Supporting Information for Microscopic Picture of the Solvent Reorganization During Electron Transfer to Flavin in Water

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Unbiasing the fractional electron transfer state simulations

The probability to measure a certain vertical energy gap, $\Delta E' = E_R(\mathbf{r}^N) - E_O(\mathbf{r}^N)$, of the neutral ($\eta = 0$) system in the canonical ensemble is:

$$P_{\eta=0}(\Delta E') = \frac{1}{Z_{\eta=0}} \int d\mathbf{r}^N e^{-\beta H_{\eta=0}} \delta(\Delta E - \Delta E') \tag{1}$$

with $Z_{\eta=0} = \int d\mathbf{r}^N e^{-\beta H_{\eta=0}}$, the partition function of the neutral system. The probability in the reduced system, $P_{\eta=1}(\Delta E')$ has the analogous expression, but will in practise be numerically different from $P_{\eta=0}(\Delta E')$ because the anionic system samples different configurations under $H_{\eta=1}$. In fact, there may even be little overlap between the two probability functions in the case of a large reorganization of the environment upon changing the charge.

To enhance the sampling of configurations in rarely visited regions of the reaction coordinate ΔE, the system can be biased by sampling configurations under a mixed Hamiltonian, $H_\eta = \eta H_R + (1-\eta)H_O$, with $\eta \in [0, 1]$ and with H_O and H_R the Hamiltonians of the neutral and anionic systems respectively. The probability function measured at some fractional value η_1 is again analogous to eq 1, but it should be reweighted to correct for the applied bias. To reweight a probability function $P_{\eta_1}(\Delta E')$ as if it was measured at a different η_2, we start from the formula for $P_{\eta_2}(\Delta E')$ (see eq 1) and multiply the Boltzmann factor by the identity $e^{-\beta H_{\eta_1}} e^{+\beta H_{\eta_1}}$ and rearrange to:

$$P_{\eta_2}(\Delta E') = \frac{1}{Z_{\eta_2}} \int d\mathbf{r}^N e^{-\beta H_{\eta_1}} e^{-\beta(H_{\eta_2} - H_{\eta_1})} \delta(\Delta E - \Delta E') \tag{2}$$

By multiplying by a second identity, Z_{η_2}/Z_{η_2}, this can be further rewritten to:

$$P_{\eta_2}(\Delta E') = \frac{Z_{\eta_1}}{Z_{\eta_2}} \frac{1}{Z_{\eta_1}} \int d\mathbf{r}^N e^{-\beta H_{\eta_1}} e^{-\beta(\eta_2 - \eta_1)\Delta E} \delta(\Delta E - \Delta E') \tag{3}$$

in which we also made use of $H_{\eta_2}(\mathbf{r}^N) - H_{\eta_1}(\mathbf{r}^N) = (\eta_2 - \eta_1)\Delta E$. As the delta function leaves only the contributions for which $\Delta E = \Delta E'$, we can place the second exponent in front of the integral, so that only the Boltzmann weight of H_{η_2} remains inside, which is simply $P_{\eta_1}(\Delta E')$ when normalized by Z_{η_1}:

$$P_{\eta_2}(\Delta E') = \frac{Z_{\eta_1}}{Z_{\eta_2}} e^{-\beta(\eta_2-\eta_1)\Delta E} P_{\eta_1}(\Delta E') \tag{4}$$