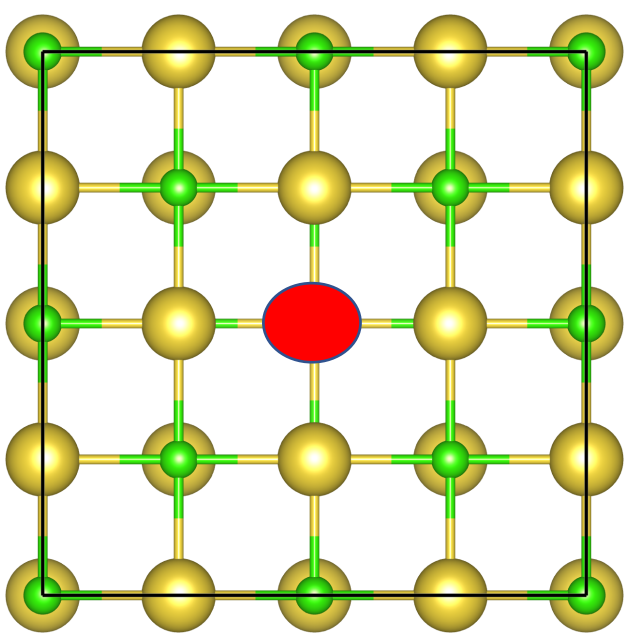
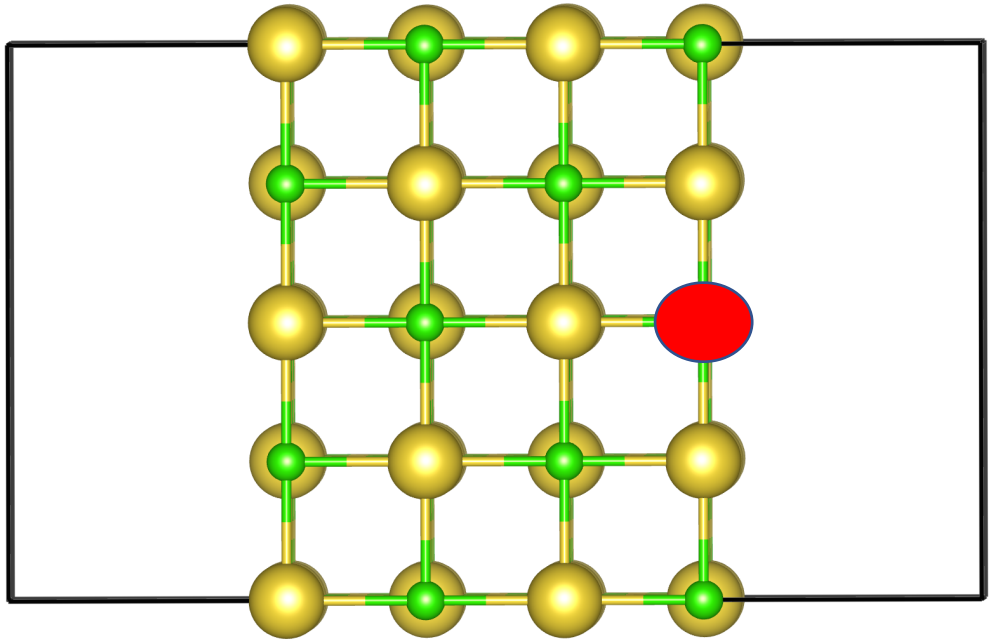
# Hands On

$V_{Cl}^{+}$ at NaCl surface

# POSCAR





# Formation Energy

$$E_f(V_{Cl}^{+}) = (E_{charged} + \mu_{cl}) - E_{pristine} + q\varepsilon_{VBM}$$

- $E_f(V_{Cl}^{+})$: it is the formation energy of the defect $V_{Cl}^{+}$.
- $E_{charged}$: it is the total energy of the charged system.
- $\mu_{Cl} \sim \left(\frac{1}{2}\right) E_{Cl2}$: it is the chemical potential of Cl atom (experimental or calculated).
- $E_{pristine}$: it is the total energy of the pristine system.
- q: the defect charge.
- $\varepsilon_{VBM}$: it is the valence band maximum energy.

