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New formulation for nonequilibrium solvation: a consistent expression of electrostatic free energy by different methods and its application to solvent reorganization energy and spectral shifts in solution

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Abstract

We present an overview of the current status of the theories of nonequilibrium solvation and their generalizations in modern chemistry. Based on the continuous medium theory, the nonequilibrium electrostatic free energy has been reformulated. We adopt three different methods, the multi-step charging approach, the field superposition principle, and the interaction energy method, to achieve the consistent expression of electrostatic free energy of nonequilibrium. The misunderstandings on the interaction energy between the polarization field and its source (free) charge have been made clear. Derivations reveal a significant feature that this interaction energy is quite different from that between two independent fields. In the present work, the solvation free energy is found entirely contributed from the interaction between the solvent polarization and its source charge, whereas the self-energy of the polarization field is deduced to zero. The spectral shifts for light absorption and emission, and solvent reorganization energy for electron transfer in solution, have been derived to new forms differing from the conventional ones. The newly developed two-sphere model for electron transfer has been employed to investigation of the intramolecular electron transfer in Closs–Miller system.

Keywords: Continuous medium theory; Nonequilibrium solvation; Polarization field; Electron transfer; Spectral shift

1. Introduction

Because most of chemistry and biochemistry occur in solution, and the solvent can have a major effect on the position of chemical equilibrium and on reaction rates, incorporation of the solvent effects into chemical models has been of great interest for several decades. In this area, continuum models have been playing a key role up till now. There are several models for the equilibrium solvation, including Onsager spherical model [1] and other arbitrary cavity ones [2–13]. Introducing the numerical solution of the appropriate electrostatic potential into the popular quantum chemical packages yields different equilibrium solvation models [10,11,14]. For the importance of evaluations for the solvent reorganization energy (SRE) in electron transfer (ET) and the spectral shifts in solution, particular attentions have been paid to nonequilibrium solvation in the last decades. Marcus introduced the nonequilibrium concept in 1950s [15–17], based on the separation of the orientational (we use orientational to represent the total of orientational and atomic) and electronic polarizations of solvent. This led to great progresses for people to understand the physics of fast processes in solution. Following the progresses of computational technique, several continuum models were proposed by means of more accurate numerical solutions for the cases of arbitrary cavities [18–24]. At present, a feature common to all the continuum solvation approximations is

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that the solute–solvent interactions are described in terms of the solute–reaction field interactions. The reaction field is due to the solvent polarization perturbed by the presence of solute, and the reaction field in turn perturbs the solute, until self-consistence is achieved. The reaction field is usually computed by solving the suitable Poisson equations.

We noticed that the expression for electrostatic free energy of nonequilibrium state of solute–solvent system was originally obtained by means of virtual work principle, and then employed to derive the generalized formulations of such as SRE for ET and spectral shifts for light absorption and emission [15–17,25,26]. On the other hand, Ooshika [27], Mataga [28] and Lippert [29] developed the single-sphere model. Lippert–Mataga relationship developed in this way was widely employed in the predictions of the solvent effects of spectra. A slightly different method was developed by Lee and Hynes at the end of 1980s [30]. In Hynes' approach, Felderhof's equation [31–33] for the solvation free energy of electrostatic field was modified. Similar treatments could be found in the subsequent literatures [18,34–36] in which the solvent effects of ultrafast processes were intensively studied. These theories mutually support each other and give good qualitative or semi-quantitative descriptions for nonequilibrium solvent effects so far.

Doubts arose recently. Basilevsky and Newton [22,23] developed a numerical method to evaluate SRE and applied it to the well-known Closs–Miller ET systems [37,38] by using conventional Marcus theory. However, the calculated values of SRE for the biphenyl–bridge–naphthalene system were exaggerated by a factor of about 2 than those fitted from the experimental rate constants [22]. In 1989, Johnson and Miller [39] tried to use Marcus two-sphere formula to evaluate SRE of the same biphenyl–bridge–naphthalene system. From the experimental value of SRE, 0.75 eV, a mean value of 0.507 nm for the cavity radii of biphenyl and naphthalene was obtained. Comparing with the available values of 0.39 nm for biphenyl and 0.37 nm for naphthalene from structural data, these authors were puzzled in finding an adequate explanation for such a large discrepancy. Although Johnson and Miller [39] attempted to apply more sophisticated alternatives to Marcus two-sphere formula, which retain the dielectric continuum approximation but use elliptical cavities, no method could substantially improve the result. When the torsion contribution of 0.13 eV [38] is subtracted from the total value of 0.75 eV, SRE due to the presence of solvent becomes an even lower value, 0.62 eV. Using this value, Basilevsky and Newton [22] obtained an even larger mean value, 0.59 nm, for the cavity radii. If we use the same donor–acceptor distance, 1.73 nm for the biphenyl–bridge–naphthalene system, the mean radius value, 0.38 nm from the structural data, the previous two-sphere formula will predict a value of SRE about twice the experimental fitting, similar to those by Basilevsky and Newton with numerical solution for arbitrary cavity [22]. Facing with these difficulties, the discrepancies were attributed to the inaccuracy of the continuum model [24,39]. However, when we notice that continuous medium theory make tremendous successes for equilibrium solvation, we ask ourselves whether some aspects of the previous theories should be improved. In our recent work [40–42], we addressed some problems on this issue, in particular the defects in virtual work approach [41]. The conclusion of zero self-energy of the polarization field was obtained by direct analysis of the polarization field [42]. In the present work, we shall make a more detailed discussion on the doubts of the previous theories. Some new features of our theory will be paid attentions. The new two-sphere formula for ET will be applied to the well-known Closs–Miller [37] ET system.

We arrange our present work as follows. In Section 2, a brief review on the present situation of nonequilibrium solvation theory has been made. The doubts in the previous theories are illustrated. Secondly, reformulations for the expression of electrostatic free energy of nonequilibrium state are carried out through different ways in Section 3. The generalized expressions of SRE for ET and spectral shifts of light absorption and emission are deduced in this section. In Section 4, the new two-sphere formula for ET and single-sphere formula for spectral shifts are presented, and the new features of our results are given particular attentions. Ab initio calculations are carried out for the model ET system, biphenyl–bridge–naphthalene (bridge = cyclohexane), in Section 5, and the newly developed two-sphere formula of ET has been applied to estimation of SRE of this system. The conclusions are given in Section 6.

We emphasize here that the approximations taken in this work are just the same as those in the previous theories, so that we can make our formulations comparable with those before. Major approximations in the reformulations throughout this work are worth describing in advance. First of all is the continuum model approximation, hence we only make derivations in the framework of electrostatics. Another one is the neglect of the influence of the solvent polarization upon the solute charge distribution. In other words, self-consistent-reaction-field treatment is not taken into account. The penetration of the solute charge distribution into the medium region is neglected, this means we ignore the volume polarization [43].

2. A brief review on theories of nonequilibrium solvation

In 1950s, Marcus [15,16] proposed the concept of nonequilibrium solvation, and treated the electrostatic free energy of nonequilibrium state of solution as the sum of virtual works done during charging process of two steps as follows

$$[\rho = 0, \Phi = 0] \xrightarrow{\mathrm{A1},\varepsilon_{\mathrm{S}}} [\rho_1, \Phi_1^{\mathrm{eq}}] \xrightarrow{\mathrm{A2},\varepsilon_{\mathrm{op}}} [\rho_2, \Phi_2^{\mathrm{non}}] \tag{1}$$

In Eq. (1), symbol Φ denotes the total electric potential. We use ρ to represent the bulk distribution of the solute (free) charge, without considering the mutual influence from solvent polarization. We let the surface distribution of the solute charge, if any, be incorporated into the bulk distribution by introducing a Dirac δ function. So the free surface charge disappears throughout this work. The superscripts ‘eq’ and ‘non’ in Eq. (1) refer to the equilibrium and the nonequilibrium, respectively. In the establishment of the nonequilibrium state, the first step, A1, charges the solute to ρ_1, and Φ reaches equilibrium in solvent of a static dielectric constant ε_s. In step A2, the solute is charged from ρ_1 to ρ_2 but only the electronic component of the solvent polarization, which corresponds to the optical dielectric constant ε_{op} of the solvent, responds. The system arrives at a new state in which the electronic polarization of solvent reaches equilibrium with ρ_2 but the orientational polari zation does not. This state, we denote it by $[\rho_2, \Phi_2^{non}]$, is referred to as the ‘nonequilibrium’ state. If we notice that the potential change in step A2 is caused by the charge distribution change of the solute, but only the electronic polarization responds, we can take the nonequilibrium as an ‘equilibrium’ in the hypothetical medium that possesses a dielectric constant of ε_{op}. We define the solute charge change as

$$\Delta\rho = \rho_2 - \rho_1 \tag{2}$$

throughout this work. The total potential Φ can be divided into two contributions: ψ from the solute charge and φ from the polarized charge. For convenience we call ψ the vacuum potential but φ the polarization potential. We need to specify equilibrium or nonequilibrium for φ but this is unnecessary for ψ since it is produced by the solute charge in vacuum. Therefore we have

$$\Phi_i^{eq} = \psi_i + \varphi_i^{eq}, \quad \Phi_i^{non} = \psi_i + \varphi_i^{non} \quad (i = 1,\ 2) \tag{3}$$

A few words are needed to make the potential definitions more clear. When the solute charge ρ_1 is placed in the medium of ε_s, the equilibrium polarization potential can be divided into two parts, i.e.

$$\varphi_1^{eq}(\rho_1, \varepsilon_s) = \varphi_{or,1} + \varphi_{op,1} \tag{4}$$

When the medium is suddenly changed from ε_s to ε_{op}, prior to the change of the solute charge distribution, $\varphi_{or,1}$ and ρ_1 will keep unchanged but the electronic polarization responds immediately. The electronic polarization in this case contains two parts: $\varphi_{or,1\text{-}op}$ equilibrated to the fixed $\varphi_{or,1}$, and $\varphi_{\rho\text{-}op}$ equilibrated to ρ_1. Therefore, the polarization potential in this stage is given by

$$\varphi_1^{eq}(\rho_1 + \sigma_{or,1}, \varepsilon_{op}) = \varphi_{or,1} + \varphi_{or,1\text{-}op} + \varphi_{\rho 1\text{-}op} \tag{5}$$

It can be proved that $\varphi_{op,1}$ in medium of ε_s is equal to the sum of $\varphi_{or,1\text{-}op}$ and $\varphi_{\rho 1\text{-}op}$ in medium of ε_{op}. Hence we have (see Appendix A)

$$\varphi_1^{eq}(\rho_1, \varepsilon_s) = \varphi_1^{eq}(\rho_1 + \sigma_{or,1}, \varepsilon_{op}) \tag{6}$$

where we use $\varphi_1^{eq}(\rho_1, \varepsilon_s)$ to denote the equilibrium potential due to ρ_1 in medium of ε_s and $\varphi_1^{eq}(\rho_1 + \sigma_{or,1}, \varepsilon_{op})$ to the potential yielded by changing the dielectric constant ε_s to ε_{op} but ρ_1 and $\sigma_{or,1}$, the orientationally polarized charge distribution, keep unchanged. In the following discussion, we use φ_1^{eq} (or Φ_1^{eq} if the vacuum potential ψ_1 included) indiscriminatingly.

