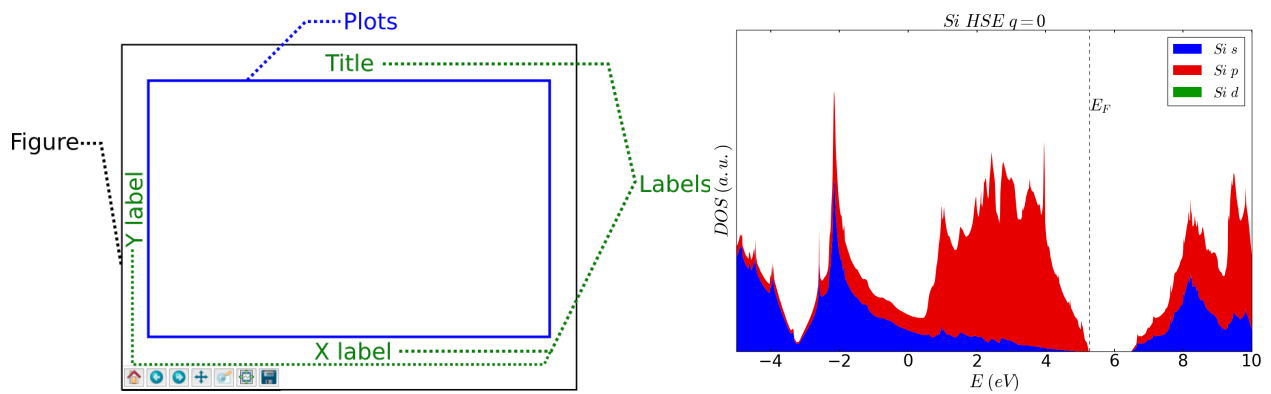
Figure 3.5: Left: schematic representation of a *figure* window containing a single *plot*. Right: Projected DOS of silicon

Using the buttons at the bottom of the *figure* window (see Figure 3.5), you can

- save the figure to a png file using the last button;

- navigate through the data in the plot using the 5th button;

- zoom on a plot using the 4th button;

- undo the last action (zoom or move) using the 2nd button or redo the last action using the 3rd button.

- reverse to the original state of all the plots using the 1st button.

It is also possible to have multiple plots next to each other in a same *figure*. To do this, you will need to create a new *figure* with a certain number of rows and columns using the *Create figure* button.

Once this is done, select the newly created figure in the selector and click on the *plot position* button to set the position of the plot in the figure. A schematic representation of and an actual *figure* composed of 2 rows and 2 columns is displayed in Figure 3.6.
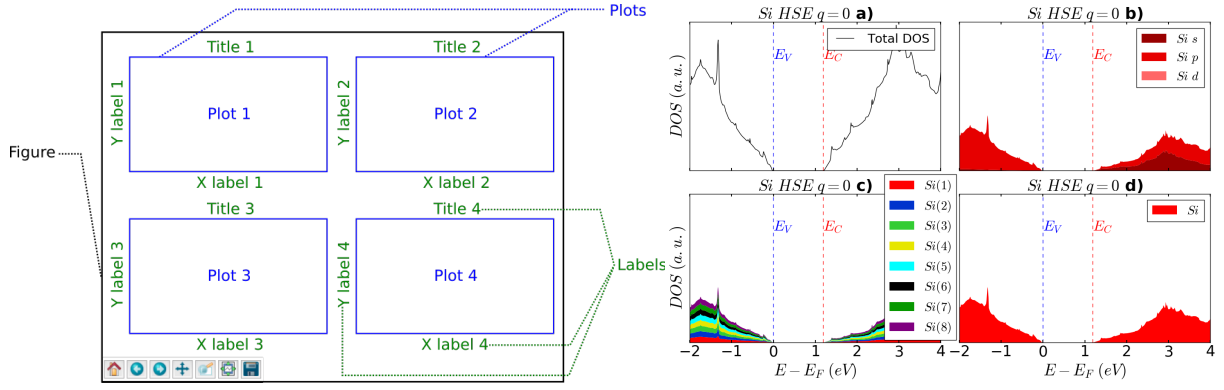
Figure 3.6: Left: schematic representation of a *figure* window containing 4 *plots.* Right: Actual *figure* composed of 4 *plots,* each one displaying different informations.