# Formation Energy

$$E_f(V_{Cl}^{+}) = E_{charged} + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

- **Energy correction (FNV)**

FNV energy correction

$$E_f(V_{Cl}^{+}) = \left(E_{charged} + E_{cor}\right) + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

- **SCPC method**

Potential Alignment

$$E_f(V_{Cl}^{+}) = \left(E'_{charged} + q\Delta V\right) + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

SCPC total energy

# VCl+ Formation Energy

$$E_f(V_{Cl}^{+}) = E_{charged} + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

- ***CHARGED :*** ***the charged system calculation***
- ***Check.bash*** ***: a bash script to check the final calculations***
- ***Cl2:*** ***the calculation for the chemical potential***
- ***FNV :*** ***the Freysoldt energy correction***
- ***NEUTRAL :*** ***the neutral defect system calculation (for reference only)***
- ***PRISTINE :*** ***the pristine system (formation energy + reference)***
- ***SCPC-1 :*** ***the SCPC method using the neutral defect as reference***
- ***SCPC-2 :*** ***the SCPC method using the pristine system as reference***

Run the default VASP for the folders

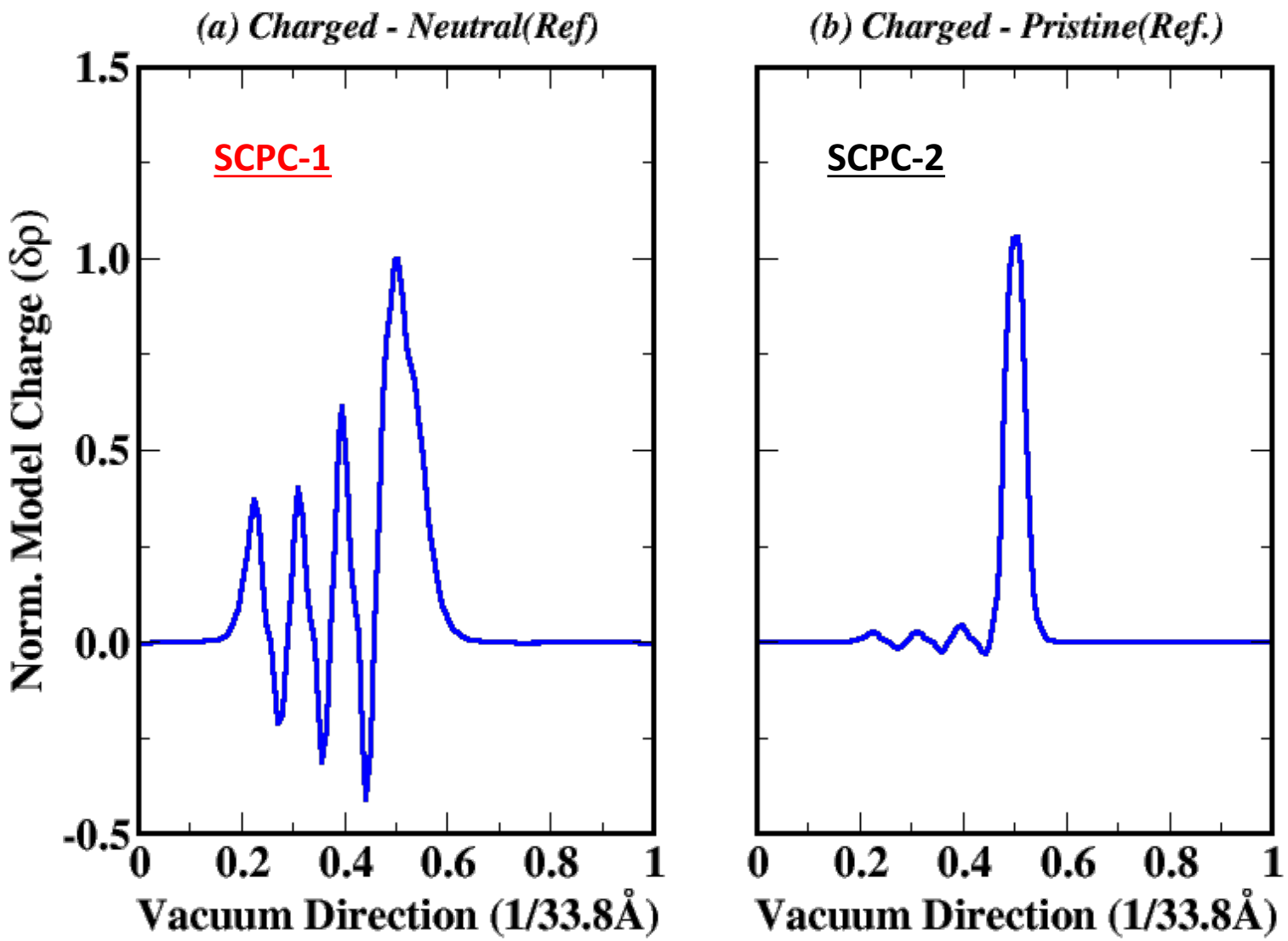
***CHARGED :*** ***the charged system calculation***

