Example Calculations of CP-VASP

Table of contents

All the following examples are for a 3x3x1 super cell of Pt(111), expect for the grand-canonical MD case which uses a unit cell of Pt(100). We have supplied the INCAR, POSCAR, and KPOINTS files.

Fixed Structure:

INCAR:

```
#  General VASP parameters
  ISTART = 0
  ENCUT = 400
  ISPIN = 1
  ISMEAR = 1
  SIGMA = 0.2
  ALGO = Normal
  ISYM = 0
  LREAL = Auto
  LWAVE = .FALSE.
  LCHARG = .FALSE.

  NSW = 0
  NELM = 120
  POTIM = 0.5
  IBRION = -1
  EDIFF = 1E-6

#  VASPsol++ Solvent Model - This corresponds to water
  LSOL = .TRUE.
  ISOL = 2
  C_MOLAR = 1.0
  R_ION = 4.0

#  CP-VASP Parameters
  LCEP = .TRUE.
  NESCHEME = 1
  CAP_MAX = 2.0
  TARGETMU = -4.57
  FERMICONVERGE = 0.01
###########
```

POSCAR:

```
slab-pt111
1.0
      8.4899997711      0.0000000000      0.0000000000
      4.2449998856      7.3525554799      0.0000000000
```

0.0000000000 0.0000000000 25.0000000000
Pt
27
Direct
0.000000000 0.000000000 0.080872335
0.000000000 0.333333343 0.080872335
0.000000000 0.666666687 0.080872335
0.333333343 0.000000000 0.080872335
0.333333313 0.333333343 0.080872335
0.333333313 0.666666687 0.080872335
0.666666687 0.000000000 0.080872335
0.666666687 0.333333343 0.080872335
0.666666627 0.666666687 0.080872335
0.111111112 0.111111112 0.172000006
0.111111112 0.444444448 0.172000006
0.111111119 0.777777791 0.172000006
0.444444448 0.111111112 0.172000006
0.444444448 0.444444448 0.172000006
0.444444448 0.777777791 0.172000006
0.777777791 0.111111112 0.172000006
0.777777791 0.444444448 0.172000006
0.777777791 0.777777791 0.172000006
0.222222224 0.222222224 0.263127685
0.222222224 0.555555582 0.263127685
0.222222224 0.888888896 0.263127685
0.555555582 0.222222224 0.263127685
0.555555642 0.555555582 0.263127685
0.555555522 0.888888896 0.263127685
0.888888896 0.222222224 0.263127685
0.888888896 0.555555582 0.263127685
0.888888896 0.888888896 0.263127685

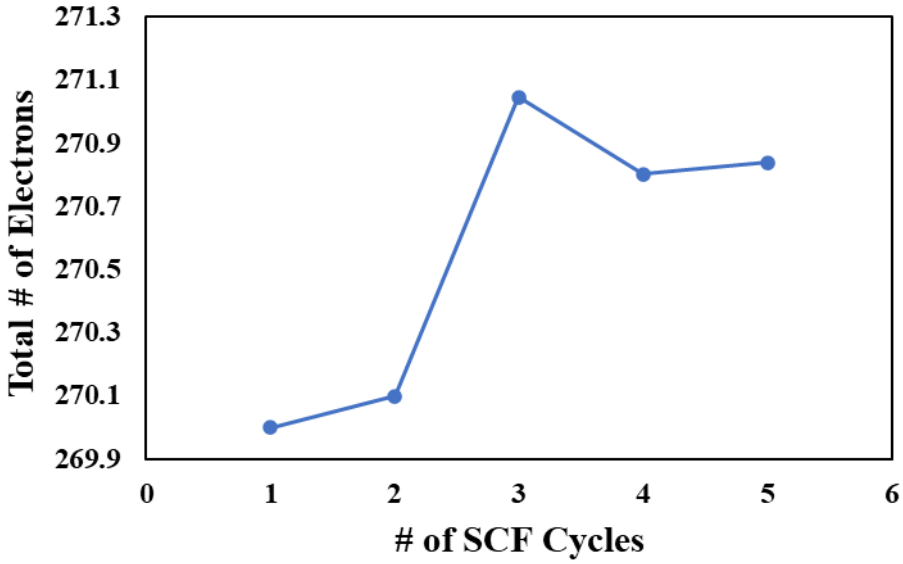
KPOINTS:

