Example Calculations of CP-VASP

All the following examples are for a 3x3x1 super cell of Pt(111). 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
  EDIFFG = -0.01
  EDIFF = 1E-6

  KPAR = 3

#  VASPsol Solvent Model - This corresponds to water
  LSOL = .TRUE.
  EB_K = 80
  LAMBDA_D_K = 3.0

#  CP-VASP Parameters
  LCEP = .TRUE.
  NESCHEME = 1
  CAP_MAX = 2.0
  TARGETMU = -4.6
  FERMICONVERGE = 0.01
############
```

POSCAR:

```
slab-pt111
```

1.0

8.4899997711	*0.0000000000*	*0.0000000000*
4.2449998856	*7.3525554799*	*0.0000000000*
0.0000000000	*0.0000000000*	*20.0000000000*

Pt
27
Direct

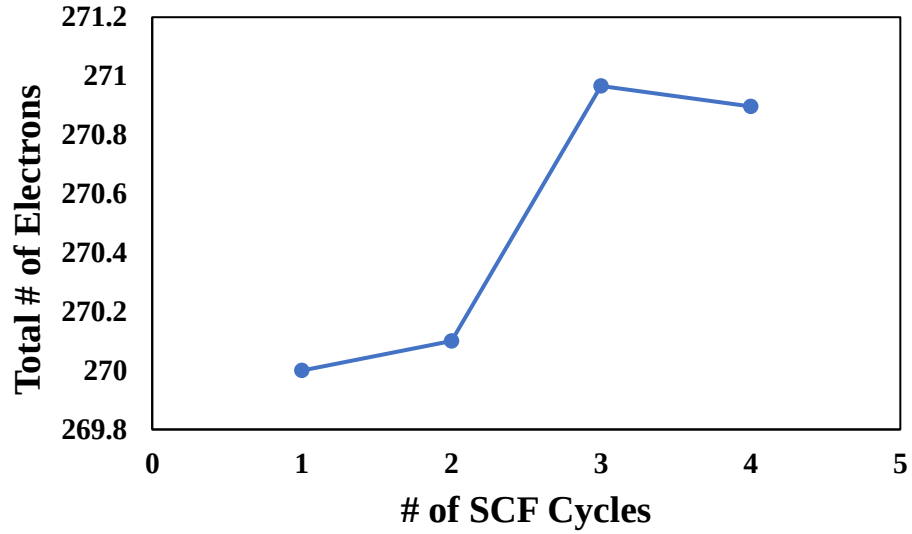
0.000000000	*0.000000000*	*0.101090416*
0.000000000	*0.333333343*	*0.101090416*
0.000000000	*0.666666687*	*0.101090416*
0.333333343	*0.000000000*	*0.101090416*
0.333333343	*0.333333343*	*0.101090416*
0.333333343	*0.666666687*	*0.101090416*
0.666666687	*0.000000000*	*0.101090416*
0.666666687	*0.333333343*	*0.101090416*
0.666666687	*0.666666687*	*0.101090416*
0.111111112	*0.111111112*	*0.215000004*
0.111111112	*0.444444448*	*0.215000004*
0.111111112	*0.777777791*	*0.215000004*
0.444444448	*0.111111112*	*0.215000004*
0.444444448	*0.444444448*	*0.215000004*
0.444444448	*0.777777791*	*0.215000004*
0.777777791	*0.111111112*	*0.215000004*
0.777777791	*0.444444448*	*0.215000004*
0.777777791	*0.777777791*	*0.215000004*
0.222222224	*0.222222224*	*0.328909576*
0.222222224	*0.555555582*	*0.328909576*
0.222222224	*0.888888896*	*0.328909576*
0.555555582	*0.222222224*	*0.328909576*
0.555555582	*0.555555582*	*0.328909576*
0.555555582	*0.888888896*	*0.328909576*
0.888888896	*0.222222224*	*0.328909576*
0.888888896	*0.555555582*	*0.328909576*
0.888888896	*0.888888896*	*0.328909576*

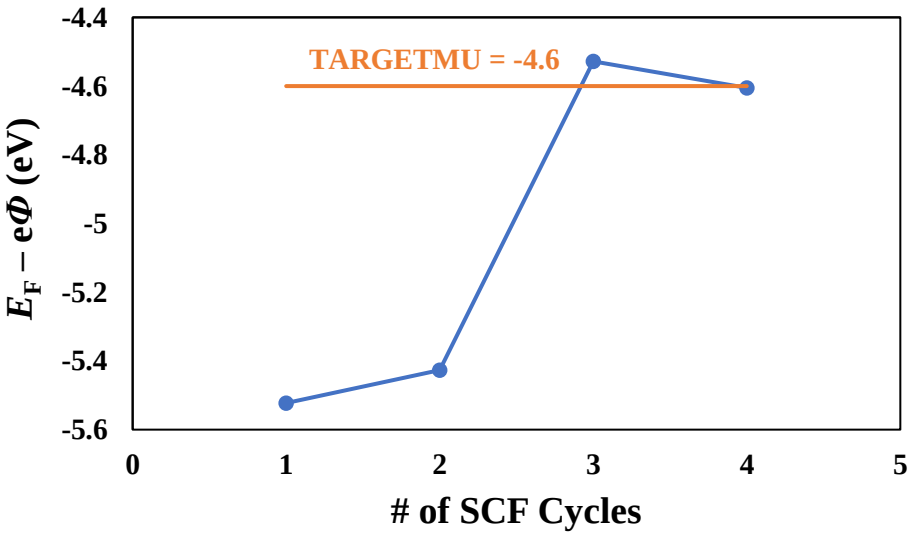
KPOINTS:

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
  POTIM = 0.5
  IBRION = 2
  EDIFFG = -0.01
  EDIFF = 1E-6

  KPAR = 3

#  VASPsol Solvent Model - This corresponds to water
  LSOL = .TRUE.
  EB_K = 80
  LAMBDA_D_K = 3.0

#  CP-VASP Parameters
  LCEP = .TRUE.
  NESCHEME = 2
  CAP_MAX = 2.0
  TARGETMU = -4.6
  FERMICONVERGE = 0.01
############
```

