Manual for CP-VASP

1. Introduction

Thank you for taking interest in CP-VASP[1, 2]! CP-VASP is a patch to the Vienna Ab-Initio Simulation Package (VASP)[3, 4] to enable DFT calculations under constant electrode potential. Using CP-VASP, the electron number, energy, and forces can be determined for any structure under a given electrode potential. Thus, CP-VASP enables structural relaxation and molecular dynamics (MD) simulation under a fixed electrode potential.

The code was originally developed by Xunhua Zhao and optimized by Saerom Yu and Zachary Levell at Yuanyue Liu's group. The code is available upon request. If you use this code in a future publication, please cite the following papers:

- Zhao, X.; Liu, Y. Origin of Selective Production of Hydrogen Peroxide by Electrochemical Oxygen Reduction. *Journal of the American Chemical Society* **2021**, *143* (25), 9423-9428.

- Yu, S.; Levell, Z.; Jiang, Z.; Zhao, X.; Liu, Y. What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe–N–C Catalysts? *Journal of the American Chemical Society* **2023**, *145* (46), 25352-25356.

2. Installation

CP-VASP is intended to be applied to VASP version 6. It also requires installing VASPsol before being applied:

https://github.com/henniggroup/VASPsol/tree/master.

If you are using VASP version 6.4 or 6.3, use the vasp6.4_6.3_cpm.patch file. If you are instead using VASP version 6.2 or 6.1, use the vasp6.2_6.1_cpm.patch file. To apply the patch, navigate to the /src directory in your VASP folder and copy the appropriate patch file into it. Then execute the following command (assuming you are using VASP version 6.4):

```
patch -p0 < vasp6.4_6.3_cpm.patch
```

This patch file modifies the main.F, pot.F, reader.F, and the solvation.F files. The .objects file does not need to be edited. Once the patch is complete, recompile VASP.

In our experience, make veryclean is typically not necessary for this step but is worth trying if compilation errors occur.

3. CP-DFT Theory

In CP-DFT, the number of electrons (n) is changed to match the Fermi level (referenced to the electrolyte) with a target value, which is set by the electrode potential. For convenience, we define the "interfacial potential" of the system (U) as:

$$E_F - e\Phi = -eU \qquad \text{(Eq. 1)}$$

where E_F is the Fermi level of the system and Φ is the electrostatic potential in the electrolyte region. The CP-DFT thus requires:

$$U = U_T \qquad \text{(Eq. 2)}$$

where U_T is the target potential.

For a given structure, determining the n to satisfy Eq. 2 corresponds to a 1D root-finding problem for the U vs n profile, which can be approached in several ways. The current version of CP-VASP uses the Secant method. Starting from two known datapoints: (n_0, U_0) and (n_1, U_1), the electron number at step i is calculated as:

$$n_i = n_{i-1} + C (U_T - U_{i-1}) \qquad \text{(Eq. 3)}$$

where C mimics the capacitance of the system, which is calculated as:

$$C = (n_{i-1} - n_{i-2})/(U_{i-1} - U_{i-2}) \qquad \text{(Eq. 4)}$$

For each step, DFT SCF cycle is performed to determine the U for given n. Eqs. 3 and 4 can be iterated until the difference between U and U_T becomes sufficiently small.

For structure relaxation, one can run multiple electronic steps (i.e. SCF cycles) for every structure encountered during the relaxation to ensure Eq. 2 is satisfied for each structure (NESCHEME = 3). However, since we are often more interested in the final structure, a more efficient approach is to only run one SCF cycle for each structure (NESCHEME = 2). Alternatively, one can run multiple SCF cycles for the first ionic step, and then run only one SCF cycle for each sequential step (NESCHEME = 1).

For CP-MD, it should be noted that, different from static calculations (e.g. relaxation) where U equals the external electrode potential ($U_{\text{ext}} = U_T$), U should fluctuate around U_T under thermodynamic equilibrium (i.e. $\langle U \rangle = U_T$). The Secant method can be used to converge the interfacial potential, but the dynamics of the potential will not be captured. Dynamic equations for this system have been developed by coupling the system to an external potentiostat[5]:

$$\dot{n} = \frac{P_n}{M_n} \qquad \text{(Eq. 5)}$$

$$\dot{P}_n = U - U_T \qquad \text{(Eq. 6)}$$

where n is the electron number at the current step, P_n is the fictitious momentum of the electron number at the current step, and M_n is the fictitious mass that controls the coupling between the system and electron bath. In CP-VASP, these equations are integrated with time using the Velocity-Verlet algorithm.

In future versions of CP-VASP, we plan to implement additional schemes for tuning the electron number, including the Bisection method and the other schemes described in reference[5].

4. CP-VASP Usage Overview

To perform CP-DFT calculations, add the following tags into INCAR:

LCEP = .TRUE.
NESCHEME = [INTEGER]
TARGETMU = [REAL]

Turning on the constant potential calculation (LCEP = .TRUE.) performs CP-DFT calculations to reach the desired electrode potential (TARGETMU) using the electronic charge scheme (NESCHEME) specified by the user. Details about these tags are shown later in section 5.

