龙讯教程

How to calculate charged defect with PWmat?

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Charged defect calculation in semiconductors

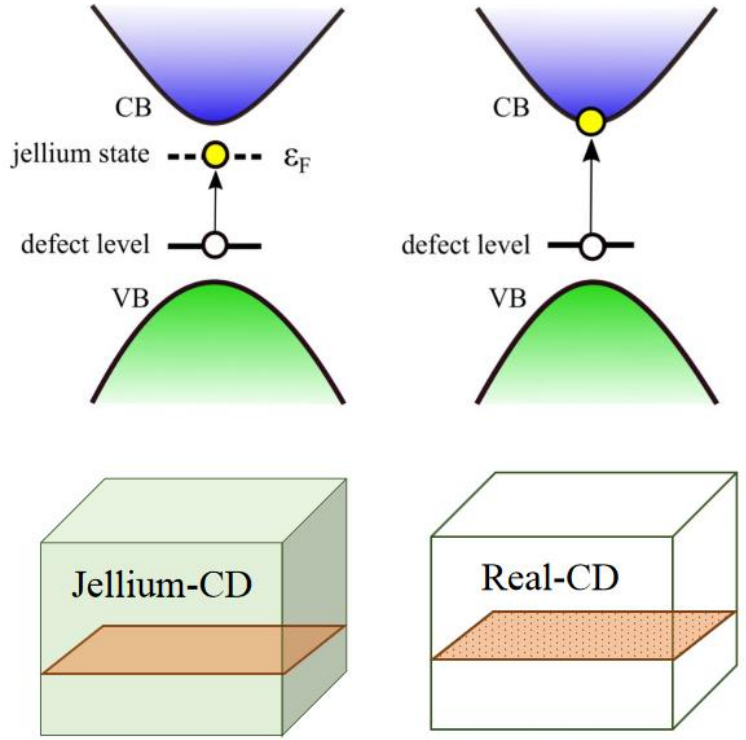
- First-principles calculations of charged defects have become a cornerstone of research in semiconductors and insulators by providing insights into their fundamental physical properties.
- But current standard approach using the so-called “jellium model” has encountered both conceptual ambiguity and computational difficulty, especially for low-dimensional semiconducting materials.
- An unavoidable “vacuum” region is added in the DFT calculations to separate the 2D material from its periodic images, it leads to a remarkable dissimilarity between a real charge put on host band-edge states and a virtual jellium charge. Specifically, when the jellium model is used, a virtual charge is uniformly filled in the whole supercell, including the vacuum region. This leads to a divergent Coulomb interaction between the jellium charge and the charge left on the 2D slab.
- In this module, we introduce a more physical and straightforward “transfer to real state” model (TRSM) to calculate the formation energies of charged defects in both three-dimensional (3D) bulk and low-dimensional semiconductors.

➢ **Refs:**

[1] J. Xion et al. Physical Review B, no. 16 (2020).

Transfer to real state model (TRSM)

- This method is based on the following concept of defect ionization that is applicable for both bulk and low-dimensional semiconductors, that is, during the defect ionization, the carriers from the defect states are excited to the unperturbed host band edge states in the limit of infinite supercell size.
- The charge density of the ionized carrier by unperturbed host band edge state, e.g., CBM or VBM states, and treat it in the same footing as all the other occupied states in the self-consistent total energy calculation, thus realize the real process of carriers exciting to host band edge states from the defect level in the same supercell (denoted as transfer to real state model or TRSM for convenience).
- Apparently, in this treatment, the whole system is charge neutral because the charged defect and the excited carrier(s) are kept in the same supercell.
- In this module, we introduce a more physical and straightforward “transfer to real state” model (TRSM) to calculate the formation energies of charged defects in both three-dimensional (3D) bulk and low-dimensional semiconductors.



➢ **Refs:**

[1] J. Xion et al. Physical Review B, no. 16 (2020).

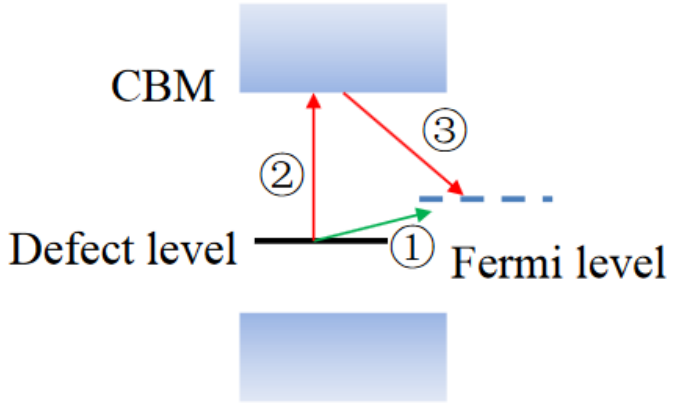
Revised formation energy formula for charged defects

- To calculate formation energy with TRSM , the formula for a defect α in a charge state q is described as:

Donor (q>0)

$$\Delta H_f(q,\alpha,\varepsilon_D \xrightarrow{①} \varepsilon_F) = \Delta H_f\left(q,\alpha,\varepsilon_D \xrightarrow{②} \varepsilon_C^h\right) - q(\varepsilon_C^h \xrightarrow{③} \varepsilon_F)$$

$$\Delta H_f\left(q,\alpha,\varepsilon_D \to \varepsilon_C^h\right) = E_{tot}(q,\alpha,\varepsilon_D \to \varepsilon_C) - E_{tot}(host) + \sum_i n_i(E_i+\mu_i) + q(\varepsilon_C^h - \varepsilon_C)$$



Acceptor (q<0)

$$\Delta H_f(q,\alpha,\varepsilon_F \to \varepsilon_D) = \Delta H_f\left(q,\alpha,\varepsilon_V^h \to \varepsilon_D\right) + q(\varepsilon_F - \varepsilon_V^h)$$

$$\Delta H_f\left(q,\alpha,\varepsilon_V^h - \varepsilon_D\right) = E_{tot}(q,\alpha,\varepsilon_V \to \varepsilon_D) - E_{tot}(host) + \sum_i n_i(E_i+\mu_i) - q(\varepsilon_V - \varepsilon_V^h)$$

- $E_{tot}(host)$, ε_C^h, ε_V^h are the total energy, CBM, VBM of the supercell for perfect host crystal, respectively.
- $E_{tot}(q,\alpha,\varepsilon_D \to \varepsilon_C)$ ($E_{tot}(q,\alpha,\varepsilon_V \to \varepsilon_D)$), ε_C, ε_V are total energy, CBM, VBM of the supercell containing a defect α in a charge state q, respectively.
- μ_i is the chemical potential of constituent i referenced to elemental solid/gas with energy E_i.
- n_i is the number of elements removed from the host in creating the defect α.
- ε_F is the fermi energy.

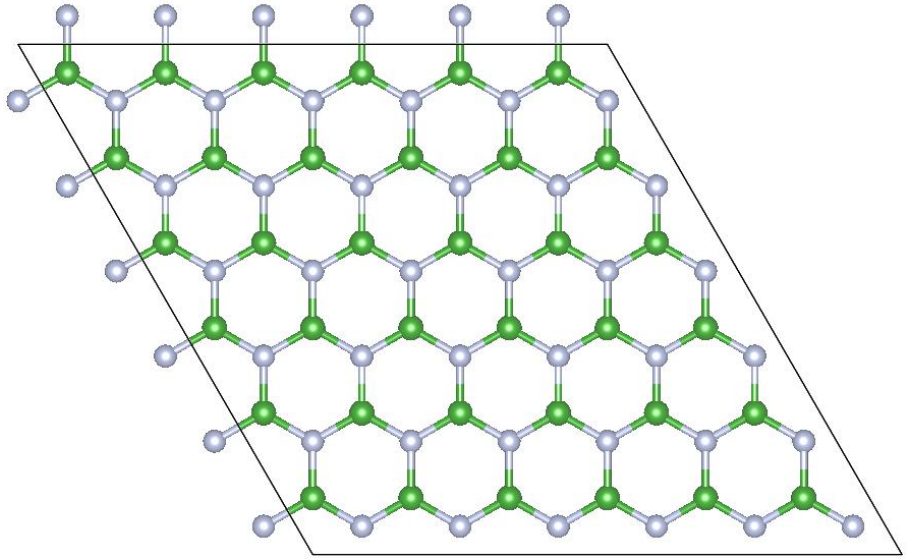
J. Xiao, H.-X. Deng* et. al. PRB 101, 165306 (2020)

