Finite-temperature density functional calculation of a molecule in electrochemical environment

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We present a method to calculate electronic structures of a molecule in electrochemical environment. In electrochemical systems, the chemical potential of electrons μ is fixed experimentally. To calculate electronic structures at a constant μ, we use a method based on Mermin's finite-temperature density functional theory (FTDFT)[1].

The FTDFT calculation can be carried out by using the conventional Kohn-Sham (KS) DFT technique. In the FTDFT calculation, the exchange-correlation potential is intrinsically a function of temperature, and the occupation numbers are associated with the Fermi-Dirac distribution given by

$$f_i = \frac{1}{1 + e^{(\epsilon_i - \mu)/(k_B T)}}. \tag{1}$$

The calculation at a constant μ is carried out in the same way as in the standard KS calculation except that the effects of the temperature and the chemical potential are taken into account through the fractional occupation numbers calculated from Eq. (1).

The numerical scheme was implemented in the GAMESS package of quantum chemistry programs and applied to the redox half reaction, $\mathrm{NO}^+ + \mathrm{e}^- \rightleftarrows \mathrm{NO}$ in aqueous solution. We practically approximated the exchange-correlation potential by the hybrid B3LYP functional given at zero-temperature. We assume outer-sphere processes in which the reactant-electrode interaction is negligible, and the solvent effect is approximated by the conductor-like polarizable continuum model (C-PCM). The radii of the cavities in C-PCM were adjusted so as to reproduce the experimental data of the hydration free energies, and they were expressed as a function of the charge.

In experiment, μ is given as an electrode potential. In the present study, the electrode potential relative to SHE of an arbitrary electrode at electrochemical equilibrium $E(\mathrm{Ox/Red})$ is given by

$$E(\mathrm{Ox/Red}) = -\frac{\mu}{e} - 4.24\ \mathrm{V\,vs\,SHE}. \tag{2}$$

Using this relation, the electronic structures were calculated as a function of the electrode potential. Fig. 1 shows the grand potential curves for the electrode potentials $E = -0.84,\ 1.16,\ \mathrm{and}\ 3, 16\ \mathrm{V\ vs\ SHE}$, respectively. This figure demonstrates that the present FTDFT/C-PCM method succeeds in directly calculating the electronic states as a function of the electrode potential.

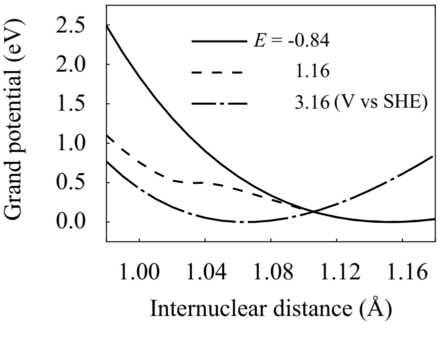

FIG. 1: Grand potential curves of NO with different electrode potentials E. The potential curves are shifted so that the grand potential at each equilibrium internuclear distance is equal to be zero.

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[1] N.D. Mermin, Phys. Rev. 137 (1965) A1441