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Self-consistent reaction field calculation of solvent reorganization energy in electron transfer: a dipole-reaction field interaction model

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Abstract. Based on the continuum dielectric model, this work has established the relationship between the solvent reorganization energy of electron transfer (ET) and the equilibrium solvation free energy. The dipole-reaction field interaction model has been proposed to describe the electrostatic solute-solvent interaction. The self-consistent reaction field (SCRF) approach has been applied to the calculation of the solvent reorganization energy in self-exchange reactions. A series of redox couples, O_2/O_2^-, NO/NO^+, O_3/O_3^-, N_3/N_3^-, NO_2/NO_2^+, CO_2/CO_2^-, SO_2/SO_2^-, and ClO_2/ClO_2^-, as well as $(CH_2)_2C$-$(\text{-}CH_2\text{-})_n$-$C(CH_2)_2$ ($n = 1 \sim 3$) model systems have been investigated using ab initio calculation. For these ET systems, solvent reorganization energies have been estimated. Comparisons between our single-sphere approximation and the Marcus two-sphere model have also been made. For the inner reorganization energies of inorganic redox couples, errors are found not larger than 15% when comparing our SCRF results with those obtained from the experimental estimation. While for the $(CH_2)_2C$–$(–CH_2–)_n$–$C(CH_2)_2$ ($n = 1 \sim 3$) systems, the results reveal that the solvent reorganization energy strongly depends on the bridge length due to the variation of the dipole moment of the ionic solute, and that solvent reorganization energies for different systems lead to slightly different two-sphere radii.

Key words: Electron transfer – Solvent reorganization energy – Dipole-reaction field interaction – Ab initio

Introduction

Electron transfer (ET) reactions in solutions are of fundamental significance in chemical and biochemical processes. In order to understand the dynamical mechanisms of those reactions, a number of theoretical and experimental studies have been carried out. The reorganization energy, which is an important dynamical parameter, commonly denoted λ, can be divided into two parts, the inner reorganization energy λ_i, and the solvent reorganization energy λ_o [1], i.e.,

$$\lambda = \lambda_i + \lambda_o \tag{1}$$

For the evaluation of the inner reorganization energy, direct quantum chemistry calculations have given rather good results in recent years. The estimation of the solvent reorganization energy, however, stays somewhat unsatisfactory. After Marcus put forward his two-sphere model a few decades ago [2, 3], the calculations of the solvent reorganization energy have been intensely researched. Due to Marcus, the solvent reorganization energy can be expressed as the free energy difference of the non-equilibrium state and the equilibrium state [3], i.e.,

$$\lambda_o = G_{n-eq} - G_{eq} \tag{2}$$

where G_{n-eq} and G_{eq} stand for the non-equilibrium free energy and the equilibrium free energy respectively.

Computational methods for evaluating the equilibrium solvation free energy have been supplemented to some popular quantum chemistry packages [4–12], while the calculation of the non-equilibrium solvation free energy is less convenient. The main aim of our present work is to establish a mathematical relationship between the solvent reorganization energy of ET reaction and the equilibrium solvation free energy and then to perform the direct calculations of the solvent reorganization energy. Using the Onsager reaction field model [4] and the standard self-consistent reaction field (SCRF) approach appended to the HONDO 95.6 package [13], the estimation of the solvent reorganization energy has been carried out. We call this method the dipole-reaction field interaction model. Test calculations have been made to some typical redox couples including O_2/O_2^-, NO/NO^+, O_3/O_3^-, N_3/N_3^-, NO_2/NO_2^+, CO_2/CO_2^-, SO_2/SO_2^-, ClO_2/ClO_2^-, and to the model systems $(CH_2)_2C$–$(CH_2)_n$–$C(CH_2)_2$ ($n = 1 \sim 3$).

This paper is organized as follows. First we introduce the expressions of the equilibrium solvation free energy

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under the SCRF approach. Then we detail the expressions of the non-equilibrium solvation free energy and the solvent reorganization energy. After this we couch the application of the approach to some samples of chemical interest, and compare the SCRF approach and the Marcus two-sphere model. Finally our conclusions are given.

Equilibrium solvation free energy

In the continuum dielectric model, for a system embedded in the solvent cavity, the free energy functional is expressed as [14]

$$\begin{aligned} G = {} & \langle\psi|\mathbf{H}_0|\psi\rangle + 1/(2\chi_\mathrm{e})\int_V |\mathbf{P}_\mathrm{e}(\mathbf{r})|^2\,\mathbf{d}^3\mathbf{r} \\ & + 1/(2\chi_\mathrm{or})\int_V |\mathbf{P}_\mathrm{or}(\mathbf{r})|^2\,\mathbf{d}^3\mathbf{r} + 1/2\int_V\int_V [\mathbf{P}_\mathrm{e}(\mathbf{r}) \\ & + \mathbf{P}_\mathrm{or}(\mathbf{r})]\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot[\mathbf{P}_\mathrm{e}(\mathbf{r}')+\mathbf{P}_\mathrm{or}(\mathbf{r}')]\mathbf{d}^3\mathbf{r}\,\mathbf{d}^3\mathbf{r}' \\ & - \int_V [\mathbf{P}_\mathrm{e}(\mathbf{r})+\mathbf{P}_\mathrm{or}(\mathbf{r})]\cdot[\mathbf{E}_\psi(\mathbf{r},\rho)\mathbf{d}^3\mathbf{r} \end{aligned} \tag{3}$$

where $\mathbf{H}_0$ is the vacuum Hamiltonian of the isolated solute; $\mathbf{E}_\psi(\mathbf{r}, \rho)$ is the electric field due to the solute charge distribution ρ of electronic state ψ in vacuum; $\mathbf{P}_\mathrm{e}$ and $\mathbf{P}_\mathrm{or}$ are electronic and orientational polarizations of the medium respectively; χ_e and χ_or are the static susceptibility for $\mathbf{P}_\mathrm{e}$ and $\mathbf{P}_\mathrm{or}$ and related to the solvent static and optical dielectric constants ε_∞ and ε_0 by

$$\chi_\mathrm{e} = (\varepsilon_\infty - 1)/4\pi \tag{4}$$

$$\chi_\mathrm{or} = (\varepsilon_0 - \varepsilon_\infty)/4\pi \tag{5}$$

The integrals in Eq. (3) are over the volume outside the cavity, and $\mathbf{T}(\mathbf{r}, \mathbf{r}')$ is the dipole tensor

$$\mathbf{T}(\mathbf{r},\mathbf{r}') = \nabla\nabla'\frac{\mathbf{1}}{|\mathbf{r}-\mathbf{r}'|} \tag{6}$$