***Cl2:*** ***the calculation for the chemical potential***

***NEUTRAL :*** ***the neutral defect system calculation (for reference only)***

***PRISTINE :*** ***the pristine system (formation energy + reference)***

# Model Charge - Reference System



## SCPC-1 (neutral system as reference)

- ***From NEUTRAL:*** copy the CHGCAR to REFCHG and LOCPOT to REFPOT files into the SCPC-1 folder
- ***From the converged CHARGED:*** copy the CHGCAR to CHGCAR and the WAVECAR to WAVECAR into the SCPC-1 folder
- ***Inside the SCPC-1 folder:***

| | |
|---|---|
| **INCAR** | **CHGCAR → from charged calc.** |
| **KPOINTS** | **WAVECAR → from charged calc.** |
| **POSCAR** | **REFCHG → from neutral CHGCAR** |
| **POTCAR** | **REFPOT → from neutral LOCPOT** |

# SCPC-1 (neutral system as reference)

## INCAR

```
# Initial Guess
  ISTART = 1 ; restart
  ICHARG = 1 ; charge read


 # self-consistent charge-potential correction
   DOVCOR   = T    ; run SCPC
   INVCOR   = 1    ; start in 1st iter.
   VCQTOT   = 1.0  ; defect charge (formal charge)
   VCZLOW   = 0.22 ; interface
   VCZHIG   = 0.53 ; interface
   VCDIEL   = 2.46 ; dielectric
   VCBROAD  = 0.40 ; broadning
```

## Charged uncorrected

```
free energy    TOTEN  =      -476.08786254 eV
free energy    TOTEN  =      -476.50089403 eV
free energy    TOTEN  =      -476.79910181 eV
free energy    TOTEN  =      -477.45963458 eV
free energy    TOTEN  =      -477.75583803 eV
free energy    TOTEN  =      -477.87531303 eV
free energy    TOTEN  =      -477.93211822 eV
free energy    TOTEN  =      -477.96335990 eV
free energy    TOTEN  =      -477.97299642 eV
free energy    TOTEN  =      -477.97555935 eV
free energy    TOTEN  =      -477.97818700 eV
free energy    TOTEN  =      -477.97906335 eV
free energy    TOTEN  =      -477.97933184 eV
free energy    TOTEN  =      -477.97952972 eV
free energy    TOTEN  =      -477.97969115 eV
free energy    TOTEN  =      -477.97971030 eV
free  energy   TOTEN  =      -477.97971030 eV
```

$E_{chg}$

## SCPC-1

$E^{1}_{SCPC-1}$

```
free energy    TOTEN  =      -477.80213469 eV
free energy    TOTEN  =      -477.80739658 eV
free energy    TOTEN  =      -477.81112623 eV
free energy    TOTEN  =      -477.81939857 eV
free energy    TOTEN  =      -477.81855768 eV
free energy    TOTEN  =      -477.81884042 eV
free energy    TOTEN  =      -477.81540833 eV
free energy    TOTEN  =      -477.81004213 eV
free energy    TOTEN  =      -477.81160178 eV
free energy    TOTEN  =      -477.81291841 eV
free energy    TOTEN  =      -477.81127037 eV
free energy    TOTEN  =      -477.81058322 eV
free energy    TOTEN  =      -477.81040836 eV
free energy    TOTEN  =      -477.81016729 eV
free energy    TOTEN  =      -477.80998014 eV
free energy    TOTEN  =      -477.80994540 eV
free  energy   TOTEN  =      -477.80994540 eV
```

$E^{N}_{SCPC-1}$

$$\Delta_1 E = E^{1}_{SCPC-1} - E_{chg} = 0.18\ eV$$

$$\Delta_N E = E^{N}_{SCPC-1} - E_{chg} = 0.17\ eV$$

- Small effect of the SCF to the total correction.
- Localize defect characteristic.