In step A2, the solute charge varies from ρ_1 to ρ_2 in the medium of ε_{op}. We understand that the slow response, $\varphi_{or,1}$ and $\varphi_{or,1\text{-}op}$, keep unchanged but the fast response changes from $\varphi_{\rho 1\text{-}op}$ to $\varphi_{\rho 2\text{-}op}$. So the nonequilibrium polarization potential is given by

$$\varphi_2^{non} = \varphi_{or,1} + \varphi_{or,1\text{-}op} + \varphi_{\rho 2\text{-}op} \tag{7}$$

If we denote the sum of $\varphi_{or,1}$ and $\varphi_{or,1\text{-}op}$ as $\varphi_{slow,1}$, $\varphi_{\rho 1\text{-}op}$ as $\varphi_{fast,1}$, and $\varphi_{\rho 2\text{-}op}$ as $\varphi_{fast,2}$, the nonequilibrium potential can be written as

$$\Phi_2^{non} = \Phi_1^{eq} + \Delta\Phi_{op} \tag{8}$$

with

$$\Delta\Phi_{op} = \psi_2 - \psi_1 + \varphi_{fast,2} - \varphi_{fast,1} \tag{9}$$

Eq. (8) can be alternatively expressed as

$$\Phi_2^{non} = \psi_2 + \varphi_{slow,1} + \varphi_{fast,2} \tag{10}$$

Using, respectively, $\varphi_{or,1}$ and $\varphi_{op,2}$ instead of $\varphi_{slow,1}$ and $\varphi_{fast,2}$ in Eq. (10) may cause some difficulties in understanding but does not affect the correct formulations and the final conclusions.

According to Eqs. (4)–(6), we can express the polarization potential as follows

$$\varphi_1^{eq} = \varphi_{slow,1} + \varphi_{fast,1} \tag{11}$$

$$\varphi_2^{non} = \varphi_1^{eq} + \Delta\varphi_{op} \tag{12}$$

with

$$\Delta\varphi_{op} = \varphi_{fast,2} - \varphi_{fast,1} \tag{13}$$

If we consider the inverse process, which we call process B, we can write the analogue of Eq. (1) as follows

$$[\rho = 0, \Phi = 0] \xrightarrow{B1,\varepsilon_s} [\rho_2, \Phi_2^{eq}] \xrightarrow{B2,\varepsilon_{op}} [\rho_1, \Phi_1^{non}] \tag{14}$$

As stated above, we ignore the influence of solvent polarization upon the solute charge, hence the charge distributions ρ_1 and ρ_2 in Eq. (14) are supposed to be exactly the same as given in Eq. (1).

It is very common to integrate the work done in the charging process by the following equation

$$\delta W = \int_V \Phi\, \delta\rho\, \mathrm{d}V \tag{15}$$

The integration is over the whole space. But if we ignore the penetration of ρ into the medium region, the integration will be in fact only carried out within the cavity occupied by the solute.

Introducing a charging fraction α during step A1, the electrostatic free energy of equilibrium state was expressed in the well-known form, i.e.

$$G_1^{\mathrm{eq}} = W_{\mathrm{A1}} = (1/2)\int_V \rho_1 \Phi_1^{\mathrm{eq}}\,\mathrm{d}V \tag{16}$$

On the basis of step A1, step A2 introduces the further charge distribution change $\Delta\rho$, and the potential accordingly responds, so the charge distribution ρ^α and the electric potential Φ^α during step A2 could be expressed as [15,16]

$$\begin{aligned}&\rho^\alpha = \rho_1 + \alpha(\rho_2 - \rho_1) \quad \text{and}\\ &\quad \Phi^\alpha = \Phi_1^{\mathrm{eq}} + \alpha(\Phi_2^{\mathrm{non}} - \Phi_1^{\mathrm{eq}}) \quad (\alpha = 0\text{–}1)\end{aligned} \tag{17}$$

Therefore, the electrostatic free energy of nonequilibrium state was expressed by Marcus as the sum of work done in steps A1 and A2 (Eq. (17) of Ref. [16]), i.e.

$$G_2^{\mathrm{non}}(\mathrm{A}) = (1/2)\int_V (\rho_2\Phi_2^{\mathrm{non}} + \rho_2\Phi_1^{\mathrm{eq}} - \rho_1\Phi_2^{\mathrm{non}})\mathrm{d}V \tag{18}$$

SRE is defined as the difference of electrostatic free energies between the nonequilibrium state $[\rho_1, \Phi_1^{\mathrm{non}}]$ and the equilibrium state $[\rho_1, \Phi_1^{\mathrm{eq}}]$, i.e.[44]

$$\lambda_0 = G_1^{\mathrm{non}} - G_1^{\mathrm{eq}} \tag{19}$$

without distinguishing the forward and backward processes since the previous theories yield

$$G_2^{\mathrm{non}} - G_2^{\mathrm{eq}} = G_1^{\mathrm{non}} - G_1^{\mathrm{eq}}$$

For the purpose of more direct derivation of SRE, another route that we call as process C was suggested as shown in Table 1 [25,26]. In this route, an equilibrium state $[\rho_1, \Phi_1^{\mathrm{eq}}]$, which corresponds to the initial state of ET in solution, is assumed to establish before. A hypothetical step, C1, which produces the proper orientational polarization and is in fact the equilibrium state $[\rho_2, \Phi_2^{\mathrm{eq}}]$ in the realistic medium of ε_s, follows. A further postulated step C2 leads to the nonequilibrium state $[\rho_1, \Phi_1^{\mathrm{non}}]$. According to the definition, SRE is expressed as the sum of work done in these two steps. Applying Eq. (15) and noticing the response given in Table 1, the deduction of SRE is rather straightforward. By the conventional treatment, the work done in the step C1 is very easy to obtain as

$$W_{\mathrm{C1}} = (1/2)\int_V (\rho_2\Phi_2^{\mathrm{eq}} - \rho_1\Phi_1^{\mathrm{eq}})\mathrm{d}V \tag{20}$$

Table 1
Quantities of start and end of the steps in process C [25]

	Start	End
Step C1	$[\rho_1, \Phi_1^{\mathrm{eq}}]$	$[\rho_2, \Phi_2^{\mathrm{eq}}]$
Response	$\rho^\alpha = \rho_1 + \alpha(\rho_2 - \rho_1)$,	$\Phi^\alpha = \Phi_1^{\mathrm{eq}} + \alpha(\Phi_2^{\mathrm{eq}} - \Phi_1^{\mathrm{eq}})$
Step C2	$[\rho_2, \Phi_2^{\mathrm{eq}}]$	$[\rho_1, \Phi_1^{\mathrm{non}}]$
Response	$\rho^\alpha = \rho_2 + \alpha(\rho_1 - \rho_2)$,	$\Phi^\alpha = \Phi_2^{\mathrm{eq}} + \alpha(\Phi_1^{\mathrm{non}} - \Phi_2^{\mathrm{eq}})$

By applying response given in Table 1, the work done in step C2 can also be deduced according to Eq. (15), i.e.

$$W_{\mathrm{C2}} = -(1/2)\int_V \Delta\rho(\Phi_1^{\mathrm{non}} + \Phi_2^{\mathrm{eq}})\mathrm{d}V \tag{21}$$

Summing over the work done in steps C1 and C2, the virtual work method finally gives SRE as follows in literatures [22,25]

$$\lambda_0 = (1/2)\int_V \Delta\rho(\Delta\varphi_{\mathrm{op}} - \Delta\varphi_{\mathrm{s}})\mathrm{d}V \tag{22}$$

with

$$\Delta\varphi_{\mathrm{s}} = \varphi_2^{\mathrm{eq}} - \varphi_1^{\mathrm{eq}}, \quad \Delta\varphi_{\mathrm{op}} = \varphi_{\mathrm{fast},2} - \varphi_{\mathrm{fast},1} \tag{23}$$

Eq. (22) does not distinguish between the forward ET and the backward ET since the virtual work method gives the same SRE for both.

Introducing the two-sphere approximation as shown in Fig. 1, the famous two-sphere model for ET was developed based on Eq. (22) and applied widely for decades, i.e.

$$\lambda_0 = \Delta q^2\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_s}\right) \tag{24}$$

where Δq is the transferred charge, r_{D}, r_{A} and d the radii of the donor, the acceptor, and the distance between these two species (see Fig. 1).

On the other hand, Felderhof [31–33] proposed an equation describing the solvation free energy due to the solvent polarization, based on the thermodynamic theory of fluctuations with electromagnetic fields and linear response theory. We use the term ‘solvation free energy’ (ΔF) throughout this work to represent the electrostatic free energy minus the self-energy, $(1/2)\int_V \rho\psi\,\mathrm{d}V$, of the solute charge. The solvation free energy ΔF was expressed in the following form by Felderhof [31,45]

$$\begin{aligned}\Delta F = \frac{1}{2}\int \chi^{-1}\mathbf{P}\cdot\mathbf{P}\,\mathrm{d}V + \frac{1}{2}\iint \frac{[\nabla\cdot\mathbf{P}(\mathbf{r})][\nabla'\cdot\mathbf{P}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}V\,\mathrm{d}V'\\ - \int \mathbf{P}\cdot\mathbf{E}_{\mathrm{f}}\,\mathrm{d}V\end{aligned} \tag{25}$$

where P is the solvent polarization, χ the dielectric susceptibility, E_{f} the electric field due to the solute charge ρ in vacuum, and $-\nabla\cdot P$ the polarized charge distribution in

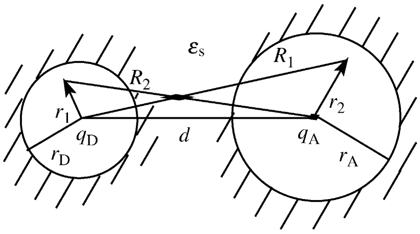


Fig. 1. A schematical description of two-sphere electron transfer.