In fact, the free energy G in Eq. (3) contains, in sequence, contributions from the expectation value of $\mathbf{H}_0$ in vacuum, the self-energy for the two types of solvent polarization, the interaction between the total polarization $\mathbf{P}$ ($\mathbf{P}(\mathbf{r}) = \mathbf{P}_\mathrm{e}(\mathbf{r}) + \mathbf{P}_\mathrm{or}(\mathbf{r})$) and the field arising from the solvent polarization, as well as the interaction between the solvent polarization and the electronic field formed by the charge distribution of the transferring electron. According to [15],

$$\mathbf{E}_\psi(\mathbf{r},\sigma_\mathrm{e},\sigma_\mathrm{or}) = -\int_V \mathbf{T}(\mathbf{r},\mathbf{r}')\cdot[\mathbf{P}_\mathrm{e}(\mathbf{r}')+\mathbf{P}_\mathrm{or}(\mathbf{r}')]\mathbf{d}^3\mathbf{r}' \tag{7}$$

and the free energy functional reads

$$\begin{aligned} G = {} & \langle\psi|\mathbf{H}_0|\psi\rangle + \\ & 1/(2\chi_\mathrm{e})\int_V |\mathbf{P}_\mathrm{e}(\mathbf{r})|^2\mathbf{d}^3\mathbf{r} + 1/(2\chi_\mathrm{or})\int_V |\mathbf{P}_\mathrm{or}(\mathbf{r})|^2\,\mathbf{d}^3\mathbf{r} \\ & - 1/2\int_V [\mathbf{P}_\mathrm{e}(\mathbf{r})+\mathbf{P}_\mathrm{or}(\mathbf{r})]\cdot\mathbf{E}_\psi(\mathbf{r},\sigma_\mathrm{e},\sigma_\mathrm{or})\cdot\mathbf{d}^3\mathbf{r} \\ & - \int_V [\mathbf{P}_\mathrm{e}(\mathbf{r})+\mathbf{P}_\mathrm{or}(\mathbf{r})]\cdot\mathbf{E}_\psi(\mathbf{r},\rho)\mathbf{d}^3\mathbf{r} \end{aligned} \tag{8}$$

Throughout this paper, we denote the charge distribution ρ from ψ within the cavity ρ^r before ET and ρ^p after ET. Here we use "r" and "p" to refer respectively to the reactant state and the product state of ET. During the ET process, the high-frequency response of the electronic polarization will keep in equilibrium with the electron transferring, whereas the orientational polarization will keep in equilibrium with the field arising from ρ, σ_e, and σ_or of "r" state, say, ρ^r, $\sigma^\mathrm{r}_\mathrm{e}$, and $\sigma^\mathrm{r}_\mathrm{or}$. Thus the orientational polarization and the electronic polarization are given by

$$\mathbf{P}_\mathrm{or}(\mathbf{r}) = \chi_\mathrm{or}\mathbf{E}_\psi(\rho^\mathrm{r},\sigma^\mathrm{r}_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) \tag{9}$$

$$\mathbf{P}_\mathrm{e}(\mathbf{r}) = \chi_\mathrm{e}\mathbf{E}_\psi(\rho^\mathrm{p},\sigma_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) \tag{10}$$

because the electric field caused by the polarizations can be divided into two parts, the contribution from the solute charge distribution and that from the surface polarization densities, i.e.,

$$\mathbf{E}_\psi(\rho^\mathrm{r},\sigma^\mathrm{r}_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) = \mathbf{E}_\psi(\sigma^\mathrm{r}_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) + \mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{r}) \tag{11}$$

$$\mathbf{E}_\psi(\rho^\mathrm{p},\sigma_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) = \mathbf{E}_\psi(\sigma_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) + \mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{p}) \tag{12}$$

Using Eqs. (11) and (12) inversely, we get the final form of G, which is given in Eq. (31) of [15]:

$$\begin{aligned} G = {} & \langle\psi|\mathbf{H}_0|\psi\rangle - 1/2\int_V (\mathbf{P}_\mathrm{e}+\mathbf{P}_\mathrm{or})\cdot E_\psi(\mathbf{r},\rho^\mathrm{p})\cdot\mathbf{d}^3\mathbf{r} \\ & + 1/2\int_V \mathbf{P}_\mathrm{or}\cdot[\mathbf{E}_\psi(\rho^\mathrm{r},\sigma^\mathrm{r}_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) - \mathbf{E}_\psi(\rho^\mathrm{p},\sigma_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or})]\cdot\mathbf{d}^3\mathbf{r} \end{aligned} \tag{13}$$

When the system is in equilibrium state ($\rho^\mathrm{r} \to \rho^\mathrm{p}$), we have

$$\mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{r}) = \mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{p}) \tag{14}$$

$$\mathbf{E}_\psi(\rho^\mathrm{r},\sigma^\mathrm{r}_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) = \mathbf{E}_\psi(\rho^\mathrm{p},\sigma_\mathrm{e},\sigma^\mathrm{r}_\mathrm{or}) \tag{15}$$

Thus the last integral in Eq. (13) vanishes, and the equilibrium free energy expression is obtained:

$$G_\mathrm{eq} = \langle\psi|\mathbf{H}_0|\psi\rangle - 1/2\int_V (\mathbf{P}_\mathrm{e}+\mathbf{P}_\mathrm{or})\cdot\mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{r})\cdot\mathbf{d}^3\mathbf{r} \tag{16}$$

On the other hand, the total energy of the system can be expressed as the energy of the solute in vacuum plus the equilibrium electrostatic solvation free energy $\Delta G^\mathrm{eq}_\mathrm{sol}$, i.e., [16, 17]

$$G_\mathrm{eq} = \langle\psi|\mathbf{H}_0|\psi\rangle + \Delta G^\mathrm{eq}_\mathrm{sol} \tag{17}$$

so we get the expression of the equilibrium electrostatic solvation free energy as

$$\Delta G^\mathrm{eq}_\mathrm{sol} = -1/2\int_V (\mathbf{P}_\mathrm{e}+\mathbf{P}_\mathrm{or})\cdot\mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{r})\cdot\mathbf{d}^3\mathbf{r} \tag{18}$$

Clearly, in the equilibrium state, $\mathbf{P}_\mathrm{e}$ and $\mathbf{P}_\mathrm{or}$ are in the same direction. Using Eqs. (4) and (5), we can express $\Delta G^\mathrm{eq}_\mathrm{sol}$ as

$$\Delta G^\mathrm{eq}_\mathrm{sol} = -\frac{(\varepsilon_0 - 1)}{2(\varepsilon_0-\varepsilon_\infty)}\int_V \mathbf{P}_\mathrm{or}(\mathbf{r})\cdot\mathbf{E}_\psi(\mathbf{r},\rho^\mathrm{r})\cdot\mathbf{d}^3\mathbf{r} \tag{19}$$

SCRF approach for the calculation of the equilibrium electrostatic solvation free energy

At present, $\Delta G_{\mathrm{sol}}^{\mathrm{eq}}$ is usually calculated by SCF techniques. Now let us give a brief description for the SCF evaluation of $\Delta G_{\mathrm{sol}}^{\mathrm{eq}}$ as follows.

