Density-functional constrained molecular dynamics energy gap (DF-CMD-EG) method for free energy calculation of chemical reaction coupled to electron transfer

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Chemical reactions with electron-transfer in solution, so called "redox reactions", play crucial roles in diverse topics such as battery, fuel cell, catalysis, corrosion, photosynthesis. Fundamental quantities of redox reactions are usually characterized by free energies, which are mainly governed by structural fluctuations of the target species (solute) as well as the environment (solvent). The free energy changes among different charged states associated with electron transfer should be taken into account as well. In most redox reactions, change of chemical bonds is coupled to the electron transfer. Therefore first-principles free energy calculation method that can involve change of the electron number as well as bond breaking/formation is quite desired for quantitative investigation of the above phenomena of interest.

For this purpose, we have recently developed novel computational methods for redox reactions [1,2]. The density-functional molecular dynamics energy gap (DF-MD-EG) method [1] is derived from statistical mechanics for redox couples and the Marcus theory of electron transfer. It is found that this formulation is quite compatible with the fundamentals of DFT. However it is only applicable to electron transfer process without bond change in practice. Then, combining this method with constrained MD (CMD) scheme of blue-moon ensemble, we have newly constructed the DF-CMD-EG method [2] that can deal with free energies of bond breaking/formation coupled to electron transfer, based on the fundamental principles of quantum and statistical mechanics.

We have applied this DF-CMD-EG method to a water cleavage reaction coupled to electron transfer on a transition metal oxide ion in aqueous solution and demonstrated that it can well reproduce experimental reaction free energy. The resultant free energy profile is shown in Fig. 1. We consider that this will open new perspectives for first-principles investigation of electron transfer reactions coupled to chemical bond breaking/formation.

These works were done in collaboration with M. Sprik, J. Blumberger, I. Tavernelli, and T. Ohno.

[1] Y. Tateyama, J. Blumberger, M. Sprik, and I. Tavernelli, J. Chem. Phys. **122**, 234505 (2005).
[2] Y. Tateyama, J. Blumberger, T. Ohno, and M. Sprik, J. Chem. Phys. **126**, 204506 (2007).

Fig. 1: Helmholtz free energy profile of the redox reaction, $RuO_4^- + H_2O + e^- \rightarrow [RuO_3(OH)_2]^{2-}$. The symbols, ξ and θ, denote the reaction coordinates with respect to the chemical bond change and the electron transfer, respectively. The overall reaction free energy is calculated to be -0.65 eV, in good agreement with the experimental value (-0.59 eV). Owing to the lower activation free energy, the reaction pathway via RuO_4^{2-} is more favourable than that through $[RuO_3(OH)_2]^-$.