POSCAR:

```
slab-pt111
1.0
      8.4899997711       0.0000000000       0.0000000000
      4.2449998856       7.3525554799       0.0000000000
      0.0000000000       0.0000000000      20.0000000000
  Pt
  27
Direct
0.006663551    -0.00250753    0.103329116
0.000521699    0.33654323     0.100124149
0.005466292    0.664497671    0.098922134
0.333856139    -0.001130454   0.097043648
0.33488808     0.324505597    0.099427716
```

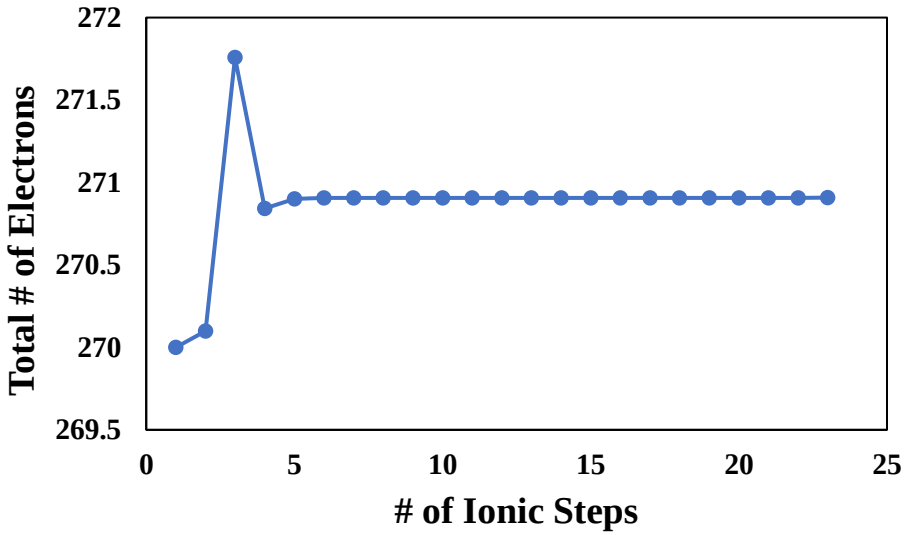
0.334581281 0.658504628 0.108204375
0.667036935 0.005466488 0.092482874
0.669289153 0.338651129 0.109587231
0.667903235 0.662064792 0.09983121
0.119142773 0.107272794 0.211351115
0.110557832 0.45272685 0.210837667
0.102894967 0.774473086 0.216519742
0.445798574 0.116315735 0.211453996
0.442165824 0.43904854 0.217996182
0.437628887 0.770166106 0.210834032
0.774587264 0.10580737 0.21783955
0.783585033 0.436009407 0.21688409
0.785915631 0.771487374 0.216173539
0.222130099 0.225648869 0.322386112
0.213626163 0.56200542 0.335482213
0.220871004 0.888177727 0.327113395
0.557420213 0.219741935 0.320199203
0.555504654 0.563429476 0.3254934
0.550366025 0.886049288 0.331377435
0.878893621 0.214194633 0.330798189
0.887896371 0.557410376 0.338215906
0.888455905 0.885109531 0.327601588