If the dielectric medium is homogeneous, we can rewrite the equilibrium free energy as [15, 18, 19]

$$\begin{aligned} G_{\mathrm{eq}} &= \langle\psi|\mathbf{H}_0|\psi\rangle - 1/2\int_V \mathbf{P}(\mathbf{r})\cdot\mathbf{E}_\psi(\mathbf{r})\mathbf{d}^3\mathbf{r} \\ &= \langle\psi|\mathbf{H}_0|\psi\rangle - 1/2\int_V \sigma(\mathbf{r})\cdot U(\mathbf{r})\mathbf{d}^2\mathbf{r} \\ &= \langle\psi|\mathbf{H}_0|\psi\rangle - 1/2\int_V \rho(\mathbf{r})\cdot U(\mathbf{r})\mathbf{d}^3\mathbf{r} \end{aligned} \tag{20}$$

where $U(\mathbf{r})$ is the electrostatic potential and $\rho(\mathbf{r})$ is the charge distribution in the cavity, with the condition that

$$\rho(\mathbf{r}) = \rho(\mathbf{r}) \quad \mathbf{r}\in V_{\mathrm{in}} \tag{21}$$

$$\rho(\mathbf{r}) = 0 \qquad \mathbf{r}\in V_{\mathrm{out}} \tag{22}$$

where V_{in} and V_{out} are respectively the volumes inside the cavity and outside the cavity. Combining Eqs. (17), (19)–(22), we have

$$\begin{aligned} \Delta G_{\mathrm{sol}}^{\mathrm{eq}} &= -\frac{(\varepsilon_0 - 1)}{2(\varepsilon_0 - \varepsilon_\infty)}\int_V \mathbf{P}_{\mathrm{or}}(\mathbf{r})\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{r}})\,\mathbf{d}^3\mathbf{r} \\ &= -1/2\int_{V_{\mathrm{in}}} \rho^{\mathrm{r}}(\mathbf{r})\cdot U(\mathbf{r})\,\mathbf{d}^3\mathbf{r} \end{aligned} \tag{23}$$

According to Onsager reaction field theory, the solute is embedded in a spherical cavity with radius a_0, surrounded by the continuous medium of dielectric constant ε_0. The dipole of the solute molecule will induce the solvent molecules to form a reaction field $\mathbf{R}$, and then the induced reaction field will in turn interact with the solute molecule dipole. In molecular orbital theory, when only a point dipole μ at the center of the sphere is considered [16], the equilibrium electrostatic solvation free energy is defined as the electrostatic interaction energy between the dipole of the solute and the reaction field arising from the solvent polarization. At present, the self-consistent reaction field method based on the Onsager model supplies an efficient approach to evaluating $\Delta G_{\mathrm{sol}}^{\mathrm{eq}}$.

In molecular orbital theory, the electrostatic solvent effect may be taken as a perturbation term, $\mathbf{H}_1$, added to the Hamiltonian of the isolated molecule, $\mathbf{H}_0$. Thus the total Hamiltonian can be written as

$$\mathbf{H}_{\mathrm{rf}} = \mathbf{H}_0 + \mathbf{H}_1 \tag{24}$$

The perturbation term $\mathbf{H}_1$ expresses the coupling between the solute dipole moment μ and the reaction field $\mathbf{R}$, that is

$$\mathbf{H}_1 = -\mu\cdot\mathbf{R} \tag{25}$$

while the reaction field $\mathbf{R}$ can be expressed as

$$\mathbf{R} = g\mu \tag{26}$$

where the constant g, which gives the strength of the reaction field, depends on both the dielectric constant of the solvent ε_0 and the radius of the spherical cavity a_0. According to Onsager [4],

$$g = 2(\varepsilon_0 - 1)/[(2\varepsilon_0 + 1)a_0^3)] \tag{27}$$

The energy of a solute molecule is calculated by solving the one-electron Fock equation. For a self-consistent field wave function, the effect of the reaction field can be incorporated as an additional term in the Fock matrix [10, 20], the resulting Fock equation is

$$(\mathbf{F}_0 - \mu\cdot\mathbf{R})\phi_{\mathrm{i}} = e_{\mathrm{i}}\phi_{\mathrm{i}} \tag{28}$$

where ϕ_{i} is the molecular orbital and e_{i} is the eigenvalue of ϕ_{i}. Solving these equations self-consistently, one can get the expression of the energy of a solute, G_{s}, by

$$G_{\mathrm{s}} = \langle\psi|\mathbf{H}_0|\psi\rangle = \langle\psi|\mathbf{H}_0|\psi\rangle - \mu\cdot\mathbf{R} \tag{29}$$

When the solvent polarization energy is included, the free energy of the system is given by [20]

$$G_{\mathrm{eq}} = G_{\mathrm{s}} + \mu\cdot\mathbf{R}/2 = \langle\psi|\mathbf{H}_0|\psi\rangle - \mu\cdot\mathbf{R}/2 \tag{30}$$

For the sake of comparison with Eq. (17), we get

$$\Delta G_{\mathrm{sol}}^{\mathrm{eq}} = -\mu\cdot\mathbf{R}/2 \tag{31}$$

Obviously, $\Delta G_{\mathrm{sol}}^{\mathrm{eq}}$, which stands for the equilibrium electrostatic solvation free energy of the system, is proportional to the product of the dipole moment of the solute and the reaction field formed from the medium polarization. Combining Eqs. (31) and (23), we can conveniently get the following equation:

$$\begin{aligned} \Delta G_{\mathrm{sol}}^{\mathrm{eq}} &= -\frac{(\varepsilon_0 - 1)}{2(\varepsilon_0 - \varepsilon_\infty)}\int_V \mathbf{P}_{\mathrm{or}}(\mathbf{r})\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{r}})\,\mathbf{d}^3\mathbf{r} \\ &= -1/2\int_{V_{\mathrm{in}}} \rho^{\mathrm{r}}(\mathbf{r})\cdot U(\mathbf{r})\,\mathbf{d}^3\mathbf{r} = -1/2\boldsymbol{\mu}\cdot\mathbf{R} \end{aligned} \tag{32}$$

Equation (32) gives the relationship among the interaction energies between the total polarization and the electric field, the charge distribution, and the electrostatic potential, as well as the solute dipole and the reaction field. So, in the following section, we will use this relationship to derive the expressions of the non-equilibrium free energy and the solvent reorganization energy.