The user can also add the following optional tags:

FERMICONVERGE = [REAL]
INIT_ECHANGE = [REAL]
ECHANGE_MAX = [REAL]
CAP_MAX = [REAL]
NEADJUST = [INTEGER]

Pn = [REAL]

Mn = [REAL]

FERMICONVERGE determines the convergence criterion of the electrolyte-referenced Fermi level to the target energy -eU_T. INIT_ECHANGE is the magnitude of the initial electron number change. ECHANGE_MAX and CAP_MAX are the maximum magnitude of the electron number change and the capacitance, respectively. NEADJUST is only used for CP-MD simulations and controls how often an electron adjustment is performed. Pn and Mn are valid when using NESCHEME = 4. These tags determine the initial momentum of the potentiostat and the fictitious mass of the potentiostat, respectively.

5. CP-VASP INCAR Setting Details

LCEP = [LOGICAL]

Default: LCEP = .FALSE.

Setting LCEP = .TRUE. will turn on the CP for DFT calculations.

NESCHEME = [INTEGER]

Default: NESCHEME = 1

NESCHEME determines which electron adjustment scheme is used.

NESCHEME = 1 (Hybrid-scheme)

The electron number is tuned via the Secant method. For the first ionic step, Eq. 3 is repeated over multiple SCF cycles until the electrolyte-referenced Fermi level is sufficiently converged. The rest of the ionic steps use a single SCF cycle to update the number of electrons. This scheme is compatible with IBRION = -1, 0, 1, 2, and 3.

NESCHEME = 2 (Single-SCF scheme)

Using the Secant method, each ionic step has a single electron number adjustment. This scheme is compatible with IBRION = 0, 1, 2, and 3.

NESCHEME = 3 (Multi-SCF scheme)

The electrolyte-referenced Fermi level is converged at each ionic step via the Secant method, performing as many electron number adjustments as necessary. This scheme is compatible with IBRION = -1, 0, 1, 2, and 3.

NESCHEME = 4 (MD-scheme)

This scheme is for MD only and uses the first scheme proposed in reference[5]. This scheme is compatible with IBRION = 0.

TARGETMU = [REAL]

Default: TARGETMU = -4.6

TARGETMU sets the targeted Fermi level referenced to the electrolyte -eU_T. For the Standard Hydrogen electrode (SHE), its Fermi level referenced to the electrolyte is calculated to be -4.6 eV with PBE functional,[6] which is default value used for TARGETMU. Therefore, if you want to simulate an electrode potential of U vs SHE, then TARGETMU should be set to -4.6 – eU. Note that the value of Fermi level referenced to the electrolyte for the SHE can change with the functional and solvation model and should be re-calculated when working with a new functional/solvation model. We recommend ensuring that TARGETMU is not within a band gap of the system, as there are no electron numbers that produce the desired potential and CP-VASP will be unable to converge the interfacial potential.

FERMICONVERGE = [REAL]

Default: FERMICONVERGE = 0.05

It sets the convergence criterion for the electrolyte-referenced Fermi level. When the difference between it and TARGETMU is smaller than FERMICONVERGE, the potential is considered to have reached the target value.

INIT_ECHANGE = [REAL]

Default: INIT_ECHANGE= 0.1

This parameter sets the magnitude of the first electron number change. The code automatically determines whether the electron number should decrease or increase based on the electrolyte-referenced Fermi level relative to the target energy.

ECHANGE_MAX = [REAL]

Default: ECHANGE_MAX = 0.0

This parameter determines the maximum magnitude of the electron number change. In most cases, this parameter is not necessary and is turned off by default (by setting ECHANGE_MAX = 0.0). Large changes in the electron number may cause the SCF cycles to fail to converge. Setting ECHANGE_MAX to a positive value can prevent the SCF cycles from failing, but also reduce the speed of convergence.

CAP_MAX = [REAL]

Default: CAP_MAX = 2.0

This parameter determines the maximum capacitance when NESCHEME = [1,2,3]. Increasing CAP_MAX will allow the electron number to change by a greater amount in a single electron adjustment step. Limiting the capacitance prevents CP-VASP from greatly overshooting the target potential at the expense of some computational speed.

NEADJUST = [INTEGER]

Default: NEADJUST = 5

This parameter is only relevant during MD simulations. We have previously observed that it is sufficiently accurate to only perform an electron adjustment every few ionic steps[1, 2]. The advantage of applying this tag is the computational efficiency without considerably disturbing the local structure and reaction near the surface. When the explicit solvation is present, the local structure won't be significantly affected since it is far from the implicit solvation region. To maximize efficiency, CP-VASP only turns on implicit solvation every NEADJUST steps, calculates the interfacial potential, and then turns off implicit solvation and proceeds with MD.

Note that the electron adjustment step is always performed on the first ionic step, and then occurs every NEADJUST steps.