Labels   Labels are texts displayed around the *plot.*

- *Title*: title of the plot;

- *Text size*: size of the labels displayed (title, axis label, fermi level label,...);

- *Axis labelling*: if this parameter is set to automatic, axis labelling will be performed automatically in such a way to optimise the size of the plots by removing non necessary labels (this is done by assuming that the x axis range is the same for all plots of a same column). In the other case, the following parameters set the behaviour of the plot.

  - *X axis label*: if checked, display the X axis label;

  - *Y axis label*: if checked, display the Y axis label;

  - *Common Y axis label*: if checked, display a common Y axis label for all plots of a same column (this option should be selected only once for a same figure);

  - *X axis values*: if checked, display the X axis values.

3.2.3   Band diagram plot parameters

PyDEF is now able to plot band diagrams if it was calculated using the method explained here https://cms.mpi.univie.ac.at/wiki/index.php/Si_bandstructure#Procedure_1:_Standard_procedure_.28DFT.2

Data displayed

- *Energy*: energy range displayed. By default, the whole energy range is displayed.

- *VBM as zero of energy*: if ticked, the zero of energy is defined as the VBM energy.

- *Highlight VBM & CBM*: if ticked, highlight the VBM and CBM.

- *High symmetry K-points*: Name of the high symmetry K-points of the band diagram (each K-point must be separated by a comma)

3.3 Defect label tool

Once all of the VASP calculations are imported (host cell and defect cells), a few informations are required about the defect studied.

In the defect label window (Figure 3.7), indicate first its type of defect amongst 'Vacancy', 'Interstitial' and 'Substitutional'. You will then have to indicate which atom has been added or/and removed and their respective chemical potential. If you study many defects in a same cell, create a defect label for each one.
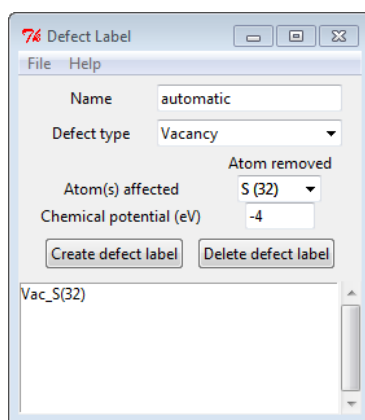
Figure 3.7: Defect label window

As usual, the *Name* of the defect label will be automatically generated if not given.

Note: the correct number of the atom(s) modified is only necessary if you plan to perform the potential alignment correction in the defect formation energy calculation.

3.4 Defect Studies

Defect studies will allow you to compute the defect formation energy and the transition energies. Creating defect studies is done using the defect studies window (Figure 3.8).
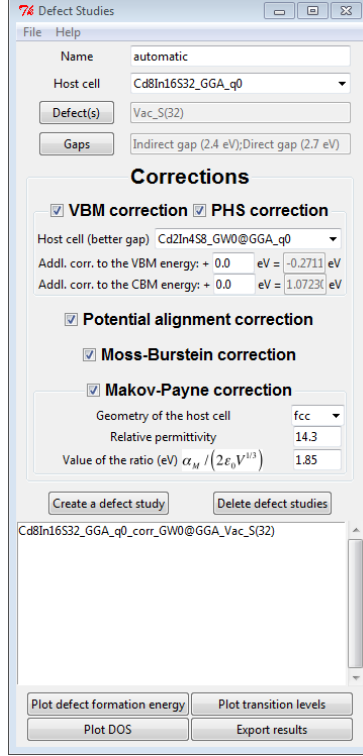
Figure 3.8: Defect studies window

The first step to create a defect study is to indicate which VASP calculation corresponds to the host cell and which defect(s) is/are studied. Experimental and theoretical gaps can also be given and will appear on the defect formation energy and transition levels plots.

As usual, the name is automatically generated if not specified otherwise.

3.4.1 Corrections

In this first version of PyDEF, fives corrections to the formation energy are available:

- *Gap corrections* (*VBM correction* and *PHS correction*). For these corrections, the gap can either be corrected using a host cell calculation with a better calculated gap (for example, GW@GGA method to correct a GGA gap), or can be corrected by hand by giving the corrections to the VBM and the CBM.

- *Potential alignment correction*

- *Moss-Burstein correction*

- *Makov-Payne correction*. For this correction you will need to provide:

  - the geometry of the host cell;

  - the relative permittivity of the material (see section 2.2.3);

  - the value of the ratio $\frac{\alpha_M}{2\epsilon_0 V^{1/3}}$ (see section 2.2.4);

These corrections can be easily enabled or disabled at will.