➢ **Energy correction (FNV)**

FNV energy correction

$$E_f(V_{Cl}^{+}) = \left(E_{charged} + E_{cor}\right) + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

CHARGED Cl2 NEUTRAL README.txt SCPC-1
Check.bash FNV PRISTINE SAVE SCPC-2

%cd FNV
%ls *

0.LOCPOT 1.LOCPOT FNV_Run.bash **system.sx**

Potentials | Script to run the method | FNV input

% vi ALIGNED.txt

Q=-1
--- Isolated
---
isolated energy = 3.97451990852 eV
periodic energy = 3.28943422032 eV
iso - periodic energy = 0.685085688205 eV

**$E_{cor}$**

➢ **SCPC-1 corrections**

$$E_f(V_{Cl}^{+}) = \left(E_{SCPC-1} + qV_{alig}\right) + \mu_{cl} - E_{pristine} + q\varepsilon_{VBM}$$

```
free energy    TOTEN  =      -477.80213469 eV
free energy    TOTEN  =      -477.80739658 eV
free energy    TOTEN  =      -477.81112623 eV
free energy    TOTEN  =      -477.81939857 eV
free energy    TOTEN  =      -477.81855768 eV
free energy    TOTEN  =      -477.81884042 eV
free energy    TOTEN  =      -477.81540833 eV
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free energy    TOTEN  =      -477.81058322 eV
free energy    TOTEN  =      -477.81040836 eV
free energy    TOTEN  =      -477.81016729 eV
free energy    TOTEN  =      -477.80998014 eV
free energy    TOTEN  =      -477.80994540 eV
free  energy   TOTEN  =      -477.80994540 eV
```

```
<<<< SCPC Cycle:   17 >>>>

Potential Alignment (X,Y,Z): 0.030583
```

# Checking the Calculation (Check.bash)

**%Check.bash 1**

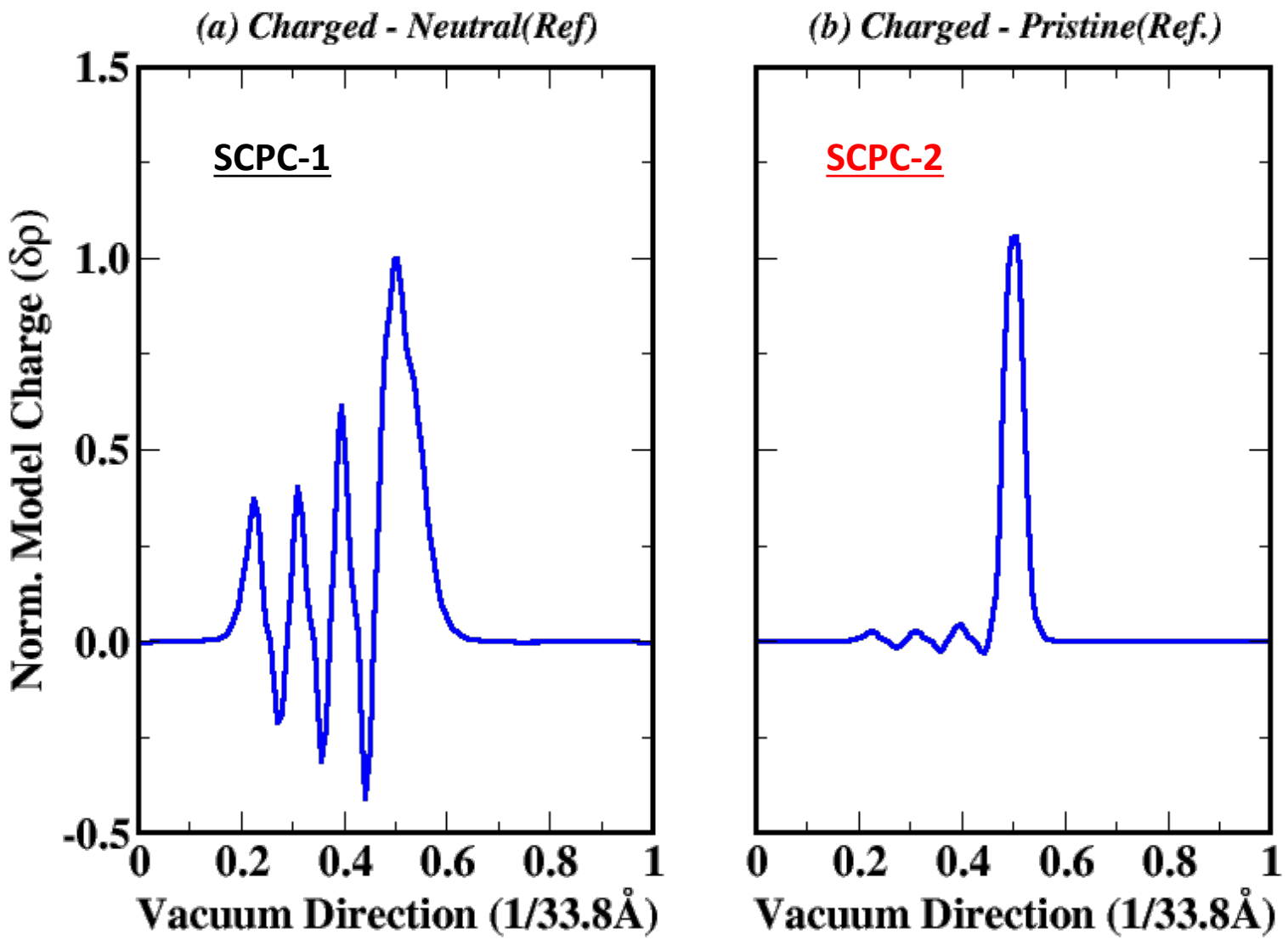
**** Reference System set to NEUTRAL DEFECT ****