Four steps to implement TRSM process

- ✓ SCF calculation for host structure to obtain total energy and real host CBM or VBM charge (make sure that you have fully optimized the host structure)
- ✓Charged defect structure relaxation using jellium model to obtain stable charged state structure
- ✓SCF calculating with charged state structure with transfer to real state model to obtain charged state total energy, VBM, CBM
- ✓Calculate formation energy according to the above formula

Defect calculation example in 2D BN : C_B(q>0)

First steps:



SCF calculation for host structure

72 atoms in the supercell
Vacuum Thickness = 20 Å

etot.input

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

We can get $E(host)$, ε_c^{host} , ε_v^{host}
and real host CBM charge or real host VBM charge

To obtain real host CBM charge

(1) Run command “convert_wg2rho.x” in the host folder

(2) Enter as prompted

number of wave functions to construct

weight of functions

weight of kpoints

name of wave functions file

which wave function

(3) The result after running is as follows

```
[qiuchen@mstation host]$ convert_wg2rho.x
 input the number of wave functions to construct rho
1
 input the prefactor for            1 wavefunction
1
 the following is the inform for           1 th wavefunction
 there are            1  kpoints
 input the ikpt to plot wg
1
 input the name of WG file
OUT.WG
 there are          161 wavefunction, input ind im to plot
145
 charge(G-space)=   1.00000002730933
 charge(R-space)=   1.00000002730937
 the constructed rho is in OUT.WG2RHO
```

$E_{tot}(host)$	ε_c^h	ε_v^h
-12615.0847 eV	0.2658 eV	-4.3688 eV

```
---------------------------------------------------
ending_scf_reason = tol Rho_err   5.000000000000000E-005
Ewald          = 0.445646114044745E+05
Alpha          = 0.897049558240035E+02
E_extV         = 0.000000000000000E+00    0.0000E+00
E_NSC          = -.332072854547325E+04    -.3406E+00
E[-rho*V_Hxc]= -.105370172690805E+06    0.3404E+00
E_Hxc          = 0.514215001361325E+05    -.3060E+00
-TS            = -.615920046918525E-11    -.3031E-12
E_tot(eV)      = -.126150847398435E+05    -.2078E-03
E_tot(Ryd)     = -.927191634455571E+03    -.7635E-05
---------------------------------------------------
```

REPORT

```
 141      -5.2796      2.00000
 142      -5.2793      2.00000
 143      -4.3688      2.00000
 144      -4.3688      2.00000
 145       0.2658      0.00000
 146       0.3580      0.00000
 147       0.3580      0.00000
 148       0.4745      0.00000
```

OUT.OCC

Second steps:

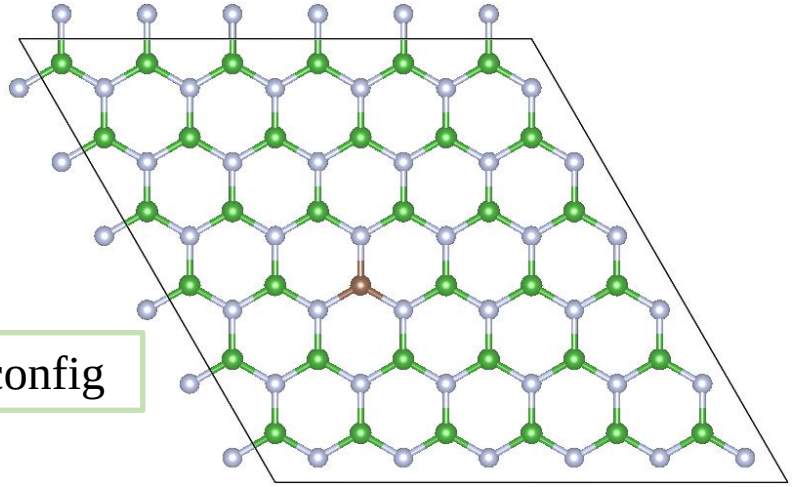
```
4   1
in.atom          = atom.config
job              = relax
relax_detail     = 1 200 0.01 0 0.03
Ecut             = 60
NUM_ELECTRON     = 288
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

etot.input

Note:

(1) The total electrons number are 289 in neutral structure.

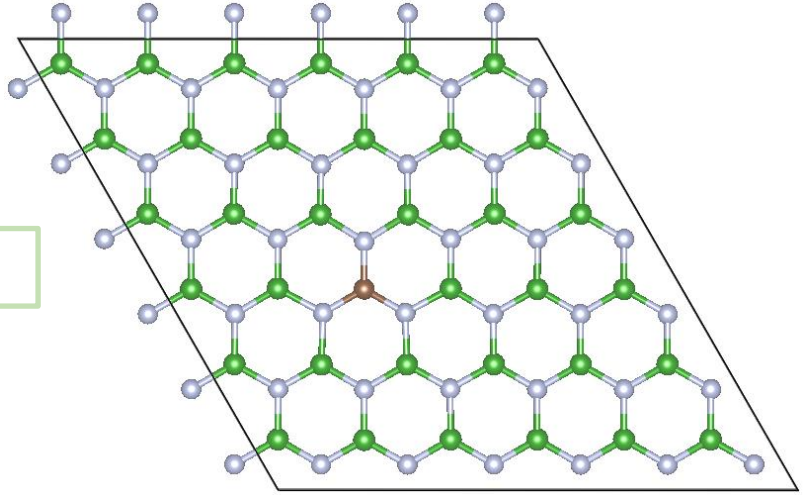
(2) We set NUM_ELECTRON=288 indicate that the total electrons number are 288 in charged structure, with a positive charge.



atom.config

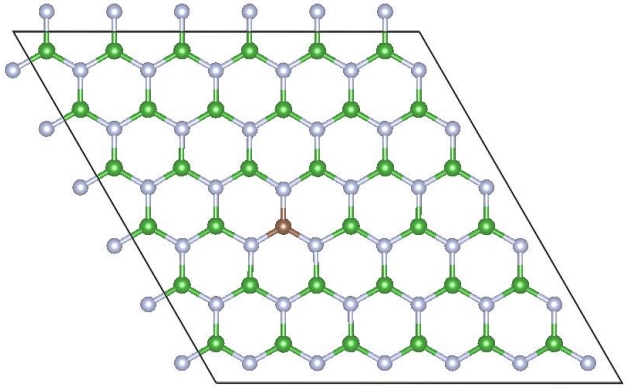
Charged defect structure before relaxation

We can get stable charged state structure



final.config

Third steps:



SCF calculation with second step final.config

To obtain IN.RHO_ADD file:

(1) Run convert_wg2rho.x in the host folder to obtain OUT.WG2RHO
(2) Copy OUT.WG2RHO to TRSM folder
(3) mv OUT.WG2RHO IN.RHO_ADD

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
in.rho_add       = T 1.0 146
in.occ=t
e_error=0.d0
```

etot.input

in.rho_add = T 1.0 146
T: read IN.RHO_ADD file
1.0: charge state of defects
146:band index of CBM of the defect supercell
Note:We set in.rho_add indicate that the host's CBM charge is added. So the charge transitions from the defect state to real host CBM.

in.occ = t
t: read IN.OCC file, you must prepare it by yourself, the content just as following:

```
144*1.0  0  1*0.5  15*0.0
```

Note: one electron is excited from defect level to CBM

Third steps:

Get $E_{tot}(q, \alpha, \varepsilon_D \rightarrow \varepsilon_C)$, ε_C

$E_{tot}(q, \alpha, \varepsilon_D \rightarrow \varepsilon_C)$	ε_c
-12687.5584 eV	-0.3201 eV

```
ending_scf_reason = tol Rho_err  5.000000000000000E-005
Ewald          = 0.449051675584 82E+05
Alpha          = 0.894909840514 88E+02
E_extV         = 0.000000000000000E+00    0.0000E+00
E_NSC          = -.35009741722870E+04     -.6074E-01
E[-rho*V_Hxc]= -.10582886853044E+06     0.6072E-01
E_Hxc          = 0.516476603872 32E+05    -.5796E-01
-TS            = -.34657359027997E-01     0.0000E+00
E_tot(eV)      = -.12687558430324E+05     -.2097E-04
E_tot(Ryd)     = -.93251835250133E+03     -.7705E-06
```

REPORT

```
142      -5.6293    2.00000
143      -4.8451    2.00000
144      -4.8450    2.00000
145      -1.7636    0.00000
146      -0.3201    1.00000
147      -0.1969    0.00000
148      -0.1456    0.00000
149      -0.1406    0.00000
150      -0.0205    0.00000
```

OUT.OCC

The fourth steps : Calculate the formation energy using TRSM

$E_{tot}(host)$	ε_c^h	ε_v^h
-12615.0847 eV	0.2658 eV	-4.3688 eV

$E_{tot}(q,\alpha,\varepsilon_D \to \varepsilon_C)$	ε_c
-12687.5584 eV	-0.3201 eV

E_B	E_C
-77.1656 eV	-155.1380 eV

$$\Delta H_f(q,\alpha,\varepsilon_D \to \varepsilon_F) = \Delta H_f\left(q,\alpha,\varepsilon_D \to \varepsilon_C^h\right) - q(\varepsilon_C^h - \varepsilon_F)$$

$$\Delta H_f\left(q,\alpha,\varepsilon_D \to \varepsilon_C^h\right) = E_{tot}(q,\alpha,\varepsilon_D \to \varepsilon_C) - E_{tot}(host) + \sum_i n_i(E_i + \mu_i) + q(\varepsilon_C^h - \varepsilon_C)$$

$$\Delta H_f(q,\alpha,\varepsilon_D \to \varepsilon_F) = E_{tot}(q,\alpha,\varepsilon_D \to \varepsilon_C) - E_{tot}(host) + \boldsymbol{E_B} - \boldsymbol{E_C} + \varepsilon_C^h - \varepsilon_C - \varepsilon_C^h + \varepsilon_F$$

$$= \text{-12687.5584} - (\text{-12615.0847}) + (\text{-77.1656}) - (\text{-155.1380} - (\text{-0.3201}) + \varepsilon_F$$

$$= 5.8118 + \varepsilon_F$$

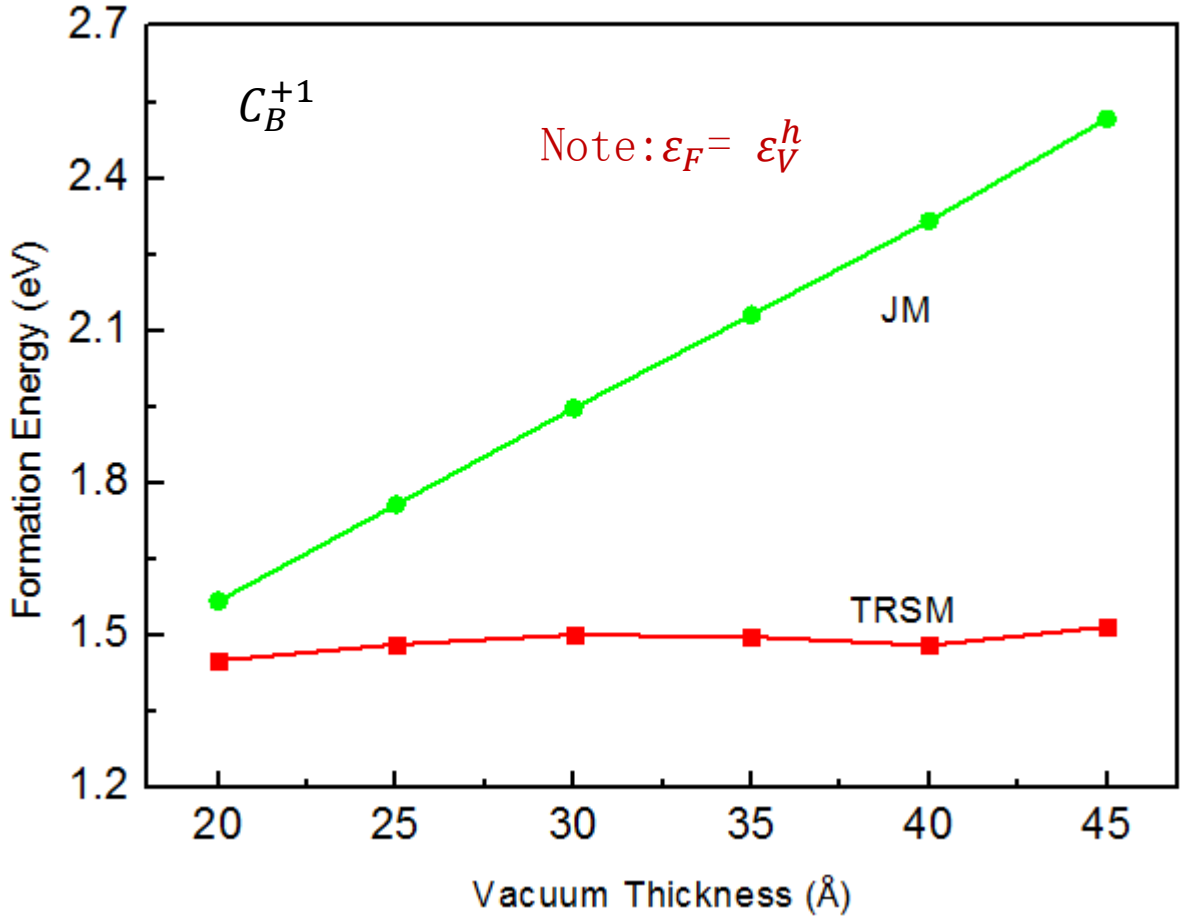
If $\varepsilon_F = \varepsilon_c^h$, $\Delta H_f = 5.8118 + 0.2668 = 6.0786$ eV

If $\varepsilon_F = \varepsilon_v^h$, $\Delta H_f = 5.8118 - 4.3688 = 1.4430$ eV

Note: $\boldsymbol{E_C}$ and $\boldsymbol{E_B}$ are the elemental energy of C and B, you can easily calculate from C and B stable element solid/gas.

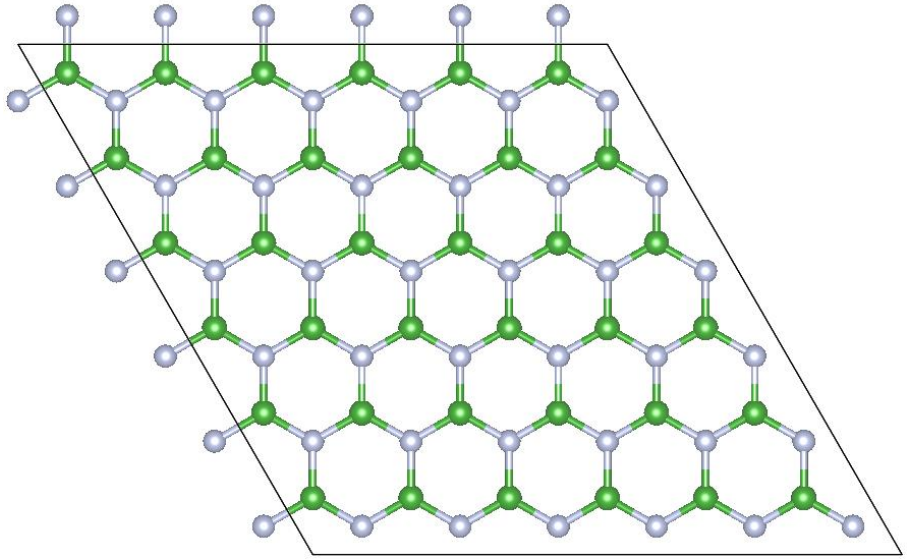
The fourth steps : Calculate the formation energy using TRSM

Change the vacuum thickness of the system, you can obtain the formation energy under different vacuum thickness.