Once the options are set, the defect study can be created using the *create defect study* button. Its properties and parameters can then be accessed by double-clicking on it in the list (Figure 3.9).
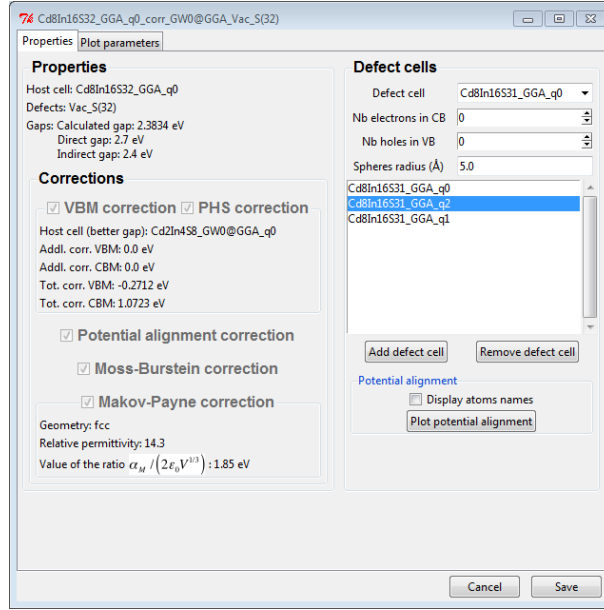

Figure 3.9: Defect study properties window

To complete the study the different defect cells need to be added to it. Depending on the activated corrections, the following parameters are required for each defect cell:

- the number of electrons in the CB and number of holes in the VB for the PHS correction;

- the radius of the spheres in Angstrom for the potential alignment.

Note: PyDEF will only display defect cells which suit the defect(s) studied and the host cell which will help the selection of these laters.

For each defect cell added, you can then plot the potential alignment correction such as displayed in Figure 1.3.

Double-clicking on a defect cell in the list opens a new window with the details of each corrections.

Once this is done, the four buttons located at the bottom of the defect studies window can be used (Figure 3.8). Those are:

- *Plot defect formation energy*: plot the defect formation energy with respect to the Fermi level energy;

- *Plot transition levels*: plot the transition levels with respect to the Fermi level energy;

- *Plot DOS*: plot the DOS of the host cell and defects cell in a same *figure* on top of each other

- *Export results*: export all defect study results (corrections values for each defect cells, transition levels, etc.) in a text file.

3.4.2 Plot parameters

Parameters of the different plots (formation energy, transition levels, DOS) are displayed in Figure 3.10.
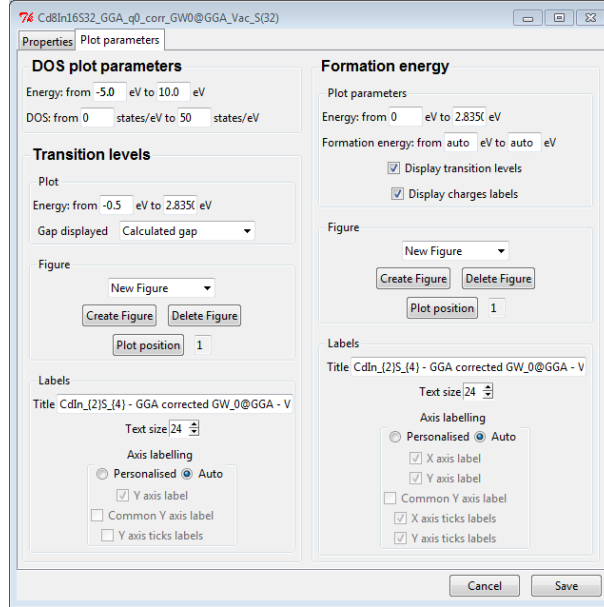
Figure 3.10: Plot parameters of a defect study

DOS

- *Energy range*: Range of energy displayed for all *plots*;

- *DOS range*: Range of DOS displayed for all *plots*.

Formation energy plot parameters

- *Energy range*: Range of the Fermi energy displayed (with respect to the VBM). It is automatically calculated from the highest gaps of the defect study;

- *Formation energy range*: Formation energy range displayed;

- *Display transition levels:* if checked, display the transition levels;

- *Display charges label*: if checked, display charge label for each formation energy line.