the medium. The variable **r** drops in our notation unless it is necessary. Later on, some authors [18,30,34–36] modified this expression by taking $(1/2)\int\chi^{-1}\mathbf{P}\cdot\mathbf{P}\,dV$ as the self-energy of the solvent polarization. Applying a decomposition to the so-called 'self-energy' term, i.e. [30]

$$(1/2)\int\chi^{-1}\mathbf{P}\cdot\mathbf{P}\,dV = (1/2)\int dV[\chi_{op}^{-1}|\mathbf{P}_{op}|^2 + \chi_{or}^{-1}|\mathbf{P}_{or}|^2] \quad (26)$$

with

$$\mathbf{P}_{or,1} = \chi_{or}\mathbf{E}_1^{eq}, \quad \mathbf{P}_{op,2} = \chi_{op}\mathbf{E}_2^{non} \quad (27)$$

an expression of electrostatic free energy of the nonequilibrium state, which coincides with the one by virtual work method as given in Eq. (18), was deduced [35]. In Eq. (26), χ_{or} and χ_{op} are the orientational and electronic susceptibilities, respectively, and the total susceptibility is

$$\chi = \chi_{op} + \chi_{or} \quad (28)$$

$\mathbf{E}_2^{non}$ in Eq. (27) can be written as follows

$$\mathbf{E}_2^{non} = -\nabla\Phi_2^{non} = -\nabla\Phi_1^{eq} - \nabla(\Delta\Phi_{op}) = \mathbf{E}_1^{eq} + \Delta\mathbf{E}_{op} \quad (29)$$

The nonequilibrium solvent polarization can be expressed as the sum of P_{or} and P_{op}. Now we turn to check what is the defect of Eq. (26). Applying Eqs. (28) and (29), we have

$$\mathbf{P}_2^{non} = \chi_{or}\mathbf{E}_1^{eq} + \chi_{op}\mathbf{E}_2^{non} = \mathbf{P}_1^{eq} + \Delta\mathbf{P}_{op} \quad (30)$$

with

$$\mathbf{P}_1^{eq} = \chi\mathbf{E}_1^{eq}, \quad \Delta\mathbf{P}_{op} = \chi_{op}\Delta\mathbf{E}_{op}$$

ΔE_{op} and ΔP_{op} have the similar definitions as $\Delta\Phi_{op}$. If we recall that $\mathbf{E}_1^{eq}$ and $\mathbf{E}_2^{non}$ in Eq. (27), respectively, represent the previous equilibrium field corresponding to ρ_1 and the nonequilibrium field corresponding to ρ_2, the left-hand side of Eq. (26) can be rewritten as

$$(1/2)\int\chi^{-1}\mathbf{P}_2\cdot\mathbf{P}_2\,dV = (1/2)\chi^{-1}\int[\chi_{op}^2(\mathbf{E}_2^{non})^2 + \chi_{or}^2(\mathbf{E}_1^{eq})^2 + 2\chi_{or}\chi_{op}\mathbf{E}_2^{non}\cdot\mathbf{E}_1^{eq}]dV \quad (31)$$

but the right-hand side of Eq. (26) is as follows

$$\begin{aligned}(1/2)&\int(\chi_{op}^{-1}\mathbf{P}_{op,2}^2 + \chi_{or}^{-1}\mathbf{P}_{or,1}^2)dV \\ &= (1/2)\chi^{-1}\int\{[\chi_{op}^2(\mathbf{E}_2^{non})^2 + \chi_{or}^2(\mathbf{E}_1^{eq})^2 \\ &\quad + \chi_{or}\chi_{op}[(\mathbf{E}_2^{non})^2 + (\mathbf{E}_1^{eq})^2]\}dV \quad (32)\end{aligned}$$

Comparison of Eqs. (31) and (32) immediately tells that Eq. (26) is false unless $\mathbf{E}_2^{non} = \mathbf{E}_1^{eq}$. In other words, Eq. (26) requires $\Delta\mathbf{E}_{op} = 0$ (see Eq. (29)) and it holds only in the equilibrium state.

SRE given in Eq. (22) can be used to perform the numerical solution for the arbitrary cavity cases. However, if we make a deeper investigation on the previous nonequilibrium theories, we can find the conventional models face with serious difficulties in both sides of theory and experiment. We list the doubts as follows.

$$\begin{tikzcd}
{[\rho_1, \Phi_1^{eq}]} \arrow[r, "\varepsilon_{op}"] \arrow[d, "\lambda_{fw}"'] \arrow[dr, "\varepsilon_s"] & {[\rho_2, \Phi_2^{non}]} \\
{[\rho_1, \Phi_1^{non}]} & {[\rho_2, \Phi_2^{eq}]} \arrow[l, "\varepsilon_{op}"] \arrow[u, "\lambda_{bw}"']
\end{tikzcd}$$

Scheme 1.

(i) Why do the physical quantities, ρ_1 and Φ_1^{eq} of the previous equilibrium state, enter the expression of electrostatic free energy of nonequilibrium state? Eq. (18) means that the nonequilibrium state needs more than two state functions to describe, but what is the physical foundation?

(ii) As shown in Scheme 1, if the integration by using Eq. (15) were appropriate, we would be able to apply it directly to the process $[\rho_1, \Phi_1^{eq}] \rightarrow [\rho_1, \Phi_1^{non}]$. But this treatment will lead to a wrong conclusion of $\lambda_0 = 0$ in any case because of $\delta\rho = 0$. This indicates the free energy difference will be path-dependent.

(iii) If the self-energy of the polarization field could be expressed as those in the previous literatures, we would face the dilemma in selecting which side of Eq. (26) for this purpose. If we take the left-hand side of that equation, derivations starting from Eq. (31) will lead to a quite different form of the electrostatic free energy for nonequilibrium. On the contrary, if we choose the right-hand side of Eq. (26) instead, we will face with the difficulty to explain why the interaction energy between the orientational component and the electronic one of solvent polarization is not involved in the total energy. Another viewpoint in the past is to suppose the orientationally polarized charge as 'free charge' at the nonequilibrium state. But if we remember that continuous medium theory is macroscopic and the average charge of the solvent molecules is zero, this presumption is lack of physical foundation. In fact, the free charge and the polarized charge are quite different in nature.

3. Reformulations for nonequilibrium solvation

3.1. *Electrostatic free energy of nonequilibrium state*

The electrostatic free energy of nonequilibrium is the dominating quantity in evaluating SRE of ET and the spectral shifts in solution. So we discuss the expression of it at first. From the illustration given in Section 2, we suspect the validity of Eq. (15) in integrating the energy changes when nonequilibrium state is involved. For the energy change of a charging process, Jackson equation [46] is more general and it serves the purpose of nonequilibrium state. According to the fundamentals of electrodynamics, the change in energy accompanying the changes $\delta\rho$ in charge distribution and $\delta\Phi$ in potential is of the form [46]

$$dG = (1/2)\int_V (\rho\,\delta\Phi + \Phi\,\delta\rho)\mathrm{d}V \tag{33}$$

We need to remind that the right-hand side of Eq. (33) could not be called the 'work' any longer, so we use here G, instead of W used before. If we use the electric displacement (**D**)–electric field (**E**) notation and notice the following relationships

$$\nabla\cdot\mathbf{D} = 4\pi\rho \tag{34}$$

$$\nabla\Phi = -\mathbf{E} \tag{35}$$

Eq. (33) can be alternatively changed to the displacement-field form, i.e.

$$dG = (1/2)\int_V (\mathbf{D}\cdot\delta\mathbf{E} + \mathbf{E}\cdot\delta\mathbf{D})\mathrm{d}V \tag{36}$$

Eqs. (33) and (36) are more applicable in practical situations involving the motion of dielectrics and in the cases that the dielectric properties change [46]. If dielectric constant keeps unchanged during the charging step, for example the different equilibrium states subject to different values of ρ in the same solvent, the two terms in the right-hand side of Eq. (33) are equal, i.e. [46]

$$\rho\,\delta\Phi = \Phi\,\delta\rho \tag{37}$$

In this case, Eq. (33) is reduced to the well-known form as given in Eq. (15) [46]. Eq. (33) apparently treats with two parts of energy contributions: influences of Φ upon $\delta\rho$ and ρ upon $\delta\Phi$. We need to emphasize that Eq. (15) is eventually a reduced form of Eq. (33) subject to Eq. (37). Unfortunately, as mentioned above, Eq. (15) has been used in a long history of nonequilibrium theory. In our opinion, the central problem in the previous virtual work method is just the inadequate employment of Eq. (15). We now turn to apply Eq. (33) in collecting the energy changes in the charging processes. At the end of our reformulations, one will find all the doubts listed in Section 2 can be automatically solved.

We begin our derivations by adopting the familiar Marcus two-step approach as given in Eq. (1), but use Eq. (33) instead of Eq. (15). According to the response given in Eq. (17) for step A2, we have

$$\rho^\alpha\,\delta\Phi^\alpha = \rho_1\Delta\Phi_{\mathrm{op}}\,\delta\alpha + \alpha\Delta\rho\Delta\Phi_{\mathrm{op}}\,\delta\alpha \tag{38}$$

$$\Phi^\alpha\,\delta\rho^\alpha = \Phi_1^{\mathrm{eq}}\Delta\rho\,\delta\alpha + \alpha\Delta\rho\Delta\Phi_{\mathrm{op}}\,\delta\alpha \tag{39}$$

It is apparent that

$$\rho^\alpha\,\delta\Phi^\alpha \neq \Phi^\alpha\,\delta\rho^\alpha \tag{40}$$

Hence applying Eq. (15) to this step would cause problems. We substitute Eqs. (38) and (39) into Eq. (33), integration will give the energy change in step A2 as follows

$$\Delta G_{\mathrm{A2}} = \frac{1}{2}\int_V (\rho_2\Phi_2^{\mathrm{non}} - \rho_1\Phi_1^{\mathrm{eq}})\mathrm{d}V \tag{41}$$

It should be mentioned that Eq. (33) yields the same G_1^{eq} as given in Eq. (16), since Eq. (37) is warranted in step A1. Collecting these two parts of energy changes, we get the correct expression of nonequilibrium electrostatic free energy as

$$G_2^{\mathrm{non}} = \frac{1}{2}\int_V \rho_2\Phi_2^{\mathrm{non}}\,\mathrm{d}V \tag{42}$$

Parallel derivation for pathway B shown in Eq. (14) can give the quantity for nonequilibrium state $[\rho_1, \Phi_1^{\mathrm{non}}]$ as

$$G_1^{\mathrm{non}} = \frac{1}{2}\int_V \rho_1\Phi_1^{\mathrm{non}}\,\mathrm{d}V \tag{43}$$

It should be emphasized again that we make the formal derivations here, without considering the influence of the polarized charge upon the solute charge distribution, otherwise Eqs. (42) and (43) will possess slightly different forms because ρ_1 (or ρ_2) takes different values in equilibrium and nonequilibrium states. We prefer to leave the more detailed description on this matter to our further work.