<<<< VCl(+) Formation Energy (eV) >>>>

| | | |
|---|---|---|
| Plain Calculation | : | 1.64 |
| Energy Correc. (FNV Method) | : | 2.08 |
| Self-cons. Pot Correc. | : | 1.84 |

- SCPC-1 is not closer to the FNV correction results.
- SCPC-1 uses NEUTRAL as reference but FNV uses PRISTINE as reference
- The difference here comes from the SCF procedure and charge model

# Using Another Reference



## SCPC-2 (pristine system as reference)

- ***From PRISTINE:*** copy the CHGCAR➔ REFCHG and LOCPOT➔ REFPOT files into the SCPC-1 folder
- ***From the converged CHARGED:*** copy the CHGCAR➔ CHGCAR and the WAVECAR ➔ WAVECAR into the SCPC-1 folder
- ***Inside the SCPC-2 folder:***

| | |
|---|---|
| **INCAR** | **CHGCAR ➔ from charged calc.** |
| **KPOINTS** | **WAVECAR ➔ from charged calc.** |
| **POSCAR** | **REFCHG ➔ from pristine CHGCAR** |
| **POTCAR** | **REFPOT ➔ from pristine LOCPOT** |

# SCPC-2 (pristine system as reference)

## INCAR

```
# Initial Guess
  ISTART = 1 ; restart
  ICHARG = 1 ; charge read
```

- INCAR is similar to SCPC-1, the reference is controlled by **REFCHG** and **REFPOT**

```
# self-consistent charge-potential correction
  DOVCOR   = T    ; run SCPC
  INVCOR   = 1    ; start in 1st iter.
  VCQTOT   = 1.0  ; defect charge (formal charge)
  VCZLOW   = 0.22 ; interface
  VCZHIG   = 0.53 ; interface
  VCDIEL   = 2.46 ; dielectric
  VCBROAD  = 0.40 ; broadning
```

# Checking the Calculation (Check.bash)

**%Check.bash 2**

```
**** Reference System set to PRISTINE ****

 <<<< VCl(+) Formation Energy (eV) >>>>

 Plain Calculation            :   1.64
 Energy Correc. (FNV Method)  :   2.08
 Self-cons. Pot Correc.       :   1.94
```

SCPC-1 1.84 eV
Neutral as Ref.

- SCPC-2 is closer to the FNV correction results.
- SCPC-2 and FNV use PRISTINE as reference
- The difference here comes from the SCF procedure

# Checking the Calculation (Check.bash)

**%Check.bash 2**

```
**** Reference System set to PRISTINE ****

 <<<< VCl(+) Formation Energy (eV) >>>>

 Plain Calculation            :   1.64
 Energy Correc. (FNV Method)  :   2.08
 Self-cons. Pot Correc.       :   1.94
```