Defect calculation example in 2D BN : C_N(q<0)

First steps:



SCF calculation for host structure

72 atoms in the supercell
Vacuum Thickness = 20 Å

etot.input

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

We can get $E(host)$, ε_c^{host} , ε_v^{host}
and real host CBM charge or real host VBM charge

To obtain real host VBM charge

(1) Run command “convert_wg2rho.x” in the host folder

(2) Enter as prompted

number of wave functions to construct

weight of functions

weight of kpoints

name of wave functions file

which wave function

(3) The result after running is as follows

```
[tianhongzhen@mstation:~/work/C-N/d-20/host]$convert_wg2rho.x
 input the number of wave functions to construct rho
1
 input the prefactor for           1 wavefunction
1.0
 the following is the inform for           1 th wavefunction
 there are            1  kpoints
 input the ikpt to plot wg
1
 input the name of WG file
OUT.WG
 there are          161 wavefunction, input ind im to plot
144
 charge(G-space)=    1.00000001690028
 charge(R-space)=    1.00000001690030
 the constructed rho is in OUT.WG2RHO
```

$E_{tot}(host)$	ε_c^h	ε_V^h
-12615.0847 eV	0.2658 eV	-4.3688 eV

```
------------------------------------------------------
ending_scf_reason = tol Rho_err   5.000000000000000E-005
Ewald          = 0.445646114044745E+05
Alpha          = 0.897049558240035E+02
E_extV         = 0.000000000000000E+00     0.0000E+00
E_NSC          = -.332072854547325E+04     -.3406E+00
E[-rho*V_Hxc]= -.105370172690805E+06     0.3404E+00
E_Hxc          = 0.514215001361325E+05     -.3060E+00
-TS            = -.615920046918525E-11     -.3031E-12
E_tot(eV)      = -.126150847398435E+05     -.2078E-03
E_tot(Ryd)     = -.927191634455571E+03     -.7635E-05
------------------------------------------------------
```

REPORT

141	-5.2796	2.00000
142	-5.2793	2.00000
143	-4.3688	2.00000
144	-4.3688	2.00000
145	0.2658	0.00000
146	0.3580	0.00000
147	0.3580	0.00000
148	0.4745	0.00000

OUT.OCC

Second steps:

```
4   1
in.atom          = atom.config
job              = relax
relax_detail     = 1 200 0.01 0 0.03
Ecut             = 60
NUM_ELECTRON     = 288
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

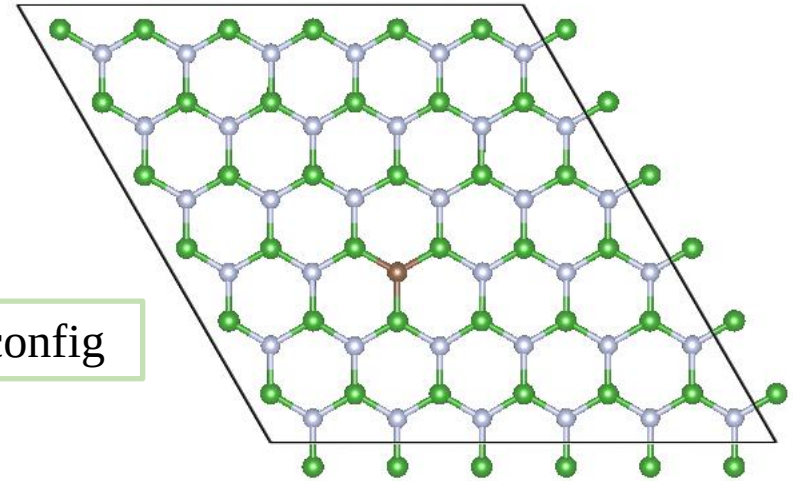
etot.input

Note:

(1) The total electrons number are 287 in neutral structure.

(2) We set NUM_ELECTRON=288 indicate that the total electrons number are 288 in charged structure, with a negative charge.

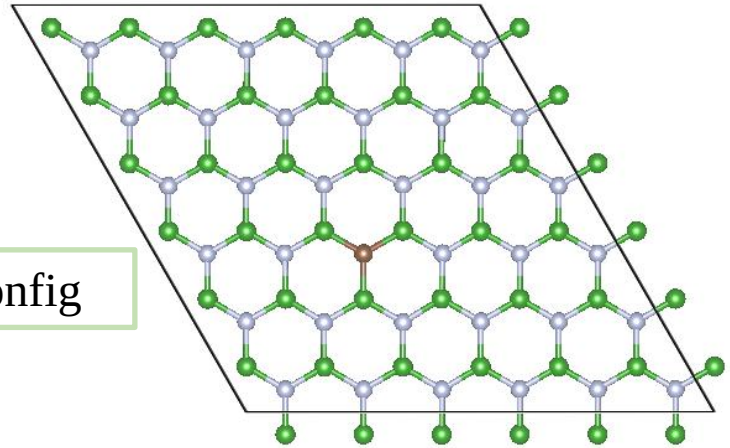
atom.config



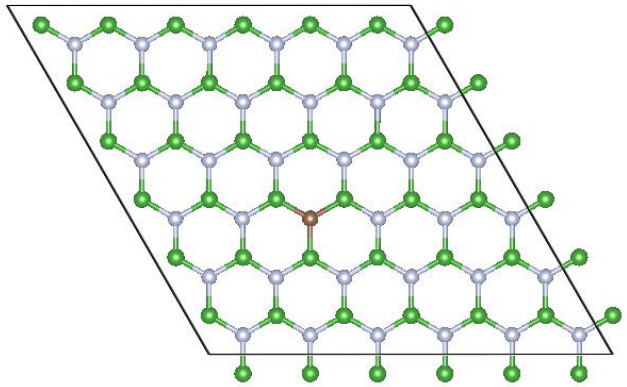
Charged defect structure before relaxation

We can get stable charged state structure

final.config



Third steps:



SCF calculation with second step final.config

To obtain IN.RHO_ADD file:

(1) Run convert_wg2rho.x in the host folder to obtain OUT.WG2RHO
(2) Copy OUT.WG2RHO to TRSM folder
(3) mv OUT.WG2RHO IN.RHO_ADD

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
in.rho_add       = T -1.0 143
in.occ=t
e_error=0.d0
```

etot.input

in.rho_add = T -1.0 143
T: read IN.RHO_ADD file
-1.0: charge state of defects
143:band index of VBM of the defect supercell
Note:We set in.rho_add indicate that the host's VBM charge is added. So the charge transitions from the real host VBM to defect state.

in.occ = t
t: read IN.OCC file, you must prepare it by yourself, the content just as following:

```
142*1.0 1*0.5 1*1 17*0.0
```

Note: one electron is excited from VBM to defect level.

Third steps:

Get $E_{tot}(q, \alpha, \varepsilon_V \rightarrow \varepsilon_D)$, ε_v

$E_{tot}(q, \alpha, \varepsilon_V \rightarrow \varepsilon_D)$	ε_V
-12493.9330 eV	-4.4119 eV

```
ending_scf_reason = tol Rho_err  5.0000000000000000E-005
Ewald          = 0.442704713243 77E+05
Alpha          = 0.887828430784 94E+02
E_extV         = 0.000000000000000E+00     0.0000E+00
E_NSC          = -.330463607892 04E+04     -.1200E+00
E[-rho*V_Hxc]= -.104585552992 17E+06     0.1198E+00
E_Hxc          = 0.510370365943 08E+05     -.1123E+00
-TS            = -.346573590279 97E-01     0.0000E+00
E_tot(eV)      = -.124939329666 83E+05     -.1684E-03
E_tot(Ryd)     = -.918287143293 66E+03     -.6188E-05
```

REPORT

```
  140      -4.6867    2.00000
  141      -4.6238    2.00000
  142      -4.6233    2.00000
  143      -4.4119    1.00000
  144      -2.8335    2.00000
  145       0.2025    0.00000
  146       0.2773    0.00000
  147       0.2774    0.00000
  148       0.3810    0.00000
```