In below we give a confirmation of the failure of Eq. (15) in general for nonequilibrium cases. As we know, at the nonequilibrium state $[\rho_1, \Phi_1^{\mathrm{non}}]$, the corresponding electric displacement $\mathbf{D}_1^{\mathrm{non}}$ and the solvent polarization $\mathbf{P}_1^{\mathrm{non}}$ are as follows

$$\mathbf{P}_1^{\mathrm{non}} = \chi_{\mathrm{or}}\mathbf{E}_2^{\mathrm{eq}} + \chi_{\mathrm{op}}\mathbf{E}_1^{\mathrm{non}} \tag{44}$$

$$\mathbf{D}_1^{\mathrm{non}} = \mathbf{E}_1^{\mathrm{non}} + 4\pi\mathbf{P}_1^{\mathrm{non}} \tag{45}$$

where χ_{or} and χ_{op} are, respectively, the orientational and electronic components of the susceptibility χ of the medium, i.e.

$$\chi = (\varepsilon_{\mathrm{s}} - 1)/4\pi, \quad \chi_{\mathrm{op}} = (\varepsilon_{\mathrm{op}} - 1)/4\pi, \quad \text{and} \quad \chi_{\mathrm{or}} = \chi - \chi_{\mathrm{op}} \tag{46}$$

Making use of Eqs. (44) and (46), Eq. (45) becomes

$$\mathbf{D}_1^{\mathrm{non}} = 4\pi\chi_{\mathrm{or}}\mathbf{E}_2^{\mathrm{eq}} + \varepsilon_{\mathrm{op}}\mathbf{E}_1^{\mathrm{non}} \tag{47}$$

Eq. (47) tells the following relationship

$$\delta\mathbf{D}_1^{\mathrm{non}} = \varepsilon_{\mathrm{op}}\,\delta\mathbf{E}_1^{\mathrm{non}} \tag{48}$$

Therefore, we have

$$\mathbf{E}_1^{\mathrm{non}}\cdot\delta\mathbf{D}_1^{\mathrm{non}} = \varepsilon_{\mathrm{op}}\mathbf{E}_1^{\mathrm{non}}\cdot\delta\mathbf{E}_1^{\mathrm{non}} \neq \mathbf{D}_1^{\mathrm{non}}\cdot\delta\mathbf{E}_1^{\mathrm{non}} \tag{49}$$

Eq. (49) indicates that the two terms in the right-hand of Eq. (36) are not equal, so the two terms in the right-hand side of Eq. (33) are not equal either in this case, that is $\Phi\,\delta\rho \neq \rho\,\delta\Phi$. We conclude that Eq. (15) becomes invalid when the step links a nonequilibrium state. In addition, it is well known that

$$\delta \mathbf{D} = \varepsilon_{\rm s}\, \delta \mathbf{E} \tag{50}$$

for any equilibrium states. A comparison between Eq. (48) and Eq. (50) shows that the linear response given by Eq. (50) holds true when the system moves from one equilibrium state to another subject to the same medium ($\varepsilon_{\rm s}$), but such a linear response is no longer valid when the properties of the medium changes (from $\varepsilon_{\rm s}$ to $\varepsilon_{\rm op}$). This indicates that the application of Eq. (15) to A2 step of Eq. (1) will lead to the wrong expression of the free energy of the nonequilibrium state.

Up to this stage, the doubts stated in Section 2 can find their answers. Let us depict as follows.

(i) In our formulation, the electrostatic free energy, $G_i^{\rm non}$ only contains the properties of the nonequilibrium state own, ρ_i and $\Phi_i^{\rm non}$. But this never means that $G_i^{\rm non}$ is independent of the previous equilibrium state. If we notice $\Phi_2^{\rm non} = \Phi_1^{\rm eq} + \Delta\Phi_{\rm op}$ from Eq. (8), the dependency of $G_i^{\rm non}$ on the potential of the previous equilibrium is clear.

(ii) Let us perform the direct integration of energy change from $[\rho_1, \Phi_1^{\rm eq}]$ to $[\rho_1, \Phi_1^{\rm non}]$ by Jackson's equation Eq. (33). The energy change becomes path-independent (see below).

Therefore, we can conclude that the troubles in the previous virtual work approach are completely caused by the inappropriate employment of Eq. (15). Adopting Eq. (33) or alternatively Eq. (36) can make these problems perfectly solved.

3.2. Spectral shifts of light absorption and emission

Fig. 2 schematically illustrates the energy levels of the solute–solvent system in Franck–Condon transitions from state 1 to state 2 and vice versa from state 2 to state 1. U_i(g) (i=1,2) is the total energy of state i, corresponding to ρ_i in vacuum, in other words, U_i(g) is the self-energy of the solute charge ρ_i. $h\nu_1$ and $h\nu_2$, respectively, denote the absorption and emission spectra in solution. We use $\Delta F_i^{\rm eq}$ and $\Delta F_i^{\rm non}$ to denote the solvation free energies of state i at equilibrium and nonequilibrium, respectively. As illustrated above, the solvation free energy can be expressed as follows by subtracting the self-energy of the solute charge from the electrostatic free energy, i.e.

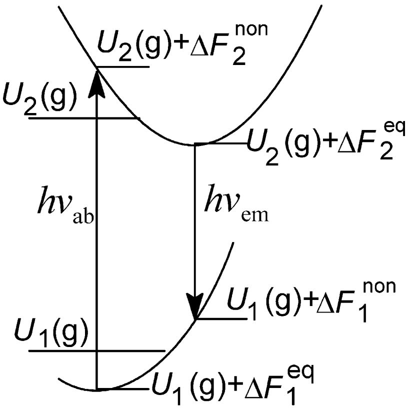


Fig. 2. Schematical depiction of solvent effect of absorption and emission spectra.

$$\Delta F_1^{\rm eq} = G_1^{\rm eq} - (1/2)\int_V \rho_1 \psi_1\, {\rm d}V = (1/2)\int_V \rho_1 \varphi_1^{\rm eq}\, {\rm d}V \tag{51}$$

$$\Delta F_2^{\rm non} = (1/2)\int_V \rho_2 \varphi_2^{\rm non}\, {\rm d}V = (1/2)\int_V \rho_2(\varphi_1^{\rm eq} + \Delta\varphi_{\rm op}){\rm d}V \tag{52}$$

For an equilibrium solvation state corresponding to ρ_2, the solvation free energies are as follows

$$\Delta F_2^{\rm eq} = (1/2)\int_V \rho_2 \varphi_2^{\rm eq}\, {\rm d}V \tag{53}$$

$$\Delta F_1^{\rm non} = (1/2)\int_V \rho_1 \varphi_1^{\rm non}\, {\rm d}V = (1/2)\int_V \rho_1(\varphi_2^{\rm eq} - \Delta\varphi_{\rm op}){\rm d}V \tag{54}$$

According to the widely accepted definitions of spectral shifts in the processes of light absorption and emission [17,27,28], we can write the spectral shift of light absorption as

$$\Delta h\nu_{\rm ab} = \Delta F_2^{\rm non} - \Delta F_1^{\rm eq} = (1/2)\int_V (\Delta\rho\varphi_1^{\rm eq} + \rho_2 \Delta\varphi_{\rm op}){\rm d}V \tag{55}$$

In the inverse process, light emission (fluorescence), the spectral shift reads

$$\Delta h\nu_{\rm em} = \Delta F_1^{\rm non} - \Delta F_2^{\rm eq} = -(1/2)\int_V (\Delta\rho\varphi_2^{\rm eq} + \rho_1 \Delta\varphi_{\rm op}){\rm d}V \tag{56}$$

Compared with Eq. (55), the minus sign in Eq. (56) is due to the definition of $\Delta\rho$. In our notation, a positive value of $\Delta h\nu_{\rm ab}$ indicates a blue shift of the light absorption in solution, and a positive value of $\Delta h\nu_{\rm em}$ indicates a red shift of the light emission. Attention should be paid since different literatures give different definitions, in particular for $\Delta h\nu_{\rm em}$. When we consider the sum of $\Delta h\nu_{\rm ab}$ and $\Delta h\nu_{\rm em}$, we have

$$\Delta h\nu_{\rm sum} = (1/2)\int_V \Delta\rho(\Delta\varphi_{\rm op} - \Delta\varphi_{\rm s}){\rm d}V \tag{57}$$

Eqs. (55)–(57) are our new formulations for spectral shift in solution.

On the other hand, if we turn to use the energy expression of nonequilibrium by the previous theories (see Eq. (18)), the spectral shift of light absorption can be written as follows

$$\Delta h\nu'_{\mathrm{ab}} = (1/2)\int_V (\rho_2\varphi_2^{\mathrm{non}} + \rho_2\varphi_1^{\mathrm{eq}} - \rho_1\varphi_2^{\mathrm{non}} - \rho_1\varphi_1^{\mathrm{eq}})\mathrm{d}V$$

$$= (1/2)\int_V \Delta\rho(2\varphi_1^{\mathrm{eq}} + \Delta\varphi_{\mathrm{op}})\mathrm{d}V \quad (58)$$

Parallel treatment gives the spectral shift of light emission as follows

$$\Delta h\nu'_{\mathrm{em}} = -(1/2)\int_V \Delta\rho(2\varphi_2^{\mathrm{eq}} - \Delta\varphi_{\mathrm{op}})\mathrm{d}V \quad (59)$$

The sum of spectral shift by the previous theories is thus given by

$$\Delta h\nu'_{\mathrm{sum}} = \int_V \Delta\rho(\Delta\varphi_{\mathrm{op}} - \Delta\varphi_{\mathrm{s}})\mathrm{d}V \quad (60)$$

Comparing our result given in Eqs. (55) and (56) with those (Eqs. (58)–(60)) given by the previous expression of electrostatic free energy of nonequilibrium, we can find the obvious differences. A significant feature of our results is that the sum of spectral shifts drops to only one half of that from the previous theories.