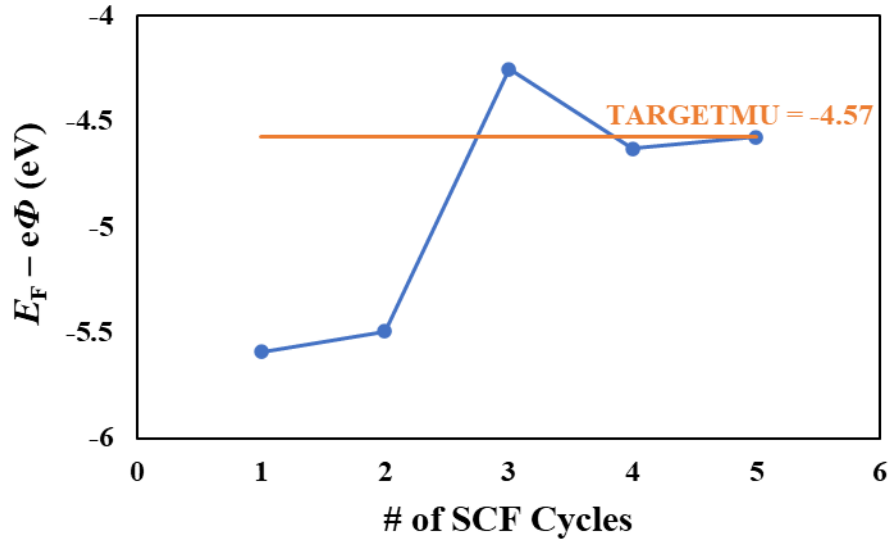
K-Points
0
M
7 7 1

Analysis:

These plots depict the change in the number of electrons and the electrolyte-referenced Fermi level (E_F – eΦ), which is related to the interfacial potential by Eq.

1 in the manual. The last printout occurs at the end of an ionic step when the target potential is reached.





Ionic Relaxation:

INCAR:

 # General VASP parameters
ISTART = 0
ENCUT = 400
ISPIN = 1

ISMEAR = 1
SIGMA = 0.2
ALGO = Normal
ISYM = 0
LREAL = Auto
LWAVE = .FALSE.
LCHARG = .FALSE.

NSW = 200
NELM = 120
IBRION = 2
EDIFFG = -0.01
EDIFF = 1E-6

 # VASPsol++ Solvent Model - This corresponds to water
LSOL = .TRUE.
ISOL = 2
C_MOLAR = 1.0
R_ION = 4.0

 # CP-VASP Parameters
LCEP = .TRUE.
NESCHEME = 2
CAP_MAX = 2.0
TARGETMU = -4.57
FERMICONVERGE = 0.01
############

POSCAR:

slab-pt111
1.0
8.4899997711 0.0000000000 0.0000000000
4.2449998856 7.3525554799 0.0000000000
0.0000000000 0.0000000000 25.0000000000
Pt
27
Direct
0.006663528 0.997492492 0.082663290
0.000521697 0.336543232 0.080099314
0.005466287 0.664497674 0.079137705
0.333856165 0.998869538 0.077634916
0.334888101 0.324505597 0.079542175
0.334581316 0.658504605 0.086563498
0.667036951 0.005466488 0.073986299

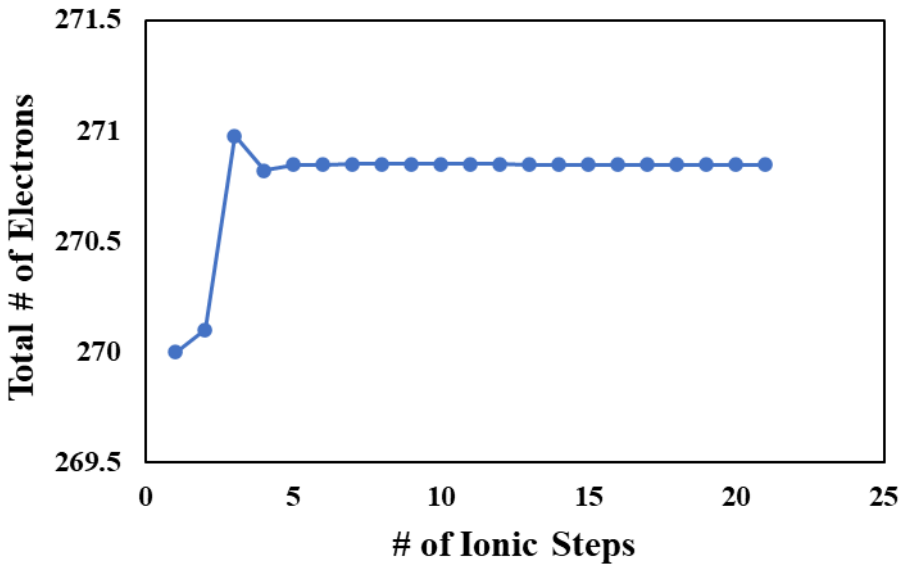
0.669289172 0.338651121 0.087669782
0.667903304 0.662064791 0.079864971
0.119142771 0.107272796 0.169080883
0.110557854 0.452726841 0.168670118
0.102894939 0.774473071 0.173215792
0.445798576 0.116315737 0.169163182
0.442165822 0.439048529 0.174396932
0.437628865 0.770166159 0.168667227
0.774587274 0.105807371 0.174271643
0.783584952 0.436009407 0.173507273
0.785915554 0.771487415 0.172938839
0.222130090 0.225648865 0.257908911
0.213626161 0.562005401 0.268385768
0.220870987 0.888177812 0.261690706
0.557420194 0.219741940 0.256159335
0.555504680 0.563429475 0.260394722
0.550366044 0.886049271 0.265101939
0.878893554 0.214194626 0.264638543
0.887896359 0.557410359 0.270572752
0.888455927 0.885109484 0.262081265

