About the computation of the free electrochemical energy

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TL;DR: The `ec-interface` package reports $\Omega = A_{\mathrm{VASP}} - N_e\, E_F$, which is **an approximation** of the correct free electrochemical energy! Depending on the case, you need either Eq. (3) or (4).

The free electrochemical energy 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.

With the PBM approach. According to Hagopian et al. (see Eq. 12 of [1]), one can introduce N_e as the number of excess electron in the system and define

$$\Phi(N_e) = E_V(N_e) - E_F(N_e) \tag{2}$$

where E_F is the Fermi energy and E_V is the vacuum potential (evaluated from `LOCPOT` in the vacuum between the electrodes). Within the Poisson-Boltzmann (PB) method, Eq. (1) becomes:

$$\Omega(\Phi) = A_{\mathrm{VASP}}(N_e) + N_e\, \Phi(N_e), \tag{3}$$

where A_{VASP} is the free energy reported by VASP (`E0` in `OSZICAR`) for a given N_e.

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

$$\Omega(\Phi) = A^0_{\mathrm{VASP}} + \alpha_s \left\{ A_{\mathrm{VASP}}(N_e) - A^0_{\mathrm{VASP}} + N_e\, \Phi(N_e) - \int_0^{N_e} E_V(n)\, dn \right\}, \tag{4}$$

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.[1] 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]

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

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

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.