3.3. Solvent reorganization energy of electron transfer

We in principle may derive SRE of ET by substituting Eqs. (16) and (43) into the definition given in Eq. (19). However, we prefer to perform the following treatments to reach our reformulations, so as to make the comparison between our results with those by Marcus [25] as described in Section 1. We adopt pathway C as shown in Table 1 for our purpose. Introducing a charging fraction α, and applying the changes of ρ and Φ in step C1, we can see that both Eqs. (15) and (33) give a same result because $\rho^{\alpha}\,\delta\Phi^{\alpha} = \Phi^{\alpha}\,\delta\rho^{\alpha} = \alpha\rho_1\Phi_1^{\mathrm{eq}}\,\delta\alpha$. So we see that the application of Eq. (15) to the first charging step, as usually seen in textbooks, can yield a correct result as given in Eq. (20). On the basis of step C1, step C2 (see Table 1) introduces further the change of the solute change $-\Delta\rho$, but only the fast polarization of the solvent alters in this step. Applying the response given in Table 1, we have

$$\rho^{\alpha}\,\delta\Phi^{\alpha} = \rho_2(\Phi_1^{\mathrm{non}} - \Phi_2^{\mathrm{eq}})\delta\alpha + \alpha(\rho_1 - \rho_2)(\Phi_1^{\mathrm{non}} - \Phi_2^{\mathrm{eq}})\delta\alpha \quad (61)$$

$$\Phi^{\alpha}\,\delta\rho^{\alpha} = \Phi_2^{\mathrm{eq}}(\rho_1 - \rho_2)\delta\alpha + \alpha(\rho_1 - \rho_2)(\Phi_1^{\mathrm{non}} - \Phi_2^{\mathrm{eq}})\delta\alpha \quad (62)$$

Consequently, only Eq. (33) is valid to this step. Substituting Eqs. (61) and (62) into Eq. (33), the energy change in step C2 is given by

$$\Delta G_{\mathrm{C2}} = (1/2)\int_V (\rho_1\Phi_1^{\mathrm{non}} - \rho_2\Phi_2^{\mathrm{eq}})\mathrm{d}V \quad (63)$$

The total change of electrostatic free energy, which is just SRE of the forward ET according to conventional definition, is thus obtained to be

$$\lambda_{\mathrm{fw}} = W_{\mathrm{C1}} + \Delta G_{\mathrm{C2}} = (1/2)\int_V \rho_1(\Phi_1^{\mathrm{non}} - \Phi_1^{\mathrm{eq}})\mathrm{d}V \quad (64)$$

Differing from the notation λ_0 given in the above statements, we distinguish here SRE of forward ET with that of backward ET and use λ_{fw} and λ_{bw} to denote these two quantities. If we notice that ρ_1 produces the same potential ψ_1 in vacuum but φ_1^{eq} in equilibrium state $[\rho_1, \Phi_1^{\mathrm{eq}}]$ and φ_1^{non} in nonequilibrium state $[\rho_1, \Phi_1^{\mathrm{non}}]$, Eq. (64) can be changed to the following identical form

$$\lambda_{\mathrm{fw}} = (1/2)\int_V \rho_1(\varphi_1^{\mathrm{non}} - \varphi_1^{\mathrm{eq}})\mathrm{d}V \quad (65)$$

Eq. (65) is our new form of SRE. Similar to Eq. (12), we have

$$\varphi_1^{\mathrm{non}} = \varphi_2^{\mathrm{eq}} - \Delta\varphi_{\mathrm{op}} \quad (66)$$

The minus sign before $\Delta\varphi_{\mathrm{op}}$ is due to the definition of $\Delta\rho$. Eq. (65) therefore can be changed to

$$\lambda_{\mathrm{fw}} = (1/2)\int_V \rho_1(\Delta\varphi_{\mathrm{s}} - \Delta\varphi_{\mathrm{op}})\mathrm{d}V \quad (67)$$

Parallel discussions can be made for the backward ET. The corresponding SRE reads

$$\lambda_{\mathrm{bw}} = (1/2)\int_V \rho_2(\Delta\varphi_{\mathrm{op}} - \Delta\varphi_{\mathrm{s}})\mathrm{d}V \quad (68)$$

Eqs. (67) and (68) indicate that SRE depends on the directions of ET and the charge distributions of the initial state. This feature is quite different from the conventional conclusion that λ_0 has nothing to do with the direction of ET and only depends on the transferred charge $\Delta\rho$ (see Eq. (22)). An average value of SRE from our derivation can thus be given by

$$\lambda_{\mathrm{av}} = (1/4)\int_V \Delta\rho(\Delta\varphi_{\mathrm{op}} - \Delta\varphi_{\mathrm{s}})\mathrm{d}V \quad (69)$$

Comparing Eq. (69) with Eq. (22) shows that the average value of SRE by us is only one half of that by the conventional theories.

3.4. Comprehension of interaction between solvent polarization and its source charge

In Section 3.1, we have deduced the expression of electrostatic free energy of nonequilibrium via the multistep charging approach. Now we present a different method, the interaction energy method for the same purpose. At first, let us show how to obtain the reasonable expressions of the interaction energy between the polarization field and its source free charge, and of the self-energy of the solvent polarization, adopting the field superposition principle. We consider two independent equilibrium electrostatic fields in solution, $[\rho_A,\Phi_A]$ and $[\rho_B,\Phi_B]$. ρ_A and ρ_B are two independent free charge distributions and Φ_A is the potential due to ρ_A and Φ_B due to ρ_B. By denoting the total free charge distribution and the total electric potential as

$$\rho = \rho_A + \rho_B, \quad \Phi = \Phi_A + \Phi_B \tag{70}$$

the electrostatic free energy $(1/2)\int\rho\Phi\,dV$ of the total field can be divided into three parts

$$\frac{1}{2}\int_V \rho\Phi\,dV = \frac{1}{2}\int_V \rho_A\Phi_A\,dV + \frac{1}{2}\int_V \rho_B\Phi_B\,dV + \frac{1}{2}\int_V (\rho_A\Phi_B + \rho_B\Phi_A)dV \tag{71}$$

The integrals in the right-hand of Eq. (70) represent, in sequence, the electrostatic free energy of the field $[\rho_A,\Phi_A]$, that of the field $[\rho_B,\Phi_B]$, and the interaction energy between these two independent fields. Eq. (71) tells that if we can divide an electrostatic field into two independent parts, we can express the electrostatic free energy of the total field by summing over their individual energies and the interaction energy between them. The interaction energy should be of the form

$$G_{A\text{–}B} = (1/2)\int_V (\rho_A\Phi_B + \rho_B\Phi_A)dV \tag{72}$$

In the case of $\int_V \rho_A\Phi_B\,dV = \int_V \rho_B\Phi_A\,dV$, the interaction energy between two independent fields takes the usual form.

However, if we divide an electric field E of equilibrium state into two parts: the vacuum field E_f and the polarization field e, the electric displacement has the form

$$\mathbf{D} = \mathbf{E}_f + \mathbf{e} + 4\pi\mathbf{P} \tag{73}$$

The total electrostatic free energy is given by

$$(1/8\pi)\int_V \mathbf{E}\cdot\mathbf{D}\,dV = (1/8\pi)\int_V \mathbf{E}_f\cdot\mathbf{D}_f\,dV + (1/8\pi)\int_V \mathbf{e}\cdot\mathbf{D}_p\,dV + (1/8\pi)\int_V (\mathbf{E}_f\cdot\mathbf{D}_p + \mathbf{e}\cdot\mathbf{D}_f)dV \tag{74}$$

where $\mathbf{D}_p = \mathbf{e} + 4_{\pi}\mathbf{P}$ and $\mathbf{D}_f = \mathbf{E}_f$. Similar to Eq. (71), the three terms in the right-hand of Eq. (74) represents, in sequence, the self-energy of the vacuum field, the self-energy of the poarization field, and the interaction energy between these two fields. Applying Eq. (34) to the vacuum case, we have

$$\nabla\cdot\mathbf{E}_f = 4\pi\rho \tag{75}$$

Making use of Eqs. (34), (35) and (75), integrals in the right-hand side of Eq. (74) can be changed to the following forms

$$\int\mathbf{E}_f\cdot\mathbf{D}_f\,dV = \int\psi\nabla\cdot\mathbf{D}_f\,dV - \int\nabla\cdot(\psi\mathbf{D}_f)dV = 4\pi\int\rho\psi\,dV \tag{76}$$

$$\int\mathbf{e}\cdot\mathbf{D}_p\,dV = \int\varphi\nabla\cdot\mathbf{D}_p\,dV - \int\nabla\cdot(\varphi\mathbf{D}_p)dV = \int\varphi\nabla\cdot(\mathbf{D} - \mathbf{D}_f)dV = 0 \tag{77}$$

$$\int\mathbf{E}_f\cdot\mathbf{D}_p\,dV = \int\psi\nabla\cdot(\mathbf{D} - \mathbf{D}_f)dV = 0 \tag{78}$$

$$\int\mathbf{e}\cdot\mathbf{D}_f\,dV = \int\varphi\nabla\cdot\mathbf{D}_f\,dV - \int\nabla\cdot(\varphi\mathbf{D}_f)dV = 4\pi\int\rho\varphi\,dV \tag{79}$$

Hence we can come to the following important conclusions

$$G_f = (1/8\pi)\int\mathbf{E}_f\cdot\mathbf{D}_f\,dV = (1/2)\int\rho\psi\,dV \tag{80}$$

$$G_p = (1/8\pi)\int\mathbf{e}\cdot\mathbf{D}_p\,dV = 0 \tag{81}$$

$$G_{f\text{–}p} = (1/8\pi)\left[\int\mathbf{e}\cdot\mathbf{D}_f\,dV + \int\mathbf{E}_f\cdot\mathbf{D}_p\,dV\right] = (1/2)\int\rho\varphi\,dV \tag{82}$$

We emphasize again that we are discussing an equilibrium solvation state here. Eqs. (80)–(82) indicate that the self-energy of the vacuum field, G_f, has the usual form, but the self-energy of the polarization field or the solvent polarization, G_p, is zero! The self-energy of the solvent polarization or polarization field is in fact the interaction energy between the molecular dipoles of the solvent. This quantity can be calculated in an exact way. When the point dipoles are placed as a cubic lattice and a macroscopic electric field is set up in the substance, the interaction energy between these parallel dipoles vanishes [46].

In addition, the interaction $G_{f\text{–}p}$ between the polarization field and its source free charge is as shown in Eq. (82). Particular attentions should be paid to Eq. (78). The zero value for the term $\int\mathbf{E}_f\cdot\mathbf{D}_p\,dV$ leads to an important conclusion as given in Eq. (82), which indicates that the interaction energy between the polarization field and its source charge no longer possesses the form similar to that between two independent fields (see Eq. (72)). Conclusions given in Eqs. (81) and (82) are quite different from the conventional understandings, which take $G_{f\text{–}p} = -\int\mathbf{P}\cdot\mathbf{E}_f\,dV$ and $G_p = (1/2)\int\mathbf{P}\cdot\mathbf{E}_f\,dV$ [47–49]. One can see that no other approximation is taken in the present derivations except taking the total equilibrium electrostatic free energy as the usual form of $G = (1/8)\int\mathbf{E}\cdot\mathbf{D}\,dV$. If we look back to the conventional understandings for $G_{f\text{–}p}$ and G_p, we guess that the previous definition for $G_{f\text{–}p}$ is just a postulation based on the analogue to Eq. (76), but Eq. (82) is ignored. So we can conclude that the interaction energy between the polarization field and its source charge does not possess the form as that between two independent fields. If we notice this point, all the doubts in the past will be solved without difficulties.

After the correct understanding of the interaction energy and the self-energy within the framework of continuum model, as illustrated above, the expression of electrostatic free energy of nonequilibrium becomes rather straightforward. Combined with Eqs. (10)–(12), G_2^{non} can be expressed as follows

$$G_2^{\mathrm{non}} = \frac{1}{2}\int_V \rho_2\psi_2\,\mathrm{d}V + \frac{1}{2}\int_V \rho_2\varphi_{\mathrm{slow},1}\,\mathrm{d}V + \frac{1}{2}\int_V \rho_2\varphi_{\mathrm{fast},2}\,\mathrm{d}V$$

The terms in the right-hand side represent, in sequence, the self-energy of the vacuum field, the interaction energy between the slow part of the polarized charge due to ρ_1 in medium of $\varepsilon_{\mathrm{op}}$ and the free charge ρ_2, as well as the interaction energy between the fast part of the polarized charge and the free charge ρ_2. This expression is essentially the same as that given in Eq. (42) when we notice that $\Phi_2^{\mathrm{non}} = \psi_2 + \varphi_{\mathrm{slow},1} + \varphi_{\mathrm{fast},2}$.