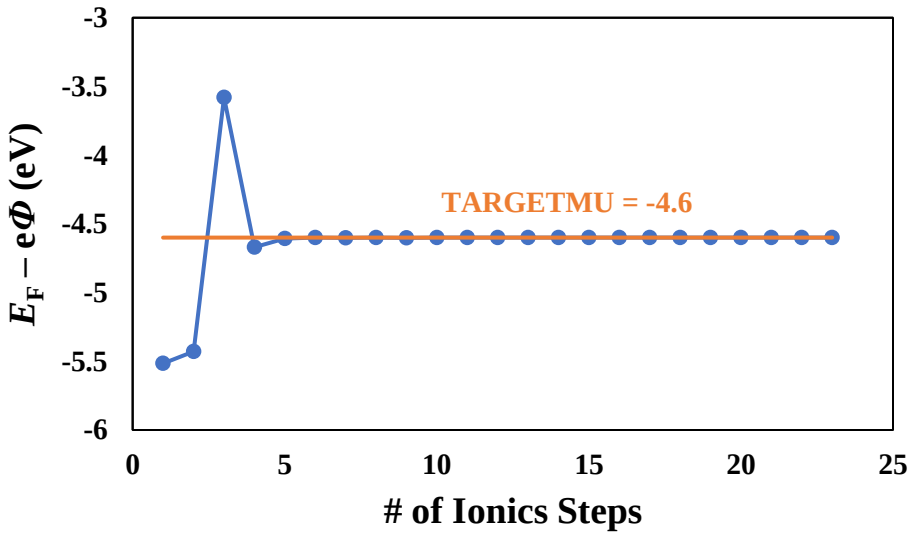
KPOINTS:

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 the large peak at the third step. The algorithm quickly corrects this overestimation 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:

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 = 0.5
  IBRION = 0
  EDIFF = 1E-6

  KPAR = 3

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

#  VASPsol Solvent Model - This corresponds to water
  LSOL = .TRUE.
  EB_K = 80
  LAMBDA_D_K = 3.0

#  CP-VASP Parameters
  LCEP = .TRUE.
  NESCHEME = 2
  CAP_MAX = 2.0
  NEADJUST = 5
  TARGETMU = -4.6
  FERMICONVERGE = 0.01
############
```

POSCAR:

```
slab-pt111
  1.00000000000000
    8.4899997711000008    0.0000000000000000    0.0000000000000000
    4.2449998856000004    7.3525554799000004    0.0000000000000000
    0.0000000000000000    0.0000000000000000   20.0000000000000000
  Pt
   27
Direct
  0.0017622944169016  0.9980476770256816  0.1006148936535466
  0.0018874858068232  0.3313477311969751  0.1005826404490572
  0.0018134464282225  0.6646673212377820  0.1005906510283874
  0.3350800652668292  0.9981233457707970  0.1005914706217550
  0.3351316603482971  0.3314138929533981  0.1006007059904995
  0.3351535567404700  0.6647810220688274  0.1005870773636369
  0.6684517428190528 -0.0019555330109288  0.1005967406772768
```

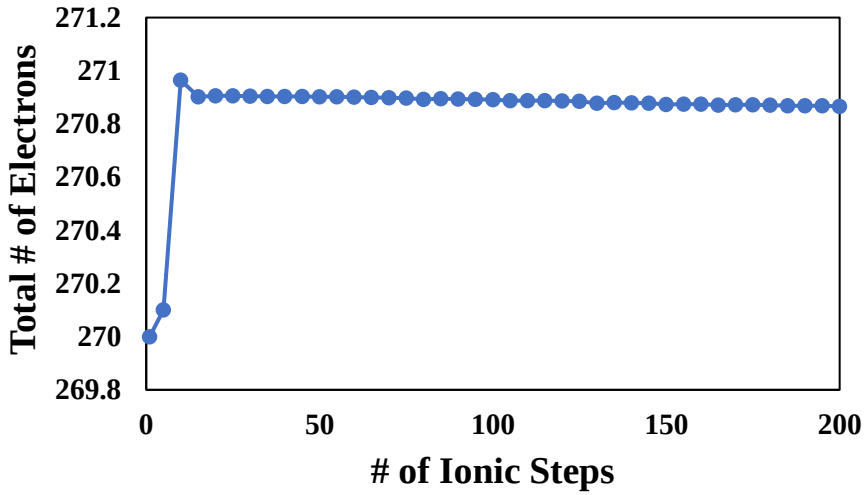
0.6684819457873808 0.3314557806023732 0.1005904191449411
0.6685593033854386 0.6646922896248416 0.1006002788716414
0.1109858021640908 0.1095510261947755 0.2147319468248442
0.1110090090375585 0.4429535505637957 0.2147375993957250
0.1109966653355097 0.7762469960346722 0.2147245022790365
0.4442823802068484 0.1095758534534205 0.2147292079070285
0.4442604024467634 0.4429633612675970 0.2147122477554258
0.4443672910981394 0.7762895034348315 0.2146719134928151
0.7776355276026382 0.1096333156411859 0.2147386273700897
0.7777938946099089 0.4429090389292731 0.2147451888158814
0.7776694076579225 0.7762870948634815 0.2147271360395371
0.2202348376086758 0.2214084516397350 0.3288412133115723
0.2203004735802859 0.5547298019567990 0.3288787915905201
0.2202581816212760 0.8880459325117109 0.3288560461275521
0.5535778353541799 0.2213599616925659 0.3288142571552120
0.5536080882019498 0.5547226643122214 0.3287998385593150
0.5535786295312164 0.8880203158627142 0.3288648286409988
0.8869443808477605 0.2214277982623108 0.3288636861880139
0.8868951102244180 0.5548582443475979 0.3288803070482775
0.8869277868714429 0.8881136295615610 0.3288375906974172

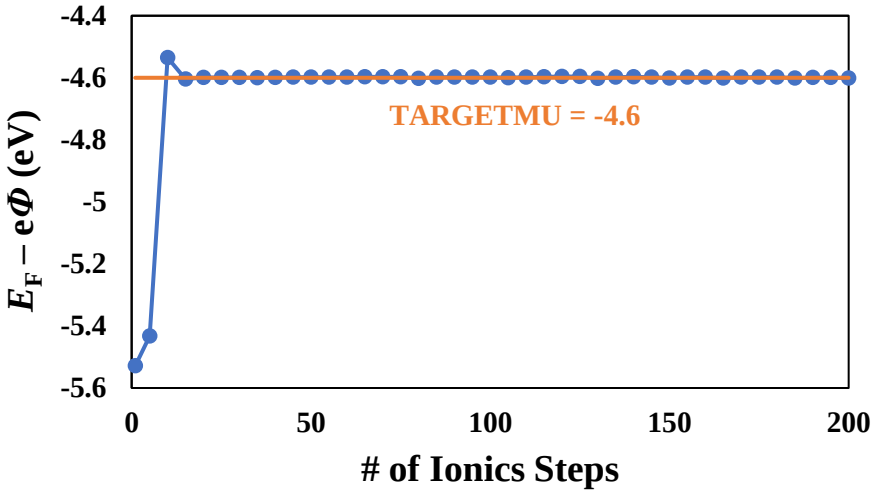
KPOINTS:

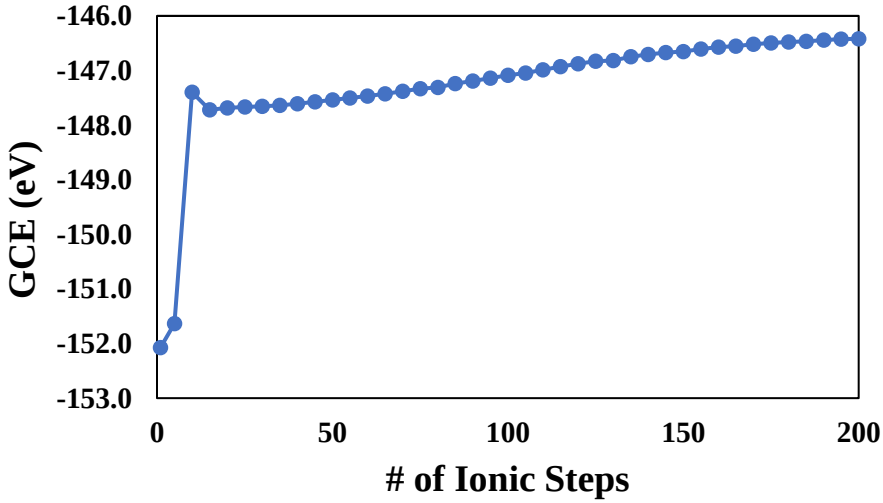
K-Points
0
M
7 7 1

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.


271.2
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 = -4.6
0
50
100
150
200
# of Ionics Steps


-146.0
-147.0
-148.0
-149.0
-150.0
-151.0
-152.0
-153.0
GCE (eV)
0
50
100
150
200
# of Ionic Steps