The fourth steps : Calculate the formation energy using TRSM

$\boldsymbol{E_{tot}(host)}$	ε_C^h	ε_V^h
-12615.0847 eV	0.2658 eV	-4.3688 eV

$E_{tot}(q,\alpha,\varepsilon_V \rightarrow \varepsilon_D)$	$\boldsymbol{\varepsilon_V}$
-12493.9330 eV	-4.4119 eV

$\boldsymbol{E_N}$	$\boldsymbol{E_C}$
-270.7770eV	-155.1380 eV

$$\Delta H_f(q,\alpha,\varepsilon_F \rightarrow \varepsilon_D) = \Delta H_f\left(q,\alpha,\varepsilon_V^h \rightarrow \varepsilon_D\right) + q(\varepsilon_F - \varepsilon_V^h)$$

$$\Delta H_f\left(q,\alpha,\varepsilon_V^h - \varepsilon_D\right) = E_{tot}(q,\alpha,\varepsilon_V \rightarrow \varepsilon_D) - E_{tot}(host) + \sum_i n_i(E_i + \mu_i) - q(\varepsilon_V - \varepsilon_V^h)$$

$$\Delta H_f(q,\alpha,\varepsilon_F \rightarrow \varepsilon_D) = E_{tot}(q,\alpha,\varepsilon_V \rightarrow \varepsilon_D) - E_{tot}(host) + \boldsymbol{E_N} - \boldsymbol{E_C} + \varepsilon_V - \varepsilon_V^h - \varepsilon_F + \varepsilon_V^h$$

$$= \text{-12493.9330} - (\text{-12615.0847}) + (\text{-270.7770}) - (\text{-155.1380} + (\text{-4.4119}) - \varepsilon_F$$

$$= 1.1008 - \varepsilon_F$$

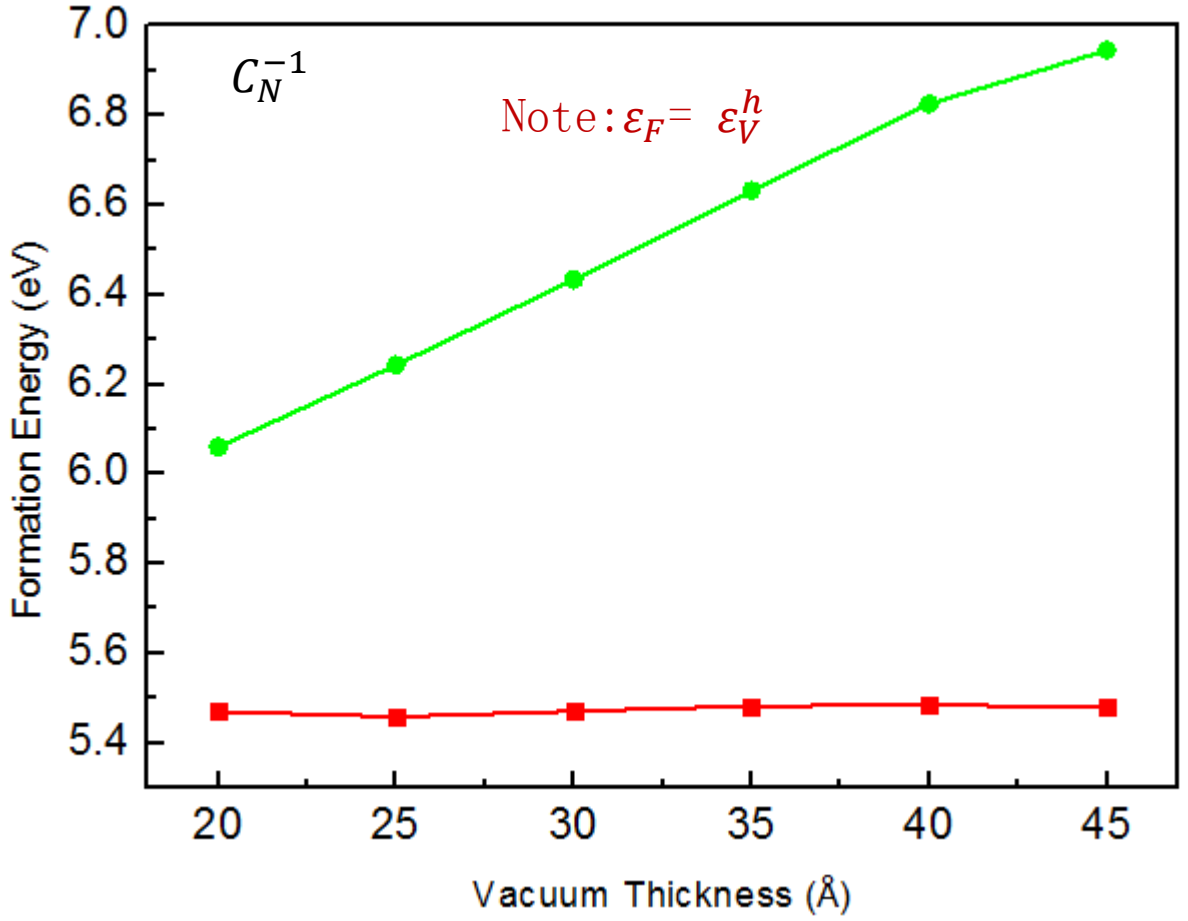
If $\varepsilon_F = \varepsilon_c^h$, ΔH_f = 1.1008 - 0.2668 = 0.8340 eV

If $\varepsilon_F = \varepsilon_v^h$, ΔH_f = 1.1008 – (-4.3688) = 5.4696 eV

Note:$\boldsymbol{E_C}$ and $\boldsymbol{E_N}$ are the elemental energy of C and B, you can easily calculate from C and B stable element solid/gas.

The fourth steps : Calculate the formation energy using TRSM

Change the vacuum thickness of the system, you can obtain the formation energy under different vacuum thickness.



Another method to calculate charged defect formation energy

- This method is based on the jellium model, in which the charge distribution of the removed or added electrons in the host band edge states which are approximated by a virtual “jellium” charge (i.e., uniform charge distribution over the whole supercell) with energy level equals ε_F.
- However, a direct employment of jellium model to 2D or other low dimensional systems (quantum dots, wires, etc.) encounters a serious problem manifested as the divergence of formation energies of the charged defects.
- An unavoidable “vacuum” region eads to a remarkable dissimilarity between a real charge put on host band-edge states and a virtual jellium charge.
- In order to settle the above problem, we can add a background charge to the charged defect system, it remarkably avoids the the divergence induced by the artificial long-range Coulomb energy of the jellium model. The background charge can be the real host CBM or VBM.

Formation energy formula for charged defects

- To calculate formation energy with this approach , the formula for a defect α in a charge state q is described as:

Donor (q>0)

$$\Delta H_f(\alpha,q) = E_{tot}(\alpha,q) + qE_{kin}^{C,h} - E_{tot}(host) + \sum_i n_i(E_i+\mu_i) + q\left(\varepsilon_C^h - \varepsilon_C\right) - q\left(\varepsilon_C^h - \varepsilon_F\right)$$

$E_{kin}^{C,h} = \varepsilon_C^h - V_{host}\rho^{C,h}$ (Note:$E_{kin}^{C,h}$ is not included in $E_{tot}(\alpha,q)$, so you need added to $E_{tot}(\alpha,q)$ by yourself.)

Acceptor (q<0)

$$\Delta H_f(\alpha,q) = E(\alpha,q) + qE_{kin}^{V,h} - E(host) + \sum_i n_i(E_i+\mu_i) - q\left(\varepsilon_V - \varepsilon_V^h\right) + q\left(\varepsilon_F - \varepsilon_V^h\right)$$

$E_{kin}^{V,h} = \varepsilon_V^h - V_{host}\rho^{V,h}$ (Note:$E_{kin}^{V,h}$ is not included in $E_{tot}(\alpha,q)$, so you need added to $E_{tot}(\alpha,q)$ by yourself.)