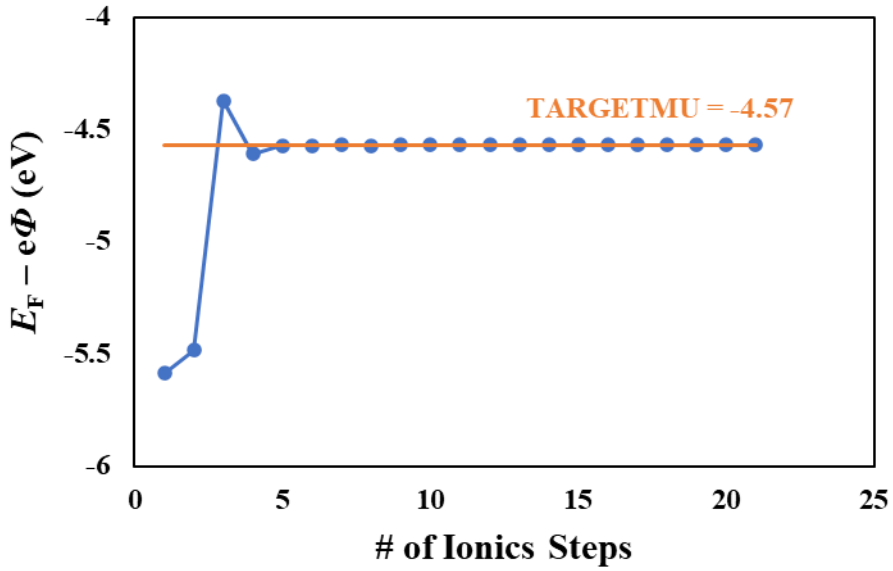
KPOINTS:

K-Points
0
M
7 7 1

Analysis:

These plots depict the change in the number of electrons and the electrolyte-referenced Fermi level with the number ionic steps. The single-SCF algorithm allows the structure to evolve before converging the interfacial potential, which leads to an overestimation in the electron number at the third step. The algorithm quickly corrects this and reaches the target potential. As we are only interested in the final structure for ionic relaxation calculations, we can conclude the relaxation was successful.





Molecular Dynamics, Exact Potential:

INCAR:

 # General VASP parameters
ISTART = 0
ENCUT = 400
ISPIN = 1
ISMEAR = 1
SIGMA = 0.2
ALGO = Normal

ISYM = 0
LREAL = Auto
LWAVE = .FALSE.
LCHARG = .FALSE.

NSW = 200
NELM = 120
POTIM = 1.0
IBRION = 0
EDIFF = 1E-6

 # MD Parameters
MDALGO = 2
SMASS = 0
TEBEG = 300 ; TEEND = 300

 # VASPsol++ Solvent Model - This corresponds to water
LSOL = .TRUE.
ISOL = 2
C_MOLAR = 1.0
R_ION = 4.0

 # CP-VASP Parameters
LCEP = .TRUE.
NESCHEME = 2
CAP_MAX = 2.0
NEADJUST = 5
TARGETMU = -4.57
FERMICONVERGE = 0.01
###########

POSCAR:

slab-pt111
1.0
8.4899997711 0.0000000000 0.0000000000
4.2449998856 7.3525554799 0.0000000000
0.0000000000 0.0000000000 25.0000000000
Pt
27
Direct
0.001762321 0.998047650 0.080491915
0.001887487 0.331347734 0.080466107
0.001813437 0.664667308 0.080472529
0.335080028 0.998123407 0.080473177