Based on the field superposition principle presented above, the expression of G_2^{non} can be directly deduced by considering the superposition of two independent fields, $[\rho_1, \Phi_1^{\mathrm{eq}}]$ and $[\Delta\rho, \Delta\Phi_{\mathrm{op}}]$. Relevant formulations are given in Appendix B. Up till now, we have in fact achieved the consistent expression of G_2^{non} via three different methods: the multi-step charging approach (see Section 3.1), the field superposition principle (see Appendix B), and the interaction energy method presented in this section.

A few words are still needed to give an explanation for the zero value for the self-energy of the solvent polarization. The continuous medium theory requires that the size of solvent molecules and the distance between them should be infinitely small, but the value of the dipole moment $\mathbf{P}_{\mathrm{i}}$ of the solvent molecule is limited. Based on these presumptions, the solvent polarization $\mathbf{P}$ is defined as $\mathbf{P} = \lim_{\Delta V\to 0}\sum q_i\mathbf{r}_i/\Delta V$, with ΔV being the volume element and $q_i r_i$ the ith dipole [50]. A corollary is the point dipole approximation of the solvent molecules for the continuum model. If we notice this, the zero value of the self-energy for the polarization field is understandable since no energy is needed to change the orientation situation of the solvent.

The detailed consideration of the interaction energy between the solvent dipoles, or the self-energy of the polarization field for the real medium, will depend on the amount of the molecular dipole, the distance between the charged pair, the intermolecular distances, and so on, but such a consideration is apparently beyond the ability of the macroscopic continuous medium theory, and is much more complicated. How to correctly evaluate the self-energy of the polarization field for the real solute–solvent system is another problem. The postulation of a non-zero self-energy G_{p} of the polarization field [47–49], without careful derivation, is just the cause leading to the incorrect expression of the nonequilibrium free energy.

4. Theoretical treatment for ideal cavity shape

4.1. Two-sphere model for electron transfer

Eqs. (67)–(69) can be easily reduced to the two-sphere form. We consider the following intramolecular ET reaction

$$\mathrm{D}^{q_{\mathrm{D}}} - \mathrm{B} - \mathrm{A}^{q_{\mathrm{A}}} = \mathrm{D}^{q_{\mathrm{D}}+\Delta q} - \mathrm{B} - \mathrm{A}^{q_{\mathrm{A}}-\Delta q} \tag{83}$$

where B is the bridge. For the reactant, we assume that there is a point charge q_{D} at the center of sphere D with a radius of r_{D}, and q_{A} at the center of sphere A of r_{A}. The two vacuum spheres are embedded in medium of ε_{S} (see Fig. 1) and separated by a distance d. Analogous to Marcus, we ignore the influence of polarized charge due to q_{A} on cavity D, and vice versa the influence of polarized charge due to q_{D} on cavity A. Thus the total potential within D is contributed from three parts: the vacuum potential due to q_{D}, i.e.

$$\psi^{\mathrm{D}}(q_{\mathrm{D}}) = q_{\mathrm{D}}/r_1 \tag{84}$$

the polarization potential due to q_{D}, i.e.

$$\varphi_{\mathrm{s}}^{\mathrm{D}}(q_{\mathrm{D}}) = (q_{\mathrm{D}}/r_{\mathrm{D}})(1/\varepsilon_{\mathrm{s}} - 1) \tag{85}$$

and the potential yielded by q_{A} in medium under the presumption of $r_{\mathrm{A}}\to 0$ and $r_{\mathrm{D}}\to 0$, i.e.

$$\Phi_{\mathrm{s}}^{\mathrm{D}}(q_{\mathrm{A}}) = q_{\mathrm{A}}/(\varepsilon_{\mathrm{s}}R_2) \tag{86}$$

The subscript ‘s’ for φ or Φ means the equilibrium in medium of ε_{S}. Summing over these three parts, the total potential within sphere D reads

$$\Phi_{\mathrm{s}}^{\mathrm{D}}(q_{\mathrm{D}} + q_{\mathrm{A}}) = (q_{\mathrm{D}}/r_{\mathrm{D}})(1/\varepsilon_{\mathrm{s}} - 1) + q_{\mathrm{D}}/r_1 + q_{\mathrm{A}}/(\varepsilon_{\mathrm{s}}R_2) \tag{87}$$

Noticing $R_2 = d$ at the center of D and cutting off the potential by q_{D} and q_{A} in vacuum, say, $q_{\mathrm{D}}/r_1 + q_{\mathrm{A}}/R_2$, we can write the polarization potential at the center of D as follows

$$\varphi_{\mathrm{s}}^{\mathrm{D}}(q_{\mathrm{D}} + q_{\mathrm{A}}) = (q_{\mathrm{D}}/r_{\mathrm{D}} + q_{\mathrm{A}}/d)(1/\varepsilon_{\mathrm{s}} - 1) \tag{88}$$

In the similar way, the polarization potential yielded by the transferred charge Δq at the center of D is given by

$$\Delta\varphi_{\mathrm{s}}^{\mathrm{D}} = (\Delta q/r_{\mathrm{D}} - \Delta q/d)(1/\varepsilon_{\mathrm{s}} - 1) \tag{89}$$

We turn to consider the polarization potential by the electronic polarization. For this case, we only need to change ε_{S} to $\varepsilon_{\mathrm{op}}$ in Eq. (89). Hence we have

$$\Delta\varphi_{\mathrm{op}}^{\mathrm{D}} = (\Delta q/r_{\mathrm{D}} - \Delta q/d)(1/\varepsilon_{\mathrm{op}} - 1) \tag{90}$$

$\Delta\varphi_{\mathrm{s}}^{\mathrm{A}}$ and $\Delta\varphi_{\mathrm{op}}^{\mathrm{A}}$ for sphere A can be given via parallel derivations, i.e.

$$\Delta\varphi_{\mathrm{s}}^{\mathrm{A}} = (-\Delta q/r_{\mathrm{A}} + \Delta q/d)(1/\varepsilon_{\mathrm{s}} - 1) \tag{91}$$

$$\Delta\varphi_{\mathrm{op}}^{\mathrm{A}} = (-\Delta q/r_{\mathrm{A}} + \Delta q/d)(1/\varepsilon_{\mathrm{op}} - 1) \tag{92}$$

Using the solute charge specified in Eq. (83), Eqs. (67) and (68) become

$$\lambda_{\mathrm{fw}} = \frac{1}{2}[q_{\mathrm{D}}(\Delta\varphi_{\mathrm{s}}^{\mathrm{D}} - \Delta\varphi_{\mathrm{op}}^{\mathrm{D}}) + q_{\mathrm{A}}(\Delta\varphi_{\mathrm{s}}^{\mathrm{A}} - \Delta\varphi_{\mathrm{op}}^{\mathrm{A}})] \tag{93}$$

$$\lambda_{\mathrm{bw}} = \frac{1}{2}[(q_{\mathrm{D}} + \Delta q)(\Delta\varphi_{\mathrm{s}}^{\mathrm{D}} - \Delta\varphi_{\mathrm{op}}^{\mathrm{D}}) + (q_{\mathrm{A}} - \Delta q)(\Delta\varphi_{\mathrm{s}}^{\mathrm{A}} - \Delta\varphi_{\mathrm{op}}^{\mathrm{A}})] \tag{94}$$

Substituting Eqs. (89)–(92) into Eqs. (93) and (94) yields the following results

$$\lambda_{\mathrm{fw}} = \frac{1}{2}\Delta q\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_{\mathrm{s}}}\right)\left[q_{\mathrm{A}}\left(\frac{1}{r_{\mathrm{A}}} - \frac{1}{d}\right) - q_{\mathrm{D}}\left(\frac{1}{r_{\mathrm{D}}} - \frac{1}{d}\right)\right] \tag{95}$$

$$\lambda_{\mathrm{bw}} = \frac{1}{2}\Delta q\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_{\mathrm{s}}}\right)\left[(q_{\mathrm{D}} + \Delta q)\left(\frac{1}{r_{\mathrm{D}}} - \frac{1}{d}\right) - \left(q_{\mathrm{A}} - \Delta q)\left(\frac{1}{r_{\mathrm{A}}} - \frac{1}{d}\right)\right)\right] \tag{96}$$

The average value thus becomes

$$\lambda_{\mathrm{av}} = \frac{1}{2}\Delta q^2\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_{\mathrm{s}}}\right)\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{d}\right) \tag{97}$$

Alternatively, if one substitutes Eqs. (89)–(92) into Eq. (22), which is based on the previous virtual work method, conventional two-sphere formula, Eq. (24), is very easy to obtain, although it was originally derived in a slightly different way [16,17,25,26]. Eqs. (95)–(97) are our new two-sphere formulae. A significant feature of our results is that SRE depends both on the direction and the charges brought by the species, unlike Eq. (24) deduced in the past. We should emphasize that present conclusion is quite straightforward when we use Eq. (33) to express the energy change or alternatively the field superposition principle, without introducing any other approximations beyond those in the conventional formulations. Owing to the inappropriate application of Eq. (15) to the steps involving nonequilibrium state, SRE was incorrectly deduced to be independent of the direction of ET and of the charges brought by the donor and accepter in the past [16,25,26].

We assume $\Delta q = e$ (e is the elementary charge) and take several typical cases of ET into account in the following.

Case 1. $q_{\mathrm{D}} = -e/2$, and $q_{\mathrm{A}} = e/2$. In this case, Eqs. (95) and (96) reduce to a same form, i.e.

$$\lambda_{\mathrm{fw}} = \lambda_{\mathrm{bw}} = \frac{e^2}{2}\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_s}\right) \tag{98}$$

Eq. (98) indicates that SRE of the forward ET and that of the backward ET are equal in this case, but SRE measures one half of the conventional expression given by Eq. (24).

