**Correction methods for the finite-size effects**

The formation enthalpy (Δ*HD,q*) of a defect with a charge state *q* was calculated through the following equation.1

(1)

, where is the total energy of the supercell with the defect (*D*) in the charge state *q*, and is that of the perfect host supercell. *ni* indicates the number of the *i*-th atoms added (*ni* < 0) or removed (*ni* > 0), and is the chemical potential of the *i*-th atom with respect to that of the corresponding elemental phase (el) by = el +. *E*F is the Fermi level relative to the valence band maximum (VBM, *E*V). is the correction value for the defect formation enthalpy. Usually, we apply three correction methods for the finite-size effects, including the image charge correction, the potential-alignment correction, and the band-filling correction.

**(1). Image charge correction:**

In actual calculations, since the size of the supercell cannot be infinite, it leads to the interaction between point defects and affects its actual defect formation enthalpy. To eliminate this effect, the image charge correction should be added.

The image charge correction (*E*i) is calculation using the simplified expression1:

(2)

Where is the Madelung constant, is the linear supercell dimension ( is the supercell volume), and is the dielectric constant.

**The steps to do it:**

**1.How to get αM/L？**

(αM/L is the same for all defects)

Choose one charged defect (for example: VSn1- )

Add IDIPOL = 4 in INCAR, then do the self-consistent calculation in the defect supercell.

Check OUTCAR and find “energy correction for charged system” by inputting [grep “energy correction for charged system” OUTCAR]

The energy correction for charged system =

So, in the following example, =1.604798, q=1, so αM/L=1.604798).

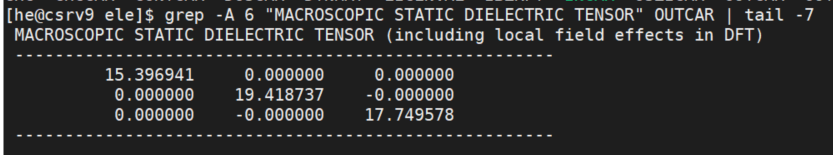


**2.How to get the dielectric constant ɛ？**

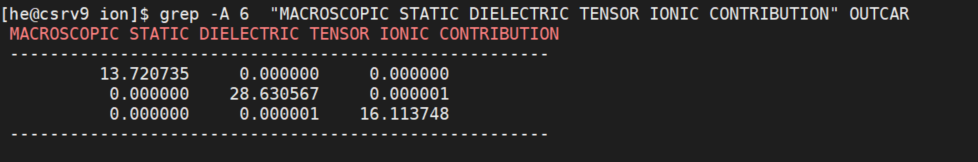
Use the primitive cell.

The dielectric constant ɛ including two parts, the electronic part and the ionic part.

1. For the electronic part, add “LEPSILON=.T.” in INCAR, then do the self-consistent calculation. Catch the value by inputting [grep -A 6 “MACROSCOPIC STATIC DIELECTRIC TENSOR” OUTCAR |tail -7]. The average electronic part is (ɛxx + ɛyy +ɛzz / 3). (For example, in the following data, the average electronic part is (15.396941 + 19.418737 +17.749578)/3 = 17.521752)



1. For the ionic part, add “LEPSILON=.T.; IBRION=8; NSW=1” in INCAR, do the self-consistent calculation. Catch the value by inputting [grep -A 6 “MACROSCOPIC STATIC DIELECTRIC TENSOR IONIC CONTRIBUTION” OUTCAR]. The average ionic part is (ɛxx + ɛyy +ɛzz / 3). (For example, in the following data, the average ionic part is (13.720735 + 28.630567 + 16.113748)/3 = 19.48835).



Then, the total ɛ = ɛ(electron) + ɛ(ion). (For example, ɛ =17.521752 + 19.48835 = 37.010102)

**3.** **Substitute αM/L and ɛ into equation**

For the larger charge state q, the correction value would be larger.

**(2). Potential-alignment correction:**

In the ideal case, defects have little effect on the local atomic-sphere-averaged electrostatic potentials in the system, but due to the limited size of the defect supercell, the electrostatic potential energy would be affected. To eliminate this effect, the potential-alignment correction should be added.