Non-equilibrium solvation free energy and solvent reorganization energy

Non-equilibrium solvation free energy

Typically, the solvent electronic polarization due to the bound electron in the polar solvent molecules adjusts quickly to any changes in, e.g., a reactive solute system or the solvent. In other words, the motions of the solvent electrons are faster than those for the solute. Thus we can invoke a Born-Oppenheimer description for $\mathbf{P}_{\mathrm{e}}$ and employ the variational principle to get the following expression (Eq. 2.6 of [14]):

$$\delta G[\psi,\mathbf{P}_{\mathrm{e}},\mathbf{P}_{\mathrm{or}}]/\delta\mathbf{P}_{\mathrm{e}} = 0 \tag{33}$$

which reads

$$\begin{aligned} \mathbf{P}_{\mathrm{e}}(\mathbf{r}) = \chi_{\mathrm{e}}\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}}) - \chi_{\mathrm{e}}\int_V \mathbf{T}(\mathbf{r},\mathbf{r}')\cdot[\mathbf{P}_{\mathrm{e}}(\mathbf{r}') \\ + \mathbf{P}_{\mathrm{or}}(\mathbf{r}')]\,\mathbf{d}^3\mathbf{r}' \end{aligned} \tag{34}$$

Due to the cavity, this is an integral equation with boundaries, and it is very difficult to solve. Under the assumption of the spherical cavity and the monopole fields, we can neglect the "dielectric image" effect and extend the volume integral over V to include the cavity. Therefore, we can invert Eq. (34) for arbitrary ψ and $\mathbf{P}_{\mathrm{or}}$ to obtain

$$\mathbf{P}_{\mathrm{e}}^{\mathrm{eq}}(\mathbf{r}) = \frac{1}{4\pi}\left(1-\frac{1}{\varepsilon_\infty}\right)[\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}}) - 4\pi\mathbf{P}_{\mathrm{or}}(\mathbf{r})] \tag{35}$$

With this $\mathbf{P}_{\mathrm{e}}^{\mathrm{eq}}(\mathbf{r})$, the second term in Eq. (13) becomes [14]

$$\begin{aligned} &-\frac{1}{2}\int_V \left\{\frac{1}{4\pi}\left(1-\frac{1}{\varepsilon_\infty}\right)[\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}}) \right.\\ &\qquad \left. - 4\pi\mathbf{P}_{\mathrm{or}}] + P_{\mathrm{or}}\right\}\cdot \mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\mathbf{d}^3\mathbf{r} \\ &\quad = -\frac{1}{8\pi}\left(1-\frac{1}{\varepsilon_\infty}\right)\int_V \left|\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\right|^2\mathbf{d}^3\mathbf{r} \\ &\qquad -\frac{1}{2\varepsilon_\infty}\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\mathbf{d}^3\mathbf{r} \end{aligned} \tag{36}$$

In the last term of Eq. (13), we have

$$\begin{aligned} 1/2&\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\rho^{\mathrm{r}},\sigma_{\mathrm{e}}^{\mathrm{r}},\sigma_{\mathrm{or}}^{\mathrm{r}})\mathbf{d}^3\mathbf{r} \\ &= 1/2\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{P}_{\mathrm{or}}/\chi_{\mathrm{or}}\mathbf{d}^3\mathbf{r} \\ &= 2\pi/(\varepsilon_0-\varepsilon_\infty)\int_V |\mathbf{P}_{\mathrm{or}}|^2\mathbf{d}^3\mathbf{r} \end{aligned} \tag{37}$$

$$\begin{aligned} -1/2&\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\rho^{\mathrm{p}},\sigma_{\mathrm{e}},\sigma_{\mathrm{or}}^{\mathrm{r}})\mathbf{d}^3\mathbf{r} \\ &= -1/(2\varepsilon_\infty)\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\mathbf{d}^3\mathbf{r} \\ &\quad -1/(2\varepsilon_\infty)\int_V \mathbf{d}^3\mathbf{r}\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}_{\mathrm{or}}(\mathbf{r}')\mathbf{d}^3\mathbf{r}' \\ &\quad -1/(2\varepsilon_\infty)\int_V \mathbf{d}^3\mathbf{r}\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}_{\mathrm{e}}(\mathbf{r}')\mathbf{d}^3\mathbf{r}' \end{aligned} \tag{38}$$

Neglecting the last term in Eq. (38), the non-equilibrium free energy $G_{\mathrm{n-eq}}$ is expressed in the following form (Eq. 2.12 of [15]):

$$\begin{aligned} &G[\psi,\mathbf{P}_{\mathrm{e}}^{\mathrm{eq}}[\psi,\mathbf{P}_{\mathrm{or}}],\mathbf{P}_{\mathrm{or}}] \\ &\quad = \langle\psi|\mathbf{H}_0|\psi\rangle - \frac{1}{8\pi}\left(1-\frac{1}{\varepsilon_\infty}\right)\int_V \left|\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\right|^2\mathbf{d}^3\mathbf{r} \\ &\qquad -\frac{1}{\varepsilon_\infty}\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\mathbf{d}^3\mathbf{r} + G_{\mathrm{or}} \end{aligned} \tag{39}$$

where G_{or} is the self-free energy associated with the orientational polarization [15]. In our case, G_{or} will keep invariant in both the equilibrium and non-equilibrium states:

$$\begin{aligned} G_{\mathrm{or}} &= 2\pi/(\varepsilon_0-\varepsilon_\infty)\int_V |\mathbf{P}_{\mathrm{or}}|^2\mathbf{d}^3\mathbf{r} \\ &\quad + 1/(2\varepsilon_\infty)\int_V \mathbf{d}^3\mathbf{r}\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}_{\mathrm{or}}(\mathbf{r}')\mathbf{d}^3\mathbf{r}' \end{aligned} \tag{40}$$

Dipole-reaction field interaction model for calculation of solvent reorganization energy

As far as we are concerned, in a self-exchange reaction,

$$\mathrm{B}^- + \mathrm{B} = \mathrm{B} + \mathrm{B}^-$$

the following equations are satisfied:

$$\langle\psi^{\mathrm{r}}|\mathbf{H}_0|\psi^{\mathrm{r}}\rangle = \langle\psi^{\mathrm{p}}|\mathbf{H}_0|\psi^{\mathrm{p}}\rangle \tag{41}$$

$$\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{r}}) = -\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}}) \tag{42}$$

$$\int_V \left|\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{r}})\right|^2\mathbf{d}^3\mathbf{r} = \int_V \left|\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{p}})\right|^2\mathbf{d}^3\mathbf{r} \tag{43}$$

Equation (41) means that the reactant state ψ^{r} and the product state ψ^{p} have the same expectation value of the vacuum Hamiltonian, and Eqs. (42) and (43) indicate that the electric field just reverses its direction, with the magnitude invariant. Assuming that the orientational polarization $\mathbf{P}_{\mathrm{or}}$ has the same self-energy before and after the transition from ψ^{r} to ψ^{p} of the transferring electron, according to Eq. (2), we can easily obtain a new expression of the solvent reorganization energy, which is the difference between the non-equilibrium free energy and the equilibrium free energy, as

$$\lambda_{\mathrm{o}} = G_{\mathrm{n-eq}} - G_{\mathrm{eq}} = 2/\varepsilon_\infty\int_V \mathbf{P}_{\mathrm{or}}\cdot\mathbf{E}_\psi(\mathbf{r},\rho^{\mathrm{r}})\mathbf{d}^3\mathbf{r} \tag{44}$$

