Grand canonical ensemble approaches for modeling electrochemical problems at constant electrode potentials in CP2K

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In many electrochemical experiments, the number of electrons of the electrode immersed in the electrolyte is variable, and the number of adsorbed substances on the surface of the electrode can also vary. However, treating electrochemical solid-liquid interfaces with the typical canonical DFT tends to be a challenge. This can be addressed by using grand canonical approaches. We present the implementation of two grand canonical approaches that go beyond the existing canonical ensemble paradigm in the open-source computational chemistry software CP2K. The first approach includes a number of recent developments: (a) grand canonical self-consistent field (GC-SCF) method[1] allowing the electron number of the system to fluctuate naturally and accordingly with the experimental electrode potential, (b) planar counter charge (PCC)[2,3] salt model completely screening the net charge of the electrode model, (c) the solvent-aware interfaces[4] between solute and solvent in continuum solvation for overcoming the unphysical isolated cavities or pockets of the dielectric function. In contrast with the previous studies, in our implementation, the work function (absolute electrode potential) is the constrained quantity during an SCF optimization instead of the Fermi energy. We derived the analytical expressions of the potential and force compatible with the Quickstep framework of the CP2K software package. The second approach (referred to as the two-surface method and the numerical litmus method)[5–7] is used to calculate the absolute electrode potential corresponding to an equilibrium electrochemical half-reaction (M^((n+m)+)+ne^-→M^(m+)) which involves DFT-MD and explicit modeling of the solvent molecules. The systematic tests have verified that the implementation of both two methods in CP2K is reliable. This opens the way for forefront electrochemical calculations in CP2K for a broad range of systems.

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