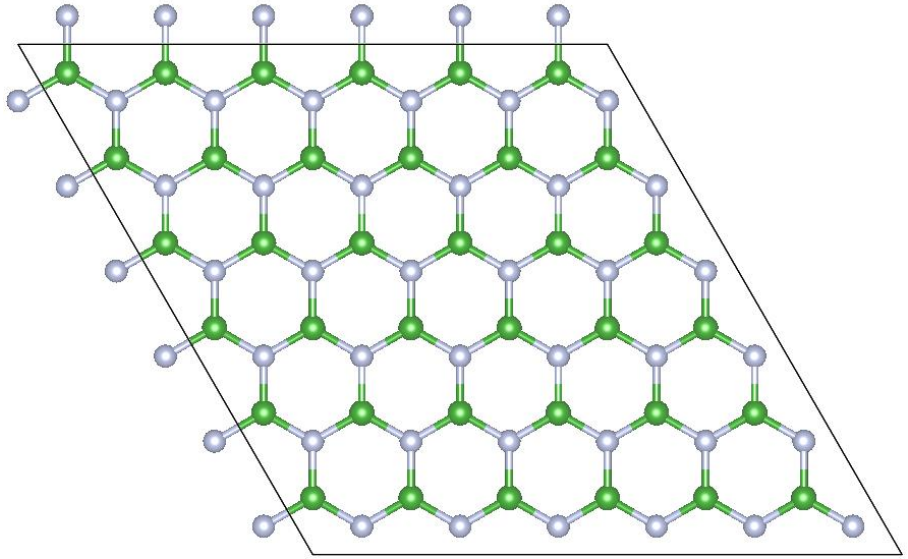
- $E_{tot}(host)$, ε_C^h, ε_V^h are the total energy, CBM, VBM of the supercell for perfect host crystal, respectively.
- $E_{tot}(q,\alpha), \varepsilon_C, \varepsilon_V$ are total energy, CBM, VBM of the supercell containing a defect α in a charge state q, respectively.
- μ_i is the chemical potential of constituent i referenced to elemental solid/gas with energy E_i.
- n_i is the number of elements removed from the host in creating the defect α.
- ε_F is the fermi energy.
- $E_{kin}^{C/V,h}$ is the kinetic energy of the host CBM or VBM
- $V_{host}\rho^{C/V,h}$ is the potential energy of host CBM or VBM

Four steps:

- ✓ SCF calculation for host structure to obtain total energy and real host CBM or VBM charge
- ✓Charged defect structure relaxation using jellium model to obtain stable charged state structure
- ✓SCF calculating for charged state structure to obtain charged state total energy, CBM or VBM
- ✓Calculate formation energy according to the above formula

Defect calculation example in 2D BN : C_B(q>0)

First steps:



SCF calculation for host structure

72 atoms in the supercell
Vacuum Thickness = 20 Å

etot.input

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

We can get $E_{tot}(host)$, $V_{host}\rho^{C,h}$, ε_c^h , ε_v^h and real host CBM charge

To obtain real host CBM charge

(1) Run convert_wg2rho.x in the host folder

(2) Enter as prompted

number of wave functions to construct

weight of functions

weight of kpoints

name of wave functions file

which wave function

(3) The result after running is as follows

```
[qiuchen@mstation host]$ convert_wg2rho.x
 input the number of wave functions to construct rho
1
 input the prefactor for            1 wavefunction
1
 the following is the inform for           1 th wavefunction
 there are            1  kpoints
 input the ikpt to plot wg
1
 input the name of WG file
OUT.WG
 there are          161 wavefunction, input ind im to plot
145
 charge(G-space)=   1.00000002730933
 charge(R-space)=   1.00000002730937
 the constructed rho is in OUT.WG2RHO
```

To obtain $V_{host}\rho^{C,h}$

(1) Run command convert_rho_multiply.x in host folder

(2) Enter as prompted

OUT.WG2RHO

OUT.VR

(3) The result after running is as follows

```
[qiuchen@mstation host]$ convert_rho_multiply.x
 input the name of rho file
OUT.WG2RHO
 Input the name of Vr
OUT.VR
 rho,rho*v(r)(eV)=   1.00000122163618       -4.48850635853885
```

$E_{tot}(host)$	$V_{host}\rho^{C,h}$	ε_C^h	ε_V^h
-12615.0847 eV	-4.4885 eV	0.2658 eV	-4.3688 eV

Second steps:

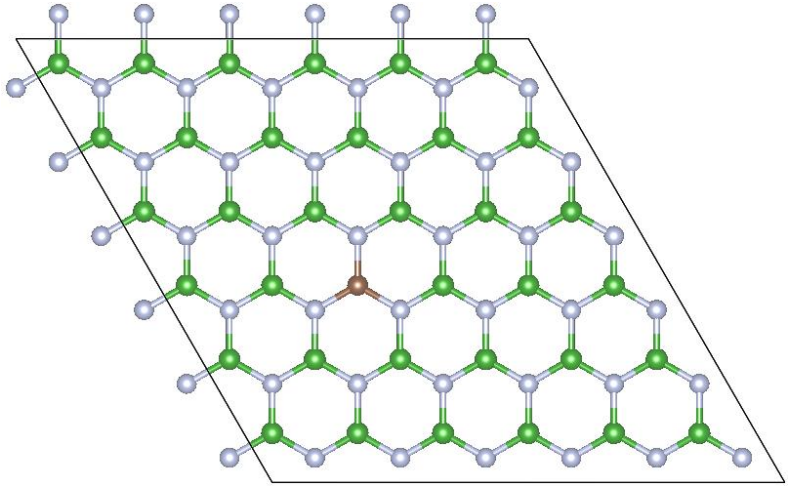
```
4   1
in.atom          = atom.config
job              = relax
relax_detail     = 1 200 0.01 0 0.03
Ecut             = 60
NUM_ELECTRON     = 288
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

etot.input

Note:

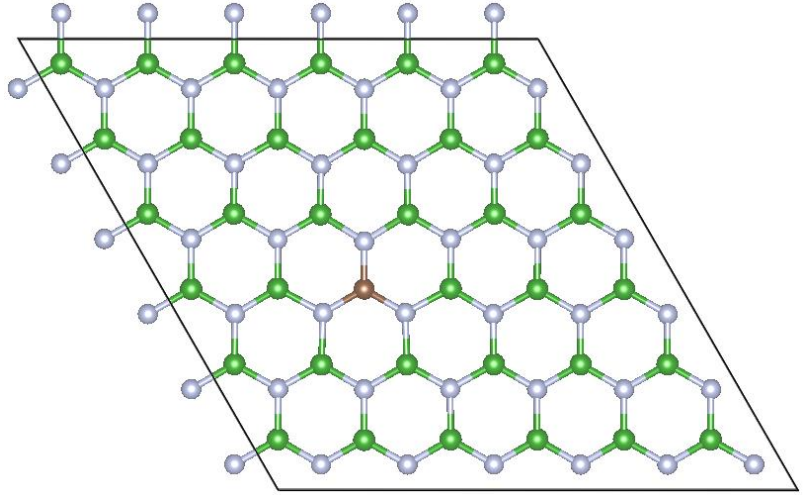
(1) The total electrons number are 289 in neutral structure.

(2) We set NUM_ELECTRON=288 indicate that the total electrons number are 288 in charged structure.

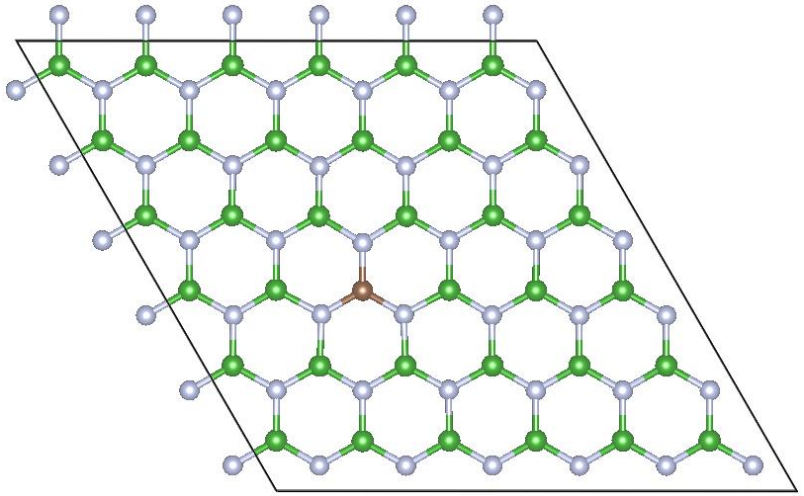


Charged defect structure before relaxation

We can get stable charged state structure



Third steps:



SCF calculation with second step final.config

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
in.rho_add       = T 1.0
NUM_ELECTRON     = 288
e_error          = 0.0
```

etot.input

in.rho_add = T 1.0
T: means read host CBM charge
1.0: is the number of defects charged

To obtain in.rho_add
(1) Run convert_wg2rho.x in the host folder to obtain OUT.WG2RHO
(2) Copy OUT.WG2RHO to TRSM folder
(3) mv OUT.WG2RHO IN.RHO_ADD

Note:
(1) The total electrons are 289 in neutral structure.
(2) We set NUM_ELECTRON=288 indicate that the charge on the defect was remaved one.
(3) We set in.rho_add indicate that the host's CBM charge is added.