Transition levels plot parameters

- *Energy range*: Range of the Fermi energy displayed (with respect to the VBM). It is automatically calculated from the highest gaps of the defect study;

- *Gap displayed*: gap (i.e. VBM and CBM position) displayed in the plot.

Figure and labels parameters are similar to the calculations parameters (see sections 3.2.2 and 3.2.2). For the formation energy, automatic axis labelling will assume that the Fermi energy range displayed is the same for all plots in a same figure and that the formation energy range is the same for all plots. For transition level plots, automatic axis labelling will assume that the Fermi energy range is the same for all plot in a same figure.

3.5 Saving data, projects and parameters

3.5.1 Saving and loading data

VASP calculations, defect labels and defect studies can be easily saved on a computer using the file menu in the corresponding window. In particular for the VASP calculations, the saved file contains all informations required to plot the DOS and thus, the OUTCAR and DOSCAR files are no longer required.

These files can then be afterward loaded from the same menu.

3.5.2 Projects

PyDEF' projects are ensembles of VASP calculations, defect labels and defect studies which allow the user to manage his data more efficiently.

Projects are created via the *File menu/New PyDEF project* menu of the main window. Once this done, the new project is opened in PyDEF (his name is displayed on top of the main window) and all elements added afterward (VASP calculations, etc.) are associated to it. Projects can then be saved and loaded on a computed using the *File* menu of the main window. Note the following

- Opening or creating a project will close the previous project opened without saving it

- Project contains all elements including the DOSCAR and POSCAR files for each calculation, hence their size which can go up to a few GB.

- By default, a new blank project is opened at PyDEF launch.

3.5.3 Parameters

Parameters can be accessed through the *Help/Parameters* menu. Currently, the user can set:

- the VASP data default directory which is the default directory opened when looking for an OUTCAR or a DOSCAR file.

- the PyDEF data default directory which is the default directory opened when saving or loading PyDEF files.

3.5.4 Error and alert messages

VASP calculation import tool

- *The OUTCAR file is missing*: this error message pop-up when the OUTCAR file location is not provided.

- *The given file is not a valid OUTCAR file*: this error message pop-up when the given file is not a valid OUTCAR file

- *An error occurred while reading the OUTCAR file*: this error message pop-up when informations in the OUTCAR file could not be retrieved. This may happen if parameters of the VASP calculation are different than the ones recommended in the previous section.

- *The given DOSCAR file is not consistent with the OUTCAR file*: this error message pop-up when the number of lines in the DOSCAR file is not consistent with the OUTCAR file. This may happen if parameters of the VASP calculation are different than the ones recommended in the previous section.

- *The given files do not exist*: this error message pop-up when the file provided does not exist.

- *Enter a correct value for the energy/DOS range*: this error message pop-up when the values given for the energy or DOS ranges is not a number.

Defect label tool

- *Select first a defect type*: this error message pop-up if the *create defect label* button is clicked while no defect type is selected.

- *You must import a VASP calculation first*: this error message pop-up if no VASP calculation was first imported.

- *The ID of a defect label can not contain a comma*: this error message pop-up if the name of the defect contains a comma

Defect studies tool

- *A host cell is required*: this error message pop-up if no host cell is given for the defect study;

- *At least one defect label is required*: this error message pop-up if no defect label is provided for the defect study

- *The correction of the CBM and VBM must be numbers*: this error message pop-up if one of the gap corrections is enabled and that the correction of the CBM and VBM are not numbers.

- *Select a geometry for the host cell*: this error message pop-up if the Makov-Payne correction is enabled and the geometry of the host cell is not given.

- *The relative permittivity must be a number*: this error message pop-up if the Makov-Payne correction is enabled and the relative permittivity provided is not a number.

- *The relative permittivity can not be zero*: this error message pop-up if the Makov-Payne correction is enabled and the relative permittivity provided zero.

- *The Makov-Payne ratio must be a number*: this error message pop-up if the Makov-Payne correction is enabled and the Makov-Payne ratio is zero.

- *Select a defect study in the list*: this error message pop-up if no defect study is selected while one of the buttons at the bottom of the defect studies window is used.

- *You must indicate at least one defect cell before*: this error message pop-up if you try to plot the formation energy or the transition levels or to export the results of a defect study while no defect cells was given.

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