Combining Eqs. (44) and (32), we reach the final expression of λ_{o}:

$$\begin{aligned} \lambda_{\mathrm{o}} &= -\frac{4(\varepsilon_0-\varepsilon_\infty)}{(\varepsilon_0-1)\varepsilon_\infty}\Delta G_{\mathrm{sol}}^{\mathrm{eq}} \\ &= -\frac{2(\varepsilon_0-\varepsilon_\infty)}{(\varepsilon_0-1)\varepsilon_\infty}\int_{V_{\mathrm{in}}} \rho^{\mathrm{r}}(\mathbf{r})\cdot U(\mathbf{r})\mathbf{d}^3\mathbf{r} \\ &= \frac{2(\varepsilon_0-\varepsilon_\infty)}{(\varepsilon_0-1)\varepsilon_\infty}\boldsymbol{\mu}\cdot\mathbf{R} \end{aligned} \tag{45}$$

Equation (45) gives the relationship between the equilibrium electrostatic solvation free energy and the solvent reorganization energy of the self-exchange ET reactions. From this relationship, we learn that the solvent reorganization energy can be obtained from the equilibrium electrostatic solvation free energy evaluated through SCRF approach and ab initio calculations, and that it is applicable to perform the direct calculation of the solvent reorganization energy by using SCRF approach. For aqueous solution, $\varepsilon_\infty = 1.8$ and $\varepsilon_0 = 78.5$ [22], the expression of λ_{o} is simplified to

$$\lambda_{\mathrm{o}} = 1.10\,\boldsymbol{\mu}\cdot\mathbf{R} \tag{46}$$

From this expression, we see that the solvent reorganization energy is proportional to the product of the solute dipole and the reaction field, so we call our calculating approach of λ_{o} is the dipole-reaction field interaction model. As a summary, we give a schematic depiction of our dipole-reaction field model in Fig. 1.

Before the ET process, the dipole $\boldsymbol{\mu}^{\mathrm{r}}$ of the solute induces a solvent reaction field $\mathbf{R}^{\mathrm{r}}$. Mutual polarizations between $\boldsymbol{\mu}^{\mathrm{r}}$ and $\mathbf{R}^{\mathrm{r}}$ make the solute-solvent system reach an equilibrium state (Fig. 1a). As long as the transfer-

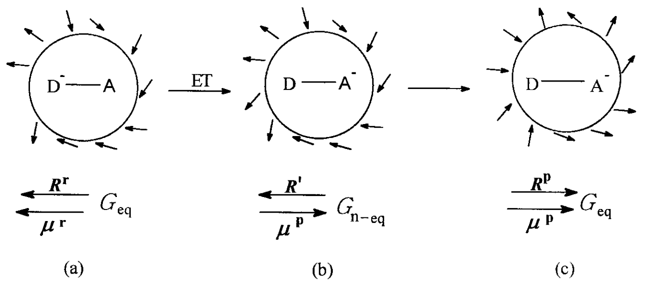


Fig. 1a–c. A schematic description of the dipole-reaction field interaction in: **a** the equilibrium state of reactant; **b** the non-equilibrium state; **c** the equilibrium state of product

ring electron "jumps" from the donor (D) to the acceptor (A), the charge distribution of the solute changes from ρ^{r} to ρ^{p}; thus the solute dipole changes, and so does the reaction field. If we denote the solute dipole and the reaction field after ET as $\boldsymbol{\mu}^{\mathrm{p}}$ and $\mathbf{R}'$, respectively (Fig. 1b), then for a self-exchange reaction, when there is only a simple electron transferring from D to A, it is safe for us to assume that

$$\boldsymbol{\mu}^{\mathrm{p}} = -\boldsymbol{\mu}^{\mathrm{r}} \tag{47}$$

and the difference of the dipole moment before and after ET reads

$$\Delta\boldsymbol{\mu} = \boldsymbol{\mu}^{\mathrm{p}} - \boldsymbol{\mu}^{\mathrm{r}} = -2\boldsymbol{\mu}^{\mathrm{r}} \tag{48}$$

On the other hand, because the low-frequency orientational polarization of solvents cannot keep up with the electronic transition, the system arrives at a non-equilibrium state, and the reaction field reduces to $\mathbf{R}'$. Although the component of the reaction field contributed from the high-frequency electronic polarization of the solute inverses, the component due to the orientational polarization is dominant, so we can expect that $\mathbf{R}'$ has the same direction as $\mathbf{R}^{\mathrm{r}}$ and only with the magnitude changed.

Combining Eqs. (26), (27), (45), and (48), we have

$$\lambda_{\mathrm{o}} = \frac{2(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 - 1)\varepsilon_\infty} g\boldsymbol{\mu}^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)}{(2\varepsilon_0 + 1)\varepsilon_\infty a_0^3} |\Delta\boldsymbol{\mu}|^2 \tag{49}$$

Equation (49) indicates that the solvent reorganization energy is proportional to $|\Delta\boldsymbol{\mu}|^2/a_0^3$, which is consistent with the conclusions obtained by Ooshika [23], Lippert [24], and Zwan and Hynes [25] in discussing some other problems, e.g., the time-dependent fluorescence solvent shift [25].

However, owing to the mutual polarization between the solute and the polar solvents, the value of $\boldsymbol{\mu}$ is usually greatly different from that in vacuum. So it should be mentioned that the dipole moment $\boldsymbol{\mu}$ in Eq. (46) is a quantity after SCRF calculation. Moreover, since ET system is generally an ionic system, the electrostatic interaction of an ET system can be divided into the dipole-reaction interaction energy, and a Born charge term which is the interaction energy between the molecular ion and the polar solvents. We denote the Born charge term as $E_{(\mathrm{Born})}$, and express it as [16]

$$E_{(\mathrm{Born})} = -\frac{\varepsilon_0 - 1}{2\varepsilon_0}\frac{Q^2}{a_0}$$

where Q is the total charge of the solute molecular ion. As shown in Fig. 1, the net charge on the solute molecule, or the "supermolecule", will remain constant when an electron transfers from D to A in the spherical cavity. Based on the assumption of fixed spherical cavity radius, the Born charge term remains invariant throughout the ET process; thus the Born charge term does not contribute to the solvent reorganization energy. This is the reason why we only discuss the dipole-reaction field interaction throughout this work.