Case 2. $q_{\mathrm{D}} = q_{\mathrm{A}} = 0$. This case indicates a charge separation process and its inverse indicates the charge recombination. λ_{fw} and λ_{bw} in this case are as follows

$$\lambda_{\mathrm{fw}} = 0 \tag{99}$$

$$\lambda_{\mathrm{bw}} = e^2\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_s}\right) \tag{100}$$

Eq. (99) indicates that SRE of a charge separation vanishes. This point deserves attentions. From our present work, the interaction energies between the polarization field of equilibrium state $[\rho_1 = 0, \varphi_1^{\mathrm{eq}} = 0]$ or nonequilibrium state $[\rho_1 = 0, \varphi_1^{\mathrm{non}}]$, and the free charge ρ_1 is zero, λ_{fw} consequently vanishes. However, in the conventional theories, a non-zero self-energy of the polarization field is incorrectly postulated, as described in Section 3.4. This misunderstanding misleads to a non-zero value of SRE by Eq. (24) for the charge separation process. There is an energy change from $[\rho_1 = 0, \varphi_1^{\mathrm{eq}} = 0]$ to $[\rho_1 = 0, \varphi_1^{\mathrm{non}}]$, owing to the entropy change caused by the ordering of the solvent molecules. But it should be noticed that the energy change due to the entropy change is in usual trivial and does not belong to the electrostatic free energy. Postulating this energy change to the same amount as solvation free energy is lack of physical foundations.

Case 3. $q_{\mathrm{D}} = -e$ and $q_{\mathrm{A}} = 0$. This is the usual situation of an excess electron transferring from the donor to the acceptor. In this case, Eqs. (95) and (96) become

$$\lambda_{\mathrm{fw}} = \frac{e^2}{2}\left(\frac{1}{r_{\mathrm{D}}} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_s}\right) \tag{101}$$

$$\lambda_{\mathrm{bw}} = \frac{e^2}{2}\left(\frac{1}{r_{\mathrm{A}}} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon_s}\right) \tag{102}$$

A parallel discussion can be made to the hole transfer, $q_{\mathrm{A}} = e$ and $q_{\mathrm{D}} = 0$. Eqs. (101) and (102) indicate that SRE in this case only depends on the radius of the charged sphere of the initial state, but the radius of the neutral sphere disappears. If we recall the statement given in Section 3.4, this feature meets the need of the physical requirement. The neutral sphere does not contribute to the change of interaction energy from the equilibrium state to the nonequilibrium state subject to the initial charge distribution, so its size and shape do not apply influence on SRE. The well-known Closs–Miller ET system belongs to this case. From our present viewpoint, we can give an estimation of radius for biphenyl group which is charged to an anion, but can not for naphthalene because it is neutral at the initial state and hence it does not contribute to SRE of the forward ET.

The average value of SRE keeps unchanged, in spite of the appearances of λ_{fw} and λ_{bw} in different cases. New features of SRE can make us have a more complete comprehension on the nature of this quantity. One can find all the doubts listed in Section 2 can be excellently explained by our new theory up till now. In Marcus' electron transfer theory, SRE is in fact incorporated into the total reorganization energy by taking the average value of $\lambda_{\rm fw}$ and $\lambda_{\rm bw}$. Therefore, the expression of the average value given by Eq. (97) will be adopted in the practical calculations in the following sections. When compared with the conventional two-sphere model, our predication of $\lambda_{\rm av}$ drops to only one half.

4.2. Single-sphere model for spectral shift

We have given the spectral shifts of light absorption and emission as well as their sum in Eqs. (55)–(57). Here, we reduce them to fit the spherical cavity. Like the model introduced by Onsager in equilibrium solvation [1], we adopt the approximation of point dipole of solute within a spherical cavity with radius a. The photoexcitation drives the point dipole to vary from initial μ_1 to the final one, μ_2. Assuming that the vacuum cavity occupied by the solute is surrounded by the medium of $\varepsilon_{\rm S}$. The electric potential of equilibrium state within the cavity is as follows (Eq. (6) of Ref. [1])

$$\Phi_1^{\rm eq} = \varphi_1^{\rm eq} + \boldsymbol{\mu}_1\cdot\mathbf{r}/r^3 \quad (103)$$

with

$$\varphi_1^{\rm eq} = -R\boldsymbol{\mu}_1\cdot\mathbf{r} \quad (104)$$

$$R = (1/a^3)[2(\varepsilon_{\rm s}-1)/(2\varepsilon_{\rm s}+1)] \quad (105)$$

It could be understood that the second term in the right-hand side of Eq. (103) is the vacuum potential due to μ_1. The reaction field (the term 'reaction field' is essentially the same as the term 'polarization field' used above, but we use here the term 'reaction field' following the literatures) within the cavity by the solvent polarization thus reads

$$\mathbf{e}_1^{\rm eq} = -\nabla\varphi_1^{\rm eq} = R\boldsymbol{\mu}_1 \quad (106)$$

Similar form is given for the equilibrium solvation case of μ_2, i.e.

$$\mathbf{e}_2^{\rm eq} = -\nabla\varphi_2^{\rm eq} = R\boldsymbol{\mu}_2 \quad (107)$$

During the Franck–Condon transition, the reaction field resulted from the dipole variation $\Delta\mu=\mu_2-\mu_1$ in medium of $\varepsilon_{\rm S}$ is of the form

$$\Delta\mathbf{e}_{\rm s} = R\Delta\boldsymbol{\mu} \quad (108)$$

In the similar way, the reaction field due to $\Delta\mu$ in medium of $\varepsilon_{\rm op}$ reads

$$\Delta\mathbf{e}_{\rm op} = \mathbf{e}_2^{\rm non} - \mathbf{e}_1^{\rm eq} = R_{\rm op}\Delta\boldsymbol{\mu} \quad (109)$$

with

$$R_{\rm op} = (1/a^3)[2(\varepsilon_{\rm op}-1)/(2\varepsilon_{\rm op}+1)] \quad (110)$$

Using the point dipole approximation, say

$$\boldsymbol{\mu} = \lim_{\substack{L\to 0\\ q\to\infty}} q\mathbf{L},$$

we have

$$\int_V \rho_i\varphi_j^{\rm eq}\,{\rm d}V = [-q_i\varphi_j^{\rm eq}(+0) + q_i\varphi_j^{\rm eq}(-0)]$$

$$= \lim_{\substack{L\to 0\\ q\to\infty}} q\mathbf{L}\cdot\nabla\varphi_j^{\rm eq} = -\boldsymbol{\mu}_i\cdot\mathbf{e}_j^{\rm eq} \quad (i,j=1,2) \quad (111)$$

$$\int_V \rho_i\varphi_j^{\rm non}\,{\rm d}V = [-q_i\varphi_j^{\rm non}(+0) + q_i\varphi_j^{\rm non}(-0)]$$

$$= \lim_{\substack{L\to 0\\ q\to\infty}} q\mathbf{L}\cdot\nabla\varphi_j^{\rm non} = -\boldsymbol{\mu}_i\cdot\mathbf{e}_j^{\rm non} \quad (i,j=1,2) \quad (112)$$

where the signs '+0' and '−0' specify the positions approaching the origin from two opposite sides. Accordingly we have

$$\int_V \Delta\rho\varphi_i^{\rm eq}\,{\rm d}V = -\Delta\boldsymbol{\mu}\cdot\mathbf{e}_i^{\rm eq} \quad (i=1,2) \quad (113)$$

$$\int_V \rho_i\Delta\varphi_{\rm op}\,{\rm d}V = \int_V \rho_i(\varphi_2^{\rm non}-\varphi_1^{\rm eq}){\rm d}V$$

$$= -\boldsymbol{\mu}_i\cdot(\mathbf{e}_2^{\rm non}-\mathbf{e}_1^{\rm eq}) \quad (i=1,2) \quad (114)$$

Applying Eqs. (113) and (114), Eq. (55) becomes

$$\Delta h\nu_{\rm ab} = -(1/2)(\Delta\boldsymbol{\mu}\cdot\mathbf{e}_1^{\rm eq} + \boldsymbol{\mu}_2\cdot\Delta\mathbf{e}_{\rm op}) \quad (115)$$

Combining Eqs. (106) and (109) with Eq. (115), we obtain the final form of the spectral shift for light absorption as follows

$$\Delta h\nu_{\rm ab} = -(1/2)(R\boldsymbol{\mu}_1 + R_{\rm op}\boldsymbol{\mu}_2)\cdot(\boldsymbol{\mu}_2-\boldsymbol{\mu}_1) \quad (116)$$

In the similar way, the spectral shift of light emission can be derived to the following form, i.e.

$$\Delta h\nu_{\rm em} = (1/2)(R\boldsymbol{\mu}_2 + R_{\rm op}\boldsymbol{\mu}_1)\cdot(\boldsymbol{\mu}_2-\boldsymbol{\mu}_1) \quad (117)$$

The sum of these two parts reads

$$\Delta h\nu_{\rm sum} = (1/2)R_{\rm or}(\boldsymbol{\mu}_2-\boldsymbol{\mu}_1)^2 \quad (118)$$

with

$$R_{\rm or} = R - R_{\rm op} \quad (119)$$

When comparing with the well-known Lippert–Mataga relationship

$$\Delta h\nu_{\rm sum}({\rm L-M}) = R_{\rm or}(\boldsymbol{\mu}_1-\boldsymbol{\mu}_2)^2 \quad (120)$$

given by Lippert [29] and Mataga [28] originally and by Marcus [17] later, our result given in Eq. (118) drops to only one half of that from the conventional models.

If one applies the expressions of electrostatic free energy by the conventional virtual work method, such as Eq. (18), and use the same spherical cavity approximation presented above, Lippert–Mataga relationship given in Eq. (120) will be easily deduced. In fact, if we notice the misunderstandings on the self-energy of the solvent polarization field in the past, the defects in the original deduction [27,28] of Eq. (120) become apparent.

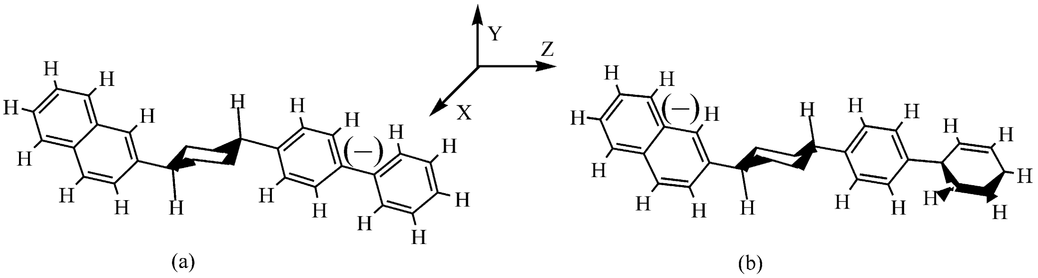
5. Application

The σ-bridge mediated ET reactions between biphenyl anion radical (Bp^-) and different acceptors were intensively investigated by Closs and Miller [37,38,51]. It has been widely believed that the experimental measurement of ET reactions between biphenyl and a series of organic systems, designed by Closs and coworkers is the first successful experimental observation of ET reactions in Marcus' inverted region. In this section, we study the electron transfer from Bp^- to naphthalene (Np) in solution. The newly developed two-sphere formula is used to estimate SRE. The cyclohexane (B) mediated ET from Bp^- to Np has been taken as the model system (Fig. 3). The coplanar orientation between the two π-electron moieties was confirmed by experiments and molecular mechanic calculations [37]. In the coplanar manner, V_{rp} will be predicted to arrive the maximum. Here 'coplanar' means that the orientation angle θ between the planar Bp^- group and Np group is set zero. In this system, the excess electron could be localized on one of the two π-electron moieties.