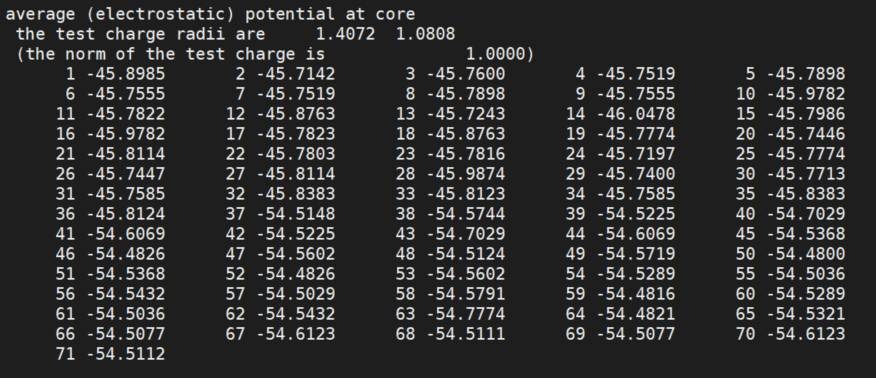
The potential-alignment correction (*E*PA) is determined by following equation1:

(3)

where and are the local atomic-sphere-averaged electrostatic potentials at atomic sites farther away from the defect in the charged-defect model and pure model, respectively.

**The steps to do it:**

1. The electrostatic potentials can be seen in the OUTCAR under the line “average (electrostatic) potential at core”. The number before the value follows the atoms order in POSCAR.



2. Choose the atom located farthest away from the defect, and get its electrostatic potential in the charged-defect model and pure model.

3. The correction value is

**(3). Band-filling correction:**

In the defect calculation, if several electrons are filled into the conduction band, the energy of the conduction band will be affected to shift down. Therefore, it needs to add the band-filling correction. Defect cells with 0 charge state also need to be corrected.

The band-filling correction (*E*bf) is calculated through the following equation1:

(4)

Where are the band energies in the defect model, is the conduction band minimum (CBM) energy in the pure model, is the Heaviside step function, is the **k**-point weight, and is the band occupation.

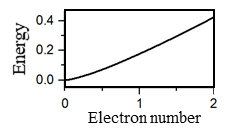
**The steps to do it:**

**1. Get DOS data for the perfect host supercell.**

Get DOS data (energy VS DOS value) from the primitive cell, then multiply the DOS values by the multiple from the primitive cell to the perfect host supercell.

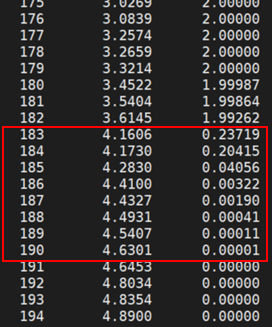
**2. Draw the relation chart between the electron number and the correction energy.**

Find the CBM energy, the electron number n=, the correction energy = . Set the electron number as x, the correction energy as y, and then draw the chart (the electron number VS the correction energy).



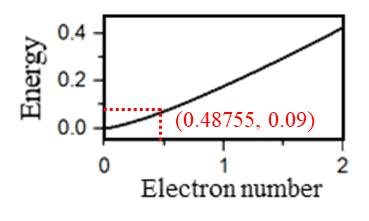
**3. Get how many electrons are filled in the conduction band**

Check each OUTCAR of the defect cells, and the filled electrons in the conduction band are counted by adding all the occupation number above CBM (The filled electrons would be integer or decimal). (For example, in following data, *e*C=4.132eV, the number of electrons that are filled to the conduction band is 0.23719 + 0.20415 + 0.04056 + 0.00322 + 0.0019 + 0.00041 + 0.00011 + 0.00001 = 0.48755.)



Get the corresponding correction energy by the chart in Step 2 (the electron number VS the correction energy).

(For example, the correction energy is around 0.09 eV).



If no electron is filled into the conduction band, no correction is needed。

Ref: [1] Lany. S.; Zunger. A. Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: Case studies for ZnO and GaAs. *Phys. Rev. B* **2008**, 78, 235104.