Pn = [REAL]

Default: Pn = 0.0

When using NESCHEME = 4, this parameter determines the initial momentum of the potentiostat. This parameter is mainly useful when running a continuation job.

Mn = [REAL]

Default: Mn = 10.0

When using NESCHEME = 4, this parameter determines the fictitious "mass" of the potentiostat; if Mn is increased, the potentiostat is more resistant to changing the electron number, thereby causing the fluctuations to have a longer period.

6. Relevant VASP INCAR Settings

IBRION = [-1, 0, 1, 2, 3]

CP-VASP is not currently compatible with all IBRION settings; the values listed above are implemented into CP-VASP. Some details for each of these settings are noted below:

IBRION = -1: This corresponds to a fixed-structure calculation. The charge at the desired potential can be calculated for a predetermined structure. The compatible schemes are NESCHEME = 1 and 3.

IBRION = 0: This runs ab initio molecular dynamics (AIMD) with DFT-calculated forces. Importantly, implicit solvation is only used to reference the interfacial potential and is turned off when calculating the atomic forces. Thus, the energies given in the output (including the grand canonical energy) are given without solvation. All values of NESCHEME are acceptable.

IBRION = 1, 2, 3: These values perform ionic-relaxation calculations. The compatible schemes are NESCHEME = 1, 2, and 3.

NELECT = [REAL]

If you know the charge of the system at the target potential, it is helpful to initialize the electron number to reduce the computational cost. This parameter and ICHARG is particularly useful for continuation jobs.

LSOL = [LOGICAL]

CP-VASP currently requires that the VASPsol solvation model is tuned on to correctly reference the Fermi level.

7. Interpreting the Results

CP-VASP includes two additional output lines to the standard VASP output and OSZICAR files:

"CPM-ion: …": This line is printed directly after the traditional VASP output line that gives the system energy at the end of each ionic step. The values on this line are as follows: the ionic step number, the total number of electrons, the electrolyte-referenced Fermi level ($E_F - e\Phi$), the target energy ($-eU_T$), and the grand canonical energy (GCE). The momentum of the potentiostat P_n is also printed on this line during MD if NESCHEME = 4. The GCE calculated by the formula below:

$$GCE = E_0 + (CNNE - n) * (-eU_T) \qquad (Eq.\ 7)$$

where E_0 is the standard VASP output energy, CNNE is the charge-neutral electron number, n is the electron number, and U_T is the external electrode potential. The GCE is given in terms of eV. Note that E_0 does *not* account for the change in electron number and is no longer an accurate representation of the system's total energy.

"CPM-scf: …": This line occurs at the end of each SCF cycle when the electrolyte-referenced Fermi level is not yet converged. The values on this line are as follows: the ionic step number, the number of SCF cycles performed this ionic step, the total number of electrons, the electrolyte-referenced Fermi level, the target energy, and the capacitance. The main purpose of this line is to evaluate how quickly the interfacial potential is converging to the target potential. If the target potential cannot be reached for whatever reason, CP-VASP will endlessly attempt to change the electron number and the simulation will not finish. This may happen if your material is an electronic insulator at the chosen potential, or if the density of states

is particularly sparse in that region. In this circumstance, try increasing the number of k-points or the orbital energy smearing width (SIGMA).

It is particularly useful to plot the ionic step vs electron number, the ionic step vs electrolyte-referenced Fermi level, the electron number vs electrolyte-referenced Fermi level, and the ionic step vs grand canonical energy. Examples showing the analysis of CP-VASP simulations are shown in a separate document.

8. Troubleshooting

If you run into any errors with compiling the VASP code with CP-VASP or the simulations do not run properly, please reach out to us via email. CP-VASP is currently under development, and we appreciate your feedback.

9. References

(1) Zhao, X.; Liu, Y. Origin of selective production of hydrogen peroxide by electrochemical oxygen reduction. *Journal of the American Chemical Society* **2021**, *143* (25), 9423-9428.
(2) Yu, S.; Levell, Z.; Jiang, Z.; Zhao, X.; Liu, Y. What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe–N–C Catalysts? *Journal of the American Chemical Society* **2023**, *145* (46), 25352-25356. DOI: 10.1021/jacs.3c09193.
(3) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6* (1), 15-50. DOI: https://doi.org/10.1016/0927-0256(96)00008-0.
(4) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Physical Review B* **1993**, *47* (1), 558-561. DOI: 10.1103/PhysRevB.47.558.
(5) Bonnet, N.; Morishita, T.; Sugino, O.; Otani, M. First-principles molecular dynamics at a constant electrode potential. *Physical Review Letters* **2012**, *109* (26), 266101.
(6) Mathew, K.; Kolluru, V. S. C.; Mula, S.; Steinmann, S. N.; Hennig, R. G. Implicit self-consistent electrolyte model in plane-wave density-functional theory. *The Journal of Chemical Physics* **2019**, *151* (23), 234101. DOI: 10.1063/1.5132354 (acccessed 9/1/2023).