$\boldsymbol{E_{tot}}(\alpha, q)$	ε_C
-12692.2035 eV	-0.3222 eV

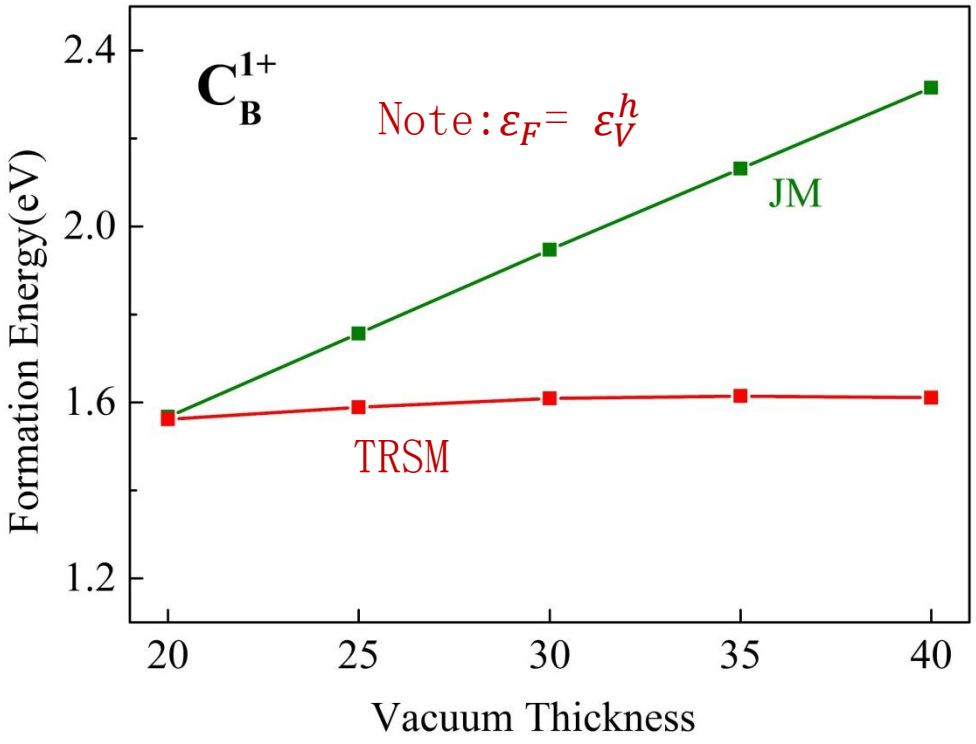
We can get $E_{tot}E(\alpha, q)$, ε_C

The fourth steps : Calculate the formation energy

$$\Delta H_f(\alpha, q) = E_{tot}(\alpha, q) + qE_{kin}^{C,h} - E_{tot}(host) + \sum_i n_i(E_i + \mu_i) + q\left(\varepsilon_C^h - \varepsilon_C\right) - q\left(\varepsilon_C^h - \varepsilon_F\right)$$

$$E_{kin}^{C,h} = \varepsilon_C^h - V_{host}\rho^{C,h}$$

Substituting the data calculated in the above three steps into the formula can be obtained
$\Delta H_f(\alpha, q)$ = 1.5613 eV

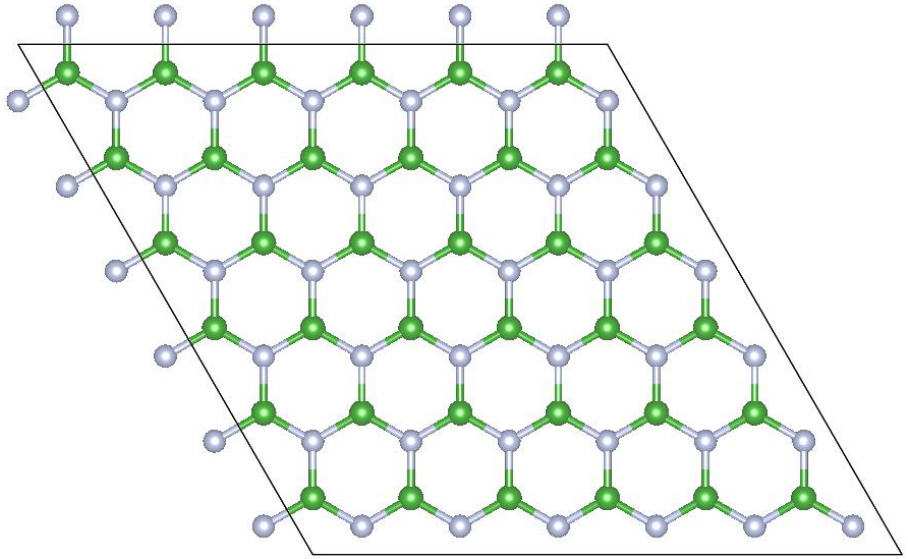


Change the vacuum thickness of the system, you can obtain the formation energy under different vacuum thickness.

As shown in Figure, one can see that TRSM results are convergent as the vacuum layer changes.

Defect calculation example in 2D BN : C_N(q<0)

First steps:



SCF calculation for host structure

72 atoms in the supercell
Vacuum Thickness = 20 Å

etot.input

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

We can get $E_{tot}(host)$, $V_{host}\rho^{C,h}$, ε_c^h , ε_v^h and real host CBM charge

To obtain real host VBM charge

(1) Run convert_wg2rho.x in the host folder

(2) Enter as prompted

number of wave functions to construct

weight of functions

weight of kpoints

name of wave functions file

which wave function

(3) The result after running is as follows

```
[tianhongzhen@mstation:~/work/C-N/d-20/host]$convert_wg2rho.x
 input the number of wave functions to construct rho
1
 input the prefactor for           1 wavefunction
1.0
 the following is the inform for          1 th wavefunction
 there are            1  kpoints
 input the ikpt to plot wg
1
 input the name of WG file
OUT.WG
 there are          161 wavefunction, input ind im to plot
144
 charge(G-space)=   1.00000001690028
 charge(R-space)=   1.00000001690030
 the constructed rho is in OUT.WG2RHO
```

To obtain $V_{host}\rho^{V,h}$

(1) Run command convert_rho_multiply.x in host folder

(2) Enter as prompted

OUT.WG2RHO

OUT.VR

(3) The result after running is as follows

```
[qiuchen@mstation host]$ convert_rho_multiply.x
 input the name of rho file
OUT.WG2RHO
 Input the name of Vr
OUT.VR
 rho,rho*v(r)(eV)=   1.00000122163618      -4.48850635853885
```

$E_{tot}(host)$	$V_{host}\rho^{C,h}$	ε_c^h	ε_v^h
-12615.0847 eV	- 41.5962 eV	0.2658 eV	-4.3688 eV

Second steps:

```
4   1
in.atom          = atom.config
job              = relax
relax_detail     = 1 200 0.01 0 0.03
Ecut             = 60
NUM_ELECTRON     = 288
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
e_error          = 0.0
```

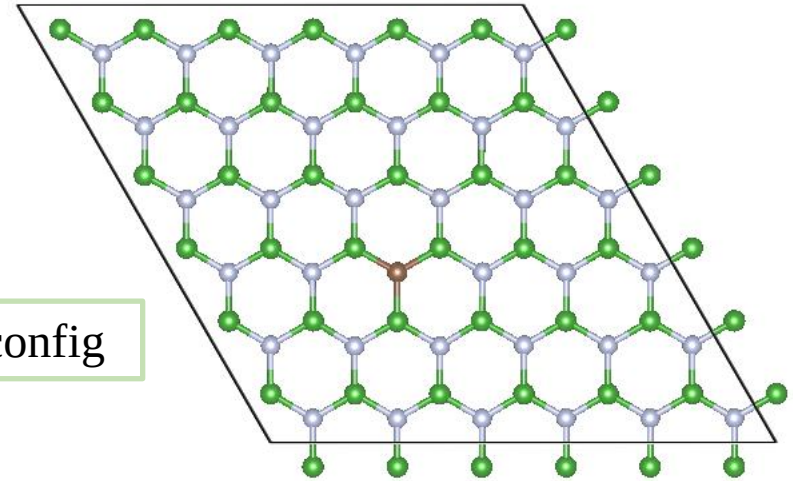
etot.input

Note:

(1) The total electrons number are 287 in neutral structure.