In the calculation of λ_{o}, a few methods based on ab initio calculation have been developed recently. Liu and Newton presented one approach to the calculation of solvent reorganization energy using the SCRF technique and Delphi Poisson equation solver [5]. The self-consistent reaction field technique is employed in both Newton's work and ours. Unlike the treatment in Newton's work, which solves the Poisson equation, our method only needs the SCRF calculation associated with the Onsager model. Under the spherical cavity approximation in our work, the calculation has been greatly simplified. Thus we can explicitly express the relationship between the solvent reorganization energy and the equilibrium solvation free energy and evaluate the solvent reorganization energy through a "single point" calculation of the solvent effects. This treatment makes our model much easier to use. A disadvantage of our model is that the application is confined to the sphere-shaped systems. The model remains to be modified for the non-sphere systems.

In addition, by replacing a suitable average value of $\boldsymbol{\mu}$ for the dipole moment before and after ET, say, $\boldsymbol{\mu}^{\mathrm{r}}$ and $\boldsymbol{\mu}^{\mathrm{p}}$ respectively, we can extend the application of Eq. (49) to the cross reaction:

$$\lambda_o = \frac{(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 - 1)\varepsilon_\infty} g\left(|\boldsymbol{\mu}^{\mathrm{p}}|^2 + |\boldsymbol{\mu}^{r}|^2\right) \tag{50}$$

Since the evaluation of λ_{o} only involves the cavity radius as well as the dipole moment after the SCRF calculation, it is very easy to perform. However, it should be mentioned that in the case that the direction of $\boldsymbol{\mu}$ and electron transfer does not fall on the same line, the dipole moment $\boldsymbol{\mu}$ used in Eq. (49) actually is its component in the direction of electron transfer.

As noted previously, in the derivation of Eq. (35), we ignored the boundary condition associated with the cavity. Actually, we can obtain a slightly different expression of $\mathbf{P}_{\mathrm{e}}^{\mathrm{eq}}$ by taking the proper boundary condition into account. (see Eq. (2.20) in [26]). Following suitable treatment, we may reach another expression of λ_{o} which differs from Eq. (49) by a factor close to unity. Given the approximations of spherical cavity and point-dipole invoked in our derivation, we think it is reasonable to neglect the boundary condition in our present paper. The more precise derivation regarding boundary conditions will be presented in later work.

In the following section, we will use Eq. (45), or equivalently Eq. (46), to evaluate λ_{o} for the selected model systems.

Test calculation

Inorganic donor-acceptor complex

Geometry optimization of the encounter complex. Using the unrestricted Hartree-Fock (UHF) wave function, we optimize the donor D, the acceptor A, and the encounter complex D...A at the level of HF/6–31G or HF/DZP (DZP represents the Dunning's (9s,5p)/(3s,2p) basis set with the polarization function on all atoms). The optimized bond parameters for the donors and the acceptors are listed in Table 1. The optimized structure of the encounter complex $A_3\ldots A_3^-$ or $AB_2\ldots AB_2^-$, which gives the largest stabilization energy (Table 2) among several nuclear configurations, has been shown in Fig. 2.

Solvent reorganization energy. In this work, in order to estimate the solvent reorganization energy, we need to determine the cavity radius at first. We employ Hyperchem package (Hyperchem programme) to determine a_0. Our procedure is as follows:

1. Replace water molecules with the optimized encounter complex in a water periodic box in Hyperchem, with the minimum distance between the solvent and solute atoms being 0.23 nm.
2. Use the number n, actually an average value, of the substituted water molecules, to obtain the solute molecular volume V_M, $V_M = nV_m$, with $V_m = 0.02992\ \text{nm}^3$ being the molecular volume of H_2O.
3. Use Eq. (51) to determine the equivalent cavity radius a_0 of the solute:

$$a_0 = (3V_M/4\pi)^{1/3} \tag{51}$$

By using the cavity radius determined by Eq. (51), we have performed the SCRF calculations and obtained the values of λ_o for a series of redox couples at the level of UHF/DZP. For the O_2/O_2^- and the NO/NO^+ systems, we take an average value of several nuclear configurations of encounter complexes [30]. For the other systems, we choose the nuclear configurations as shown in Fig. 2 to perform the calculation of λ_o. Results are listed in Table 3.

In experimental studies, some authors measured ET rate constants of redox systems in aqueous solution, and used empirical models to estimate the solvent reorganization energies [31–33] (Table 3). We can see that our results are in good agreement with those values estimated by other authors.

Discussion on the single-sphere approximation. As mentioned previously, we suppose that the encounter complex is placed into a single sphere cavity, and the solvent

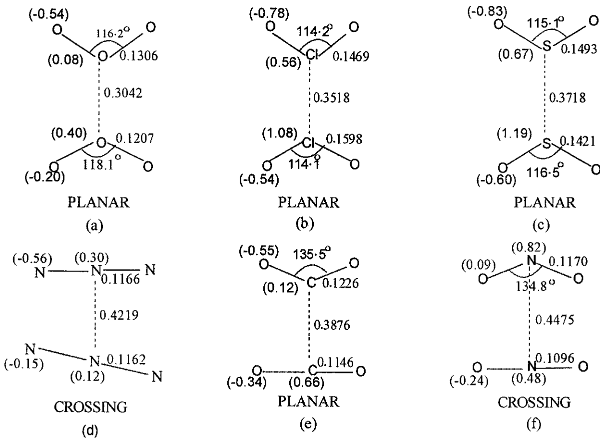


Fig. 2. Optimized geometries (C_{2v}) of some encounter complexes $A_3\ldots A_3^-$ or $AB_2\ldots AB_2^-$. *The value within parentheses* is the net charge on atom. "Planar" means all the six atoms are in a same plane, whereas "crossing" indicates the donor moiety and the acceptor moiety are in 90° orientation

Table 1. Bond parameters of species[a]

System	Bond length	Bond angle	System	Bond length	Bond angle
O_2	0.1195 (0.1207)		O_2^-	0.1347 (0.1347)	
NO	0.1165 (0.1151)		NO^+	0.1053 (0.1063)	
O_3	0.1207 (0.1278)	118.9 (116.8)	O_3^-	0.1307 (0.134)	116.0 (113)
N_3	0.1166 (0.1182)	180.0	N_3^-	0.1163 (0.1188)	180.0
NO_2	0.1169 (0.1194)	135.8 (133.9)	NO_2^+	0.1096 (0.1104)	180.0
CO_2	0.1145 (0.1162[b])	180.0 (180.0[b])	CO_2^-	0.1228	135.1
SO_2	0.1416 (0.1431)	118.4 (119.3)	SO_2^-	0.1497 (0.1520)	114.5 (116.0)
ClO_2	0.1467 (0.1470)	115.9 (117.4)	ClO_2^-	0.1598 (0.1590)	113.2 (114.0)

[a] Except where noted, the values within parentheses are from ref. 28, bond lengths are in nm and bond angles are in degree
[b] From [29]

Table 2. Stabilization energy E_s[a] and dipole moment μ for $A_3\ldots A_3^-$ and $AB_2\ldots AB_2^-$ encounter complexes

