About the computation of the free electrochemical energy with `ei-compute-fee`.

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Abstract

The program `ei-compute-fee` from the `ec-interface` package,[1] can be used to compute the free electrochemical energy of a system (Ω) following the works of Prof. J.S. Filhol.

In theory, the free electrochemical energy (or grand potential) of a system is given by:

$$\Omega(\Phi) = H(\Phi) - q\Phi, \tag{1}$$

where q is the surface charge at a given electrode potential Φ and $H(\Phi)$ is the enthalpy of the system. However, introducing or removing a certain amount of electron to the system, $N_e = N - N_0$ (where N is the number of electrons used in the calculation and N_0 is the number for the neutral system), provide a way to estimate Ω. According to Hagopian et al. (see Eq. 12 and 13 of [1]), a good approximation is given by:

$$\Omega(\Phi) = A_{\mathrm{VASP}}(N_e) - N_e\, E_F(N_e), \tag{2}$$

where A_{VASP} and E_F are the free (`E0` in `OSZICAR`) and Fermi energies reported by VASP for a given N_e, respectively. However, the "true" work function Φ is better approximated by:

$$\Phi(N_e) = E_V(N_e) - E_F(N_e), \tag{3}$$

where E_V is the vacuum potential (evaluated from `LOCPOT` at the location of the center of the vacuum between the electrodes). These formulas are used to compute the values of Ω reported by default (or using `--hbm-fermi`).

With the PBM approach. Within the Poisson-Boltzmann (PB) method, Eq. (1) becomes:

$$\Omega(\Phi) = A_{\mathrm{VASP}}(N_e) + N_e\, \Phi(N_e). \tag{4}$$

This formula is used to compute the values of Ω reported using `--pbm`.

With the HBM approach. According to Kopač Lautar et al. [2], given a fraction of active electrode α_s so that $N_s = \alpha_s\, N_e$, one gets:

$$\Omega(\Phi) = A^0_{\mathrm{VASP}} + \alpha_s \left\{ A_{\mathrm{VASP}}(N_e) - A^0_{\mathrm{VASP}} + N_e\, \Phi(N_e) - \int_0^{N_e} E_V(n)\, dn \right\}, \tag{5}$$

[1] `https://github.com/pierre-24/ec-interface/`

where A^0_{VASP} is the free energy reported by VASP without any excess electron. The integral accounts for the homogeneous background (HB) of compensating charges.[2] This formula is used to compute the values of Ω reported using `--hbm` α_s.

One way to evaluate α_s is:

$$\alpha_s^c = \frac{d_0}{d},$$

where d_0 and d are the vacuum thickness and the size of the unit cell, respectively. However, it is also possible to extract this quantity from a ratio of capacitances evaluated with two different techniques: [1]

$$\alpha_s = \frac{C_{\Omega\Phi}}{C_{\Phi N}}, \text{ where } \frac{1}{C_{\Phi N}} = -\frac{1}{e}\frac{\partial \Phi}{\partial N_e}\bigg|_{N_e=0} \text{ and } C_{\Omega\Phi} = -\frac{\partial^2 \Omega}{\partial \Phi^2}\bigg|_{N_e=0},$$

where Φ is evaluated using Eq. (3), but Ω is approximated using Eq.(2). When using `--hbm-ideal`, this formula is used to evaluate α_s, and then Eq. (5) is used to compute the values of Ω.

References

[1] Arthur Hagopian, Marie-Liesse Doublet, Jean-Sébastien Filhol, and Tobias Binninger. Advancement of the Homogeneous Background Method for the Computational Simulation of Electrochemical Interfaces. *Journal of Chemical Theory and Computation*, 18(3):1883–1893, March 2022.

[2] Anja Kopač Lautar, Arthur Hagopian, and Jean-Sébastien Filhol. Modeling interfacial electrochemistry: Concepts and tools. *Physical Chemistry Chemical Physics*, 22(19):10569–10580, 2020.

[2] And the evolution of E_V with n is not linear, so this integral does not simply evaluate to $E_V(N_e)$!