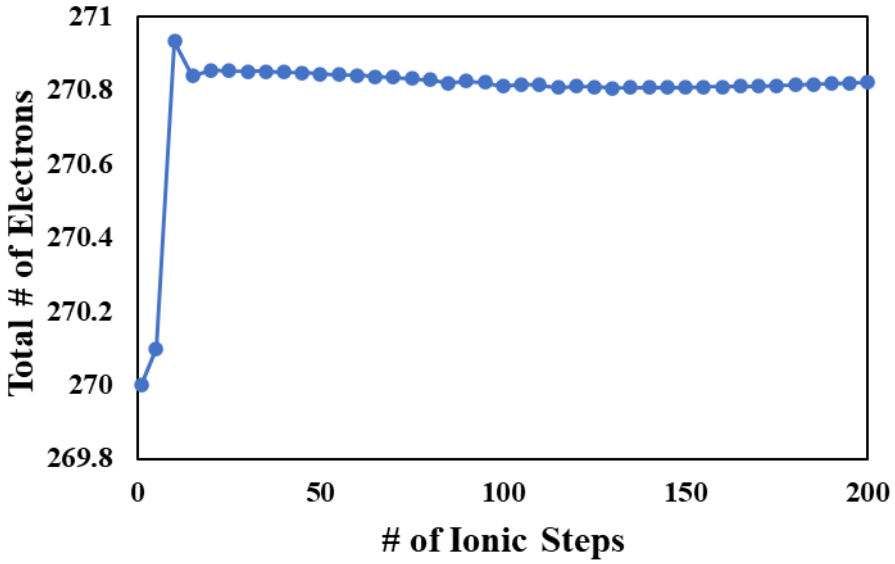
0.335131705 0.331413895 0.080480568
0.335153550 0.664781034 0.080469668
0.668451726 0.998044491 0.080477387
0.668481946 0.331455767 0.080472335
0.668559313 0.664692283 0.080480225
0.110985793 0.109551027 0.171785563
0.111008994 0.442953557 0.171790078
0.110996664 0.776247025 0.171779588
0.444282383 0.109575853 0.171783373
0.444260418 0.442963362 0.171769798
0.444367290 0.776289523 0.171737522
0.777635515 0.109633319 0.171790898
0.777793884 0.442909002 0.171796143
0.777669430 0.776287138 0.171781719
0.220234841 0.221408457 0.263072968
0.220300481 0.554729819 0.263103038
0.220258161 0.888045967 0.263084829
0.553577840 0.221359968 0.263051420
0.553608060 0.554722667 0.275039881
0.553578556 0.888020337 0.263091862
0.886944354 0.221427798 0.263090938
0.886895120 0.554858267 0.263104260
0.886927843 0.888113618 0.263070077

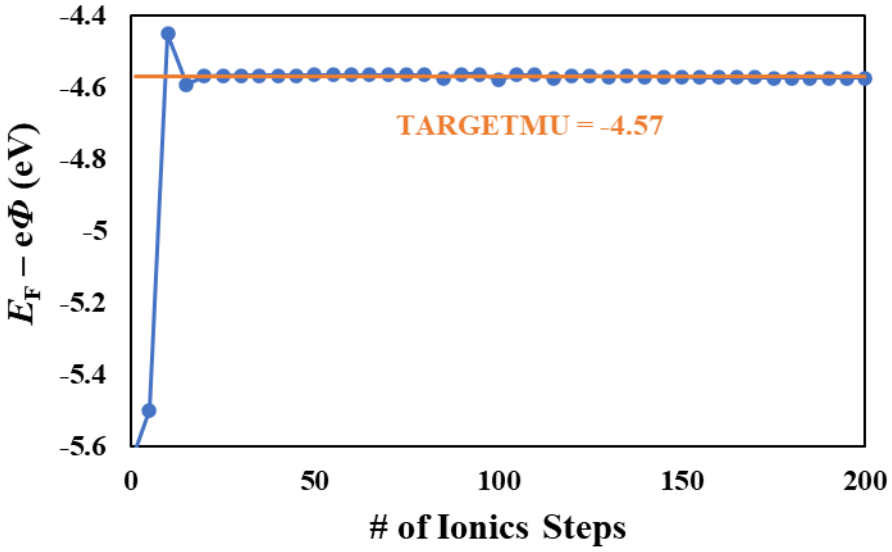
KPOINTS:

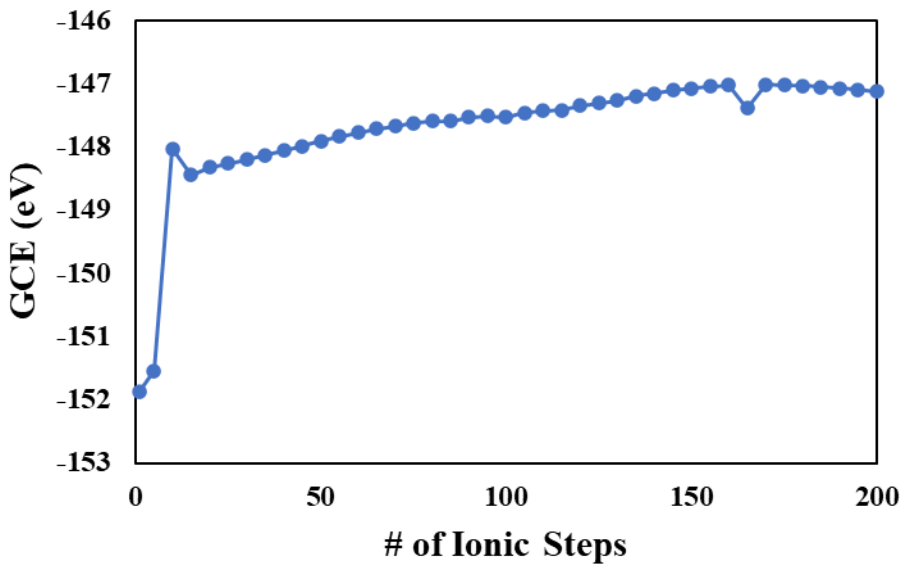
K-Points
0
M
7 7 1

Analysis:

These plots depict the change in the number of electrons, the electrolyte-referenced Fermi level, and the grand canonical energy (GCE) with the number of ionic steps. Because we set NEADJUST = 5, the electron number is only adjusted every 5 steps. Consequently, the electronic information is only printed every 5 steps. The initial jump in the GCE is due to the potentiostat reaching convergence with the single-SCF algorithm. The steady increase in the GCE overtime is due to the sluggish dynamics of the Pt system, as Pt has a high mass and the interatomic vibrations have large periods. The GCE would begin to drop if the simulation were continued over additional ionic steps. Performing MD without the constant-potential condition will yield a similar behavior.


271
270.8
270.6
270.4
270.2
270
269.8
Total # of Electrons
0
50
100
150
200
# of Ionic Steps


-4.4
-4.6
-4.8
-5
-5.2
-5.4
-5.6
$E_F - e\Phi$ (eV)
TARGETMU = -4.57
0
50
100
150
200
# of Ionics Steps



Molecular Dynamics, Grand-Canonical:

INCAR:

 # General VASP parameters
ISTART = 0
ENCUT = 400
ISPIN = 1
ISMEAR = 1
SIGMA = 0.2
ALGO = Fast
ISYM = 0
LREAL = .FALSE.
LWAVE = .FALSE.
LCHARG = .FALSE.

NSW = 200
NELM = 120
POTIM = 1.0
IBRION = 0
EDIFF = 1E-6

 # MD Parameters
MDALGO = 2
SMASS = 0
TEBEG = 300 ; TEEND = 300

```
#  VASPsol++ Solvent Model - This corresponds to water
  LSOL = .TRUE.
  ISOL = 2
  C_MOLAR = 1.0
  R_ION = 4.0

#  CP-VASP Parameters
   LCEP = .TRUE.
   NESCHEME = 5
   NEADJUST = 1
   TARGETMU = -4.57
   T_eta = 300
   eta_length = 1
############
```

POSCAR:

```
slab-pt100
1.0
       2.7882300000      0.0000000000      0.0000000000
       0.0000000000      2.7882300000      0.0000000000
       0.0000000000      0.0000000000     35.0000000000
   Pt
    3
Cartesian
     0.000000000      0.000000000      1.000000000
     1.394115000      1.394115000      2.971575000
     0.000000000      0.000000000      4.943150000
```

KPOINTS:

```
K-Points
 0
M
 13 13 1
```

Analysis:

These plots depict the change in the number of electrons and the electrolyte-referenced Fermi level with the number of ionic steps. Unlike the previous examples where the Fermi level is aggressively tuned to the target potential, the electron number is allowed to fluctuate so that the grand-canonical ensemble is correctly

sampled. The behavior of these fluctuations is highly sensitive to the input parameters and may require tuning when simulating new systems.