System	Configuration[b]	μ/debye	E_s/kJ · mol^{-1}	System	Configuration[b]	μ/debye	E_s/kJ · mol^{-1}
O_3/O_3^-	Planar	9.33	15.9	N_3/N_3^-	Crossing	9.81	11.7
NO_2^+/NO_2	Crossing	8.94	17.6	SO_2/SO_2^-	Planar	9.97	28.4
CO_2/CO_2^-	Planar	9.97	12.6	ClO_2/ClO_2^-	Planar	10.17	29.4

[a] $E_s = E_t(D) + E_t(A) - E_t(D\ldots A)$
[b] See Fig. 2

Table 3. SCRF results of the solvent reorganization energy[a]

System	O_2^-/O_2	NO^+/NO	O_3/O_3^-	N_3/N_3^-	NO_2^+/NO_2	CO_2/CO_2^-	SO_2/SO_2^-	ClO_2/ClO_2^-
a_o/nm	0.301	0.295	0.322	0.336	0.346	0.329	0.340	0.346
μ/debye	11.04[b]	10.39[c]	10.16	10.62	9.49	11.03	11.44	11.22
$\lambda_o/kJ \cdot mol^{-1}$	221.5	204.0	194.7	186.4	149.2	214.1	212.0	193.8
$\lambda'_o/kJ \cdot mol^{-1}$	214.2[d]	205.0[e]	200.8[d]	189.1[d]	150.6[f]	200.8[d]	180.8[d]	180.8[d]

[a] HF/DZP values in this work
[b] For a T-shaped configuration
[c] For a co-linear configuration
[d] From [31]
[e] From [32]
[f] From [33]

reorganization energy actually depends only on the single-sphere radius. On the other hand, we consider the well-known Marcus two-sphere model, which gives the solvent reorganization energy as follows [1–3]:

$$\lambda_o = \Delta e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d_{DA}} \right) \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \tag{52}$$

where Δe is the transferred charge, and r_D, r_A, d_{DA} are the donor sphere radius, the acceptor sphere radius, and the ET distance, respectively. We assume that the two spheres have the same radius and are in contact with each other, i.e., $r_D = r_A = a$ and $d_{DA} = 2\ a$. By taking $\varepsilon_\infty = 1.8$ and $\varepsilon_0 = 78.5$ for aqueous solution, we can simplify Eq. (52) to the following form:

$$a/\mathrm{nm} = \frac{38.296}{\lambda_o/\mathrm{kJ} \cdot \mathrm{mol}^{-1}} \tag{53}$$

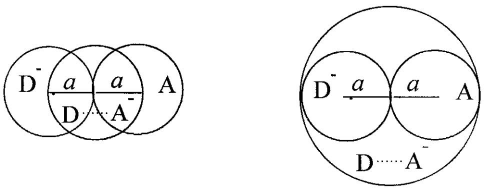
In Fig. 3, we draw the sphere cavity for both the single-sphere case and two-sphere case. We can see that the suitable value of a_0 in the single-sphere case should lie in the range from a (Fig. 3a) to $2a$ (Fig. 3b). Moreover, if we define a single-sphere which has a cavity volume equal to the total volume of the two-sphere, i.e.,

$$V_c = 4\pi r_c^3/3 = 2 \times 4\pi a^3/3 \tag{54}$$

we can obtain the equivalent single-sphere radius

$$r_c = \sqrt[3]{2}\ a \tag{55}$$

Substituting our SCRF values of λ_o into Eq. (53), we can obtain the values of two-sphere radius for different redox couples. The values of a_0, a, and r_c are listed in Table 4 and presented in Fig. 4. It can be seen that a_0, the radius of the single-sphere used in he SCRF calculation, is indeed in the range $a < a_0 < 2a$, and is close to r_c. By comparing the value of a from our SCRF results with the two-sphere radius a' estimated previously by other authors (Table 4), we have found that the difference between a and a' is acceptably small.



(a) a_0=a (b) a_0=$2a$

Fig. 3a,b. A schematic description of the relationship between single-sphere cavity and the two-sphere cavity

Application to intramolecular ET systems with π-type donor and the π type acceptor

ET reactions between the π-type donor and the π-type acceptor have been widely used to investigate the ET mechanisms on the basis of the two-site model. For the existence of π orbital, allyl radical and its anion have been used as the acceptor and the donor by several groups [34, 35]. In order to check the suitability of the SCRF model for the intramolecular ET system with a not-too-long bridge, we select the model systems $(CH_2)_2C\text{–}(\text{–}CH_2\text{–})_n\text{–}C(CH_2)_2$ ($n = 1 \sim 3$), as shown in Fig. 5, to calculate the solvent reorganization energy. In preparing the starting geometry, we optimize the structures of 2-methylallyl radical ($CH_3\text{–}C(CH_2)_2$) and its

Table 4. Two-sphere radius estimated from the SCRF results

System	O_2^-/O_2	NO^+/NO	O_3/O_3^-	N_3/N_3^-	NO_2^+/NO_2	CO_2/CO_2^-	SO_2/SO_2^-	ClO_2/ClO_2^-
a_o/nm[a]	0.301	0.295	0.322	0.336	0.346	0.329	0.340	0.346
a/nm[b]	0.173	0.188	0.197	0.205	0.257	0.179	0.181	0.197
r_c/nm	0.218	0.237	0.248	0.259	0.323	0.225	0.228	0.249
a'/nm[c]	0.177	0.187[d]	0.19	0.20	0.254[d]	0.19	0.21	0.21

[a] Single-sphere cavity radius used for the SCRF calculation
[b] Two-sphere cavity radius from our SCRF calculation of solvent reorganization energy
[c] From [33] except where noted
[d] Recalculated from the experimentally estimated value by using Eq. (53) and λ'_o in Table 3

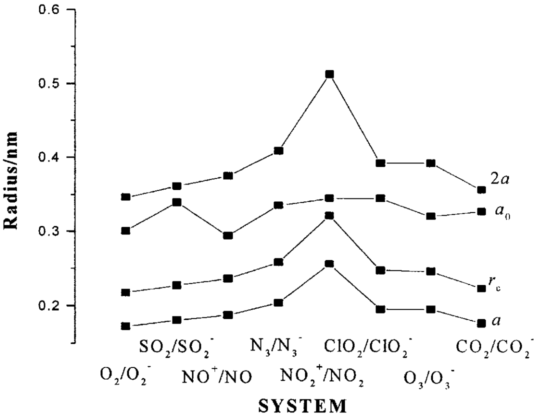


Fig. 4. a_0, a, $2a$, and r_c for different redox systems

anion at the level of UHF/DZP. Thus we can determine the bond parameters of the π-type donor and acceptor as shown in Fig. 6. All the C-H and the C–C bond lengths of the intervening bridge in Fig. 5 have been set to 0.1100 nm and 0.1530 nm respectively, and in the bridge, all the bond angles have been set tetrahedral. The C-C bond length linking the allyl radical to the bridge is 0.1527 nm, whereas that linking allyl anion to the bridge is 0.1512 nm, the bond lengths being obtained from the geometry optimizations (Fig. 6). As shown in Fig. 5, all the bridges employ *trans*-staggered carbon skeletons, with terminal donor/acceptor group in perpendicular orientation to the bridge skeleton plane.