(2) We set NUM_ELECTRON=288 indicate that the total electrons number are 288 in charged structure, with a negative charge.

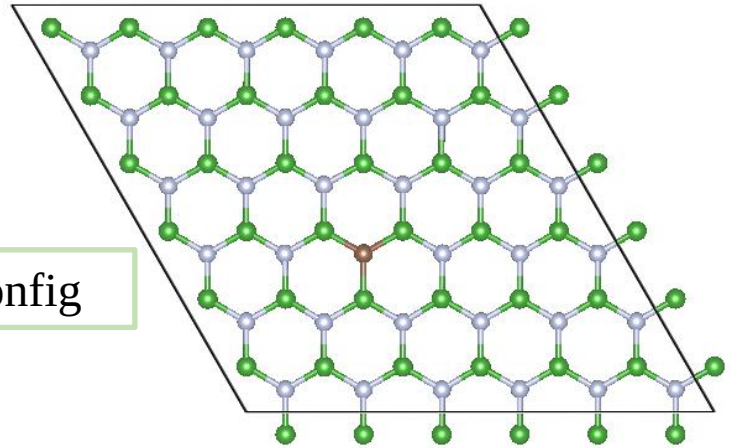
atom.config



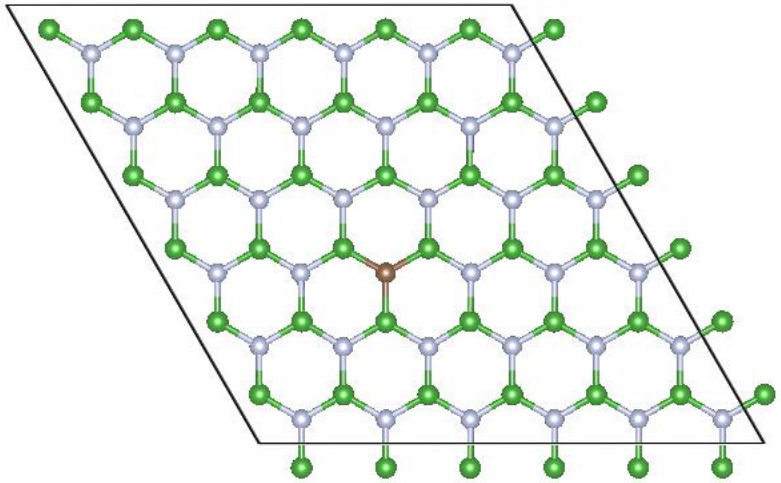
Charged defect structure before relaxation

We can get stable charged state structure

final.config



Third steps:



SCF calculation with second step final.config

```
4   1
in.atom          = atom.config
job              = scf
Ecut             = 60
in.psp1          = B.SG15.PBE.UPF
in.psp2          = C.SG15.PBE.UPF
in.psp3          = N.SG15.PBE.UPF
mp_n123          = 1 1 1 0 0 0
in.rho_add       = T 1.0
NUM_ELECTRON     = 288
e_error          = 0.0
```

etot.input

in.rho_add = T 1.0
T: means read host VBM charge
1.0: is the number of defects charged

To obtain in.rho_add
(1) Run convert_wg2rho.x in the host folder to obtain OUT.WG2RHO
(2) Copy OUT.WG2RHO to TRSM folder
(3) mv OUT.WG2RHO IN.RHO_ADD

Note:
(1) The total electrons are 287 in neutral structure.
(2) We set NUM_ELECTRON=288 indicate that the charge on the defect was remaved one.
(3) We set in.rho_add indicate that the host's CBM charge is added.

$E_{tot}(\alpha, q)$	ε_V
-12456.6543 eV	-4.4136 eV

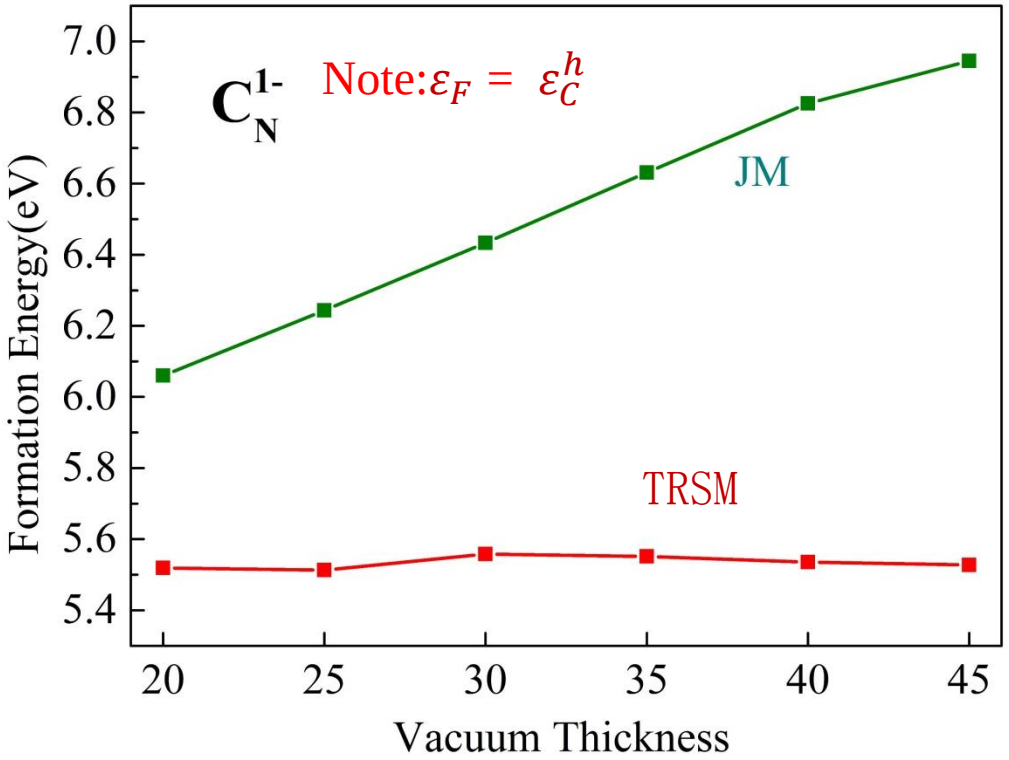
We can get $E_{tot}E(\alpha, q)$, ε_V

The fourth steps : Calculate the formation energy

$$\Delta H_f(\alpha, q) = E(\alpha, q) + qE_{kin}^{V,h} - E(host) + \sum_i n_i(E_i + \mu_i) - q\left(\varepsilon_V - \varepsilon_V^h\right) + q\left(\varepsilon_F - \varepsilon_V^h\right)$$

$$E_{kin}^{V,h} = \varepsilon_V^h - V_{host}\rho^{V,h}$$

Substituting the data calculated in the above three steps into the formula can be obtained
$\Delta H_f(\alpha, q)$ = 5.5191 eV



Change the vacuum thickness of the system, you can obtain the formation energy under different vacuum thickness.

As shown in Figure, one can see that TRSM results are convergent as the vacuum layer changes.