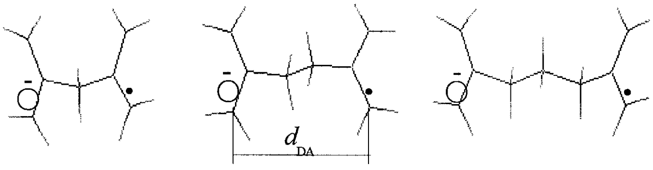


Fig. 5. Model systems for intramolecular ET

For the determination of the cavity radius of the intramolecular ET systems, the following procedure has been adopted: determining the smallest box (with box parameters l_1, l_2, and l_3) enclosing the solute by Hyperchem package; calculating the equivalent cavity volume by

$$V_M = (l_1 + 0.23\,\mathrm{nm})(l_2 + 0.23\,\mathrm{nm})(l_3 + 0.23\,\mathrm{nm}) \tag{56}$$

where 0.23 nm is twice the van der Waals radius of H atom; and using Eq. (49) to obtain the cavity radius a_0. In such a way, the only adjustable parameter a_0 is essentially not arbitrary in our calculations. The values of a_0 for the ionic systems in Fig. 5 have been listed in Table 5.

SCRF calculations have been carried out at the level of UHF/DZP. Electron localization in the ionic systems has been achieved due to the bond parameter differences between the donor group and the acceptor group. The equilibrium solvation free energy (actually the electrostatic interaction energy), the dipole moment after the SCRF calculation, and the solvent reorganization energy according to Eq. (52) have also been listed in Table 5.

Let us consider the two-sphere model again. In Eq. (56), we take the distance between the allylyl radical fragment and the allylyl anion fragment to be d_{DA} (see Fig. 5). Obviously, in our case, $r_D = r_A = a$, and the value of a for different systems becomes

$$a = \frac{76.592 d_{DA}}{d_{DA} \cdot \lambda_o + 76.592} \tag{57}$$

In Eq. (57), a and d are in nm and λ_o in kJ · mol^{-1}. Using the values from the SCRF calculation, we have obtained the two-sphere radius as listed in Table 5.

From Table 5 one can find that the values of a for different systems are slightly different. Since the shape of D-C$_1$-A is the most spherical among those three systems, it is reasonable for us to choose 0.261 nm as Marcus two-sphere radius. On the other hand, a frequently adopted method for estimating a_0 is to measure the greatest dimension of the donor and acceptor [20]. In our case, the greatest dimension in both allylyl radical and allylyl anion is the internuclear distance between H′ atom and H″ atom (see Fig. 6). This value is about 0.430 nm from the donor/acceptor geometry optimization. Adding the van der Waals radius of H atom (0.115 nm) to half of the greatest dimension, we obtain the radius value of 0.330 nm. However, if the greatest dimension model is employed, we will overestimate the

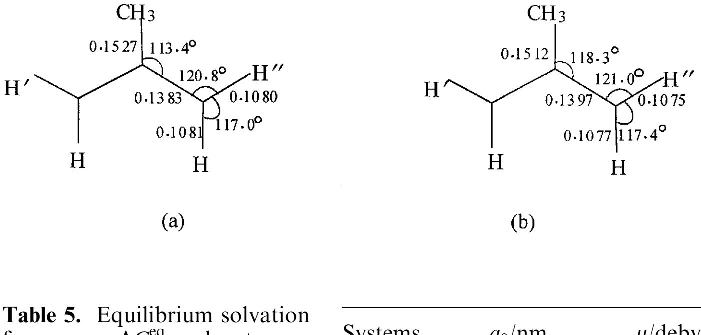


Fig. 6a, b. Bond parameters of: **a** the radical; **b** the anion used in the geometry preparations of the model systems in Fig. 5

Table 5. Equilibrium solvation free energy ΔG^{eq}_{sol}, solvent reorganization energy, and the two-sphere radius

Systems	a_0/nm	μ/debye	ΔG^{eq}_{sol}	λ_o/kJ · mol^{-1}	a/nm	d_{DA}/nm
D-C$_1$-A	0.385	8.10	−32.86	72.29	0.261	0.349
D-C$_2$-A	0.412	12.65	−65.33	143.73	0.255	0.497
D-C$_3$-A	0.424	15.20	−87.12	191.66	0.237	0.600

donor/acceptor sphere radius due to the planar donor/acceptor structure. Therefore, the value of 0.261 nm from the SCRF calculation of solvent reorganization energy in this work is a suitable estimation for radius of the donor/acceptor sphere.

Conclusion

In this paper, we have described the expressions of the equilibrium free energy, the equilibrium electrostatic solvation free energy, and the non-equilibrium free energy in detail. Based on the Onsager reaction field model, we proposed the dipole-reaction field interaction model for the solvent reorganization energy calculation. After necessary derivation, we have established the relationship between the solvent reorganization energy and the equilibrium electrostatic solvation free energy. It enables us to evaluate the solvent reorganization energy through the standard calculation of equilibrium electrostatic solvation free energy. Employing Onsager reaction field theory and the self-consistent reaction field technique, we have conveniently expressed the solvent reorganization energy to the final form of Eq. (45). For the self-exchange ET, an alternative form in which the factor $(|\Delta\mu|^2/a_0^3)$ is included, has been given in Eq. (49). The dipole-reaction field interaction model permits the direct evaluation of the solvent reorganization energy by using the molecular orbital SCF technique. Clearly, the solvent reorganization energy in our treatment strongly depends on the radius of the spherical solvent cavity. In our calculation, we have made an attempt to determine the cavity radius in some more reliable way, and the results reflect the suitability of our procedure.

By applying the SCRF calculations to several solute-solvent systems, values of solvent reorganization energy have been estimated. The calculated solvent reorganization energies show good agreement with the experimental observations. It can be seen that in the dipole-reaction field interaction model, there exists only one adjustable parameter, say, the cavity radius. For the solvent reorganization energy of the inorganic couples, the errors are found in an acceptable range. However, in the cases of $(CH_2)_2C\text{–}(\text{–}CH_2\text{–})_n\text{–}C(CH_2)_2$ ($n = 1 \sim 3$) systems, the results show that the solvent reorganization energy strongly depends on the bridge length, and solvent reorganization energies for different systems lead to slightly different two-sphere radii.

In our present work, we confine our discussions to the self-exchange ET. In fact, this method can be extended to the cross ET reaction. Further work is in preparation.

All the ab initio calculations have been carried out with the HONDO95.6 package [13].

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