When the nuclear tunneling effect is small enough so that we can ignore it and the ET matrix element V_{rp} is small, the semi-classical model become applicable for predicting the ET rate constant [52]. Several parameters, the ET matrix element V_{rP}, the standard free energy ΔA_0, the inner reorganization energy IR and the solvent reorganization energy λ_{fw}, dominate the ET rate.

We carry out the investigation using the double-well potential picture. In this case, the ET reaction is assumed to start from the energy minima of the charge-localized reactant and reach its transition state at the crossing of the two charge-localized potential curves for reactant and product states. Such charge-localized potential curves are sometimes called the quasi-diabatic potential energy surfaces [53] so as to distinguish from the adiabatic potential constructed under the Born–Oppenheimer approximation. Systems shown in Fig. 3 are composed of three fragments: the donor, the acceptor and the bridge. In order to get the reasonable electronic structure, we need to obtain the electronically localized state in which the excess electron is localized on the donor or the acceptor. First of all, we optimize the three isolated species, NpH^-, NpH, and cyclohexane at the UHF/6-31G** level. We do not pursue the higher level here because we need to warrant that the geometries obtained in this stage can produce the energy minima in the further constructions of the charge-localized potential curves.

After the geometry optimization of the isolated species, we link these three parts to form the Bp^-–B–Np system by cutting off the terminal hydrogen atoms at proper positions, with the internal coordinates of the isolated species unchanged. Finally, the two C–C bonds linking the species undergo optimization with the other internal coordinates fixed. In the connection, Bp^- and Np are linked to the bridge molecule by substituting them for the *para*-hydrogen atoms in the chair-shaped cyclohexane. In addition, the donor and the acceptor fragments in Bp^-–B–Np prefer to sit perpendicular to the average plane of the cyclohexane ring. This consideration is also based on the results from X-ray structure determination on *trans*-1,4-diphenylcyclohexane [37]. Similarly, we can prepare the starting nuclear configuration of charge-localized state for product Bp–B–Np^-. The starting geometries of Bp^-–B–Np and Bp–B–Np^- prepared in this way are assumed the optimal geometries for the electronically localized state. So it does not undergo further full geometry optimization. In our experience, a full geometry optimization will drive the system to the energy minima with the excess electron delocalized. Such a geometry is of course not desirable because it is not the optimal geometry in which the excess electron is localized on donor or on acceptor.



(a)

(b)

Fig. 3. Schematic drawing of model system of intramolecular electron transfer. The orientation angle between the planar Bp^- group and Np group is set zero. (a) Reactant system Bp^-–B–Np; (b) product system Bp–B–Np^-.

Table 2
Dipole moment and net charge of different parts

System	Dipole moment (Debye)				Net charge		
	X	*y*	*z*	Total	Bp	Bridge	Np
Bp^-–B–Np	0.00	0.50	−10.65	10.66	−0.89	−0.06	−0.05
Bp–B–Np^-	0.08	−0.84	11.10	11.14	−0.06	−0.07	−0.87

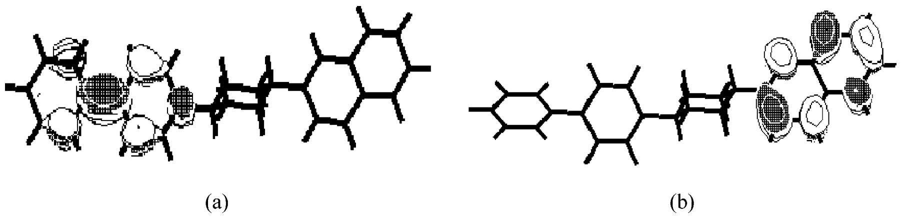

(a) (b)

Fig. 4. Highest occupied molecular orbitals of the reactant state (Bp^-–B–Np) (a) and the product state (Bp–B–Np^-) (b) See Fig. 3 for the definition of the Cartesian coordinate.

We check the validity of the localization of the excess electron. Single point calculations at the same level, UHF/6-31G**, have been carried out for the two starting geometries of Bp^-–B–Np and Bp–B–Np^- prepared in the above steps. The net charges on the three moieties by Mulliken population analysis and the dipole moment are collected in Table 2. The frontier orbitals of these two systems are shown in Fig. 4. Population analysis indicates the successful localization of the excess electron. Therefore, the starting geometries could be safely used to construct the charge-localized potential curves. Negligibly small net charge brought by the bridge permits us to make the bridge molecule fixed in the construction of the double-well potentials.

In the construction of the double-well potential curves, we need to determine the reaction coordinates at first. However, the accurate determination of the ET reaction pathway for an even small system is not practicable at present. Therefore, we apply the linear coordinate R in this paper to describe the nuclear configuration variation during ET [53,54], i.e.

$$Q_i = RQ_i^{\mathrm{p}} + (1-R)Q_i^{\mathrm{r}} \qquad (121)$$

where Q_i represents the ith internal nuclear coordinate, Q_i^{r} and Q_i^{p} represent the ith internal nuclear coordinates at the starting geometries of reactant and product, respectively. $R=0$ corresponds to the starting geometry of Bp^-–B–Np and $R=1$ to that of Bp–B–Np^-. The choice of the $3N-6$ independent internal coordinates ($Q_i, i=3N-6$) out of $3N$, which dominate the nuclear configuration of the system during ET, is somewhat arbitrary in this work but it does not apply large influence to the potential curves according to our experience.

The molecular orbital sets from UHF-SCF calculations at the starting geometries of Bp^-–B–Np and Bp–B–Np^-, which yield different charge-localized states, are used to induce the potential energy calculation of the charge-localized state. Such an induction usually maintains the electronic structure of the reactant even if at the optimal geometry of the product. We call this as the charge-localized-initial-guess induced SCF technique. In this way, the charge-localized potential curves for electronic structures of both reactant and product have been constructed at UHF/6-31G** level. The conductor-like-screening-model [14] (COSMO), a continuum model for the equilibrium solvation and arbitrary cavity coded into HONDO package [55], has been adopted to simulate the solvent effect in the energy calculation. The potential energy curves of U_{r} for Bp^-–B–Np and U_{p} for Bp–B–Np^- in tetrahydrofuran (THF, $\varepsilon_{\mathrm{S}}=10.37$ [22]) are calculated and shown in Fig. 5. The crossing of two curves, which determines the nuclear configuration of the transition state of ET, is found at $R_{\mathrm{C}}=0.53$. If we use the energy difference $\Delta U_0=U_{\mathrm{p}}(1)-U_{\mathrm{X}}(0)$ to approximate the standard free energy ΔA_0, this ET is found slightly exothermic, and ΔA_0 is obtained $-2.5\ \mathrm{kJ\ mol^{-1}}$ in gas phase and $-3.6\ \mathrm{kJ\ mol^{-1}}$ in THF

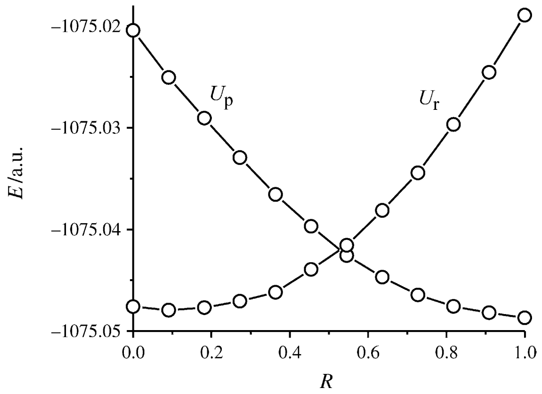


Fig. 5. Double-well potential of coplanar system in THF.

Table 3
Reorganization energy and ET matrix element[a]

	IR	λ_{av}	ΔA_0	V_{rp}
This work	74.4	47.5	−3.6	2.7
Exp.[b]	56.0[c]	53.0[c]	−4.8	1.7

[a] Energy is in kJ mol^{-1}.

[b] Experimentally estimated parameters from Ref. [37].

[c] The contribution from biphenyl torsion of 0.13 eV given in Ref. [38] is subtracted from λ_{fw} and added to IR.

solvent. Experimental estimation for this quantity is about −4.8 kJ mol^{-1} in solution [37].

Based on the energy curves of charge-localized states shown in Fig. 5, the inner reorganization energy can be expressed as the average value, i.e.

$$\mathrm{IR} = [U_{\mathrm{r}}(1) - U_{\mathrm{r}}(0) + U_{\mathrm{p}}(0) - U_{\mathrm{p}}(1)]/2 \tag{122}$$

Here $U_{\mathrm{r}}(R)$ and $U_{\mathrm{p}}(R)$ are the energy curves corresponding to Bp^{-}–B–Np and Bp–B–Np^{-}, respectively. The value of IR is listed in Table 3. One of the authors [54,56] performed IR calculations for this system by only taking the isolated donor and acceptor into account. In this way, the inner reorganization energy in gas-phase was approximated by

$$\mathrm{IR} = [\mathrm{IR}(\mathrm{BpH}^{-}/\mathrm{BpH}) + \mathrm{IR}(\mathrm{NpH}^{-}/\mathrm{NpH})]/2 \tag{123}$$

where IR(B^{-}/B) (B = BpH or NpH) represent the inner reorganization energy of the self-exchange reactions $\mathrm{B}^{-} + \mathrm{B} = \mathrm{B} + \mathrm{B}^{-}$. The results obtained by one of the authors [54,56] with Eq. (123) are 81.7 kJ mol^{-1} (UHF/4-31G), 77.8 kJ mol^{-1} (UHF/DZP), 81.3 kJ mol^{-1} (UHF/6-31G*) and 75.3 kJ mol^{-1} (CASSCF/6-31G*). The computation level is given in the parentheses. DZP represents Dunning's (9s,5p)/(3s,2p) basis functions with the polarization function on all atoms; CASSCF refers to the complete active space SCF. In the experimental aspect, Closs et al. [37] obtained the value of 0.45 eV without inclusion of the contribution from the torsion motion around the C–C bond linking the two phenyl rings. If the contribution −13 kJ mol^{-1} from this low-frequency torsion motion from another experimental measurement [38] is involved, the inner reorganization energy fitted by experiment should be about 56 kJ mol^{-1}.

The two-sphere formula given in Eq. (97) is used to make the estimation of SRE. The ET distance from the mass center of the donor fragment to that of the acceptor for the present system (this system is denoted C-1,4-e,e in Ref. [37]) is found to be 1.171 nm. Adopting the crystallographic determinations [39] of the radii, 0.39 nm for biphenyl and 0.37 nm for naphthalene, and taking $\varepsilon_{\mathrm{S}} = 10.37$ and $\varepsilon_{\mathrm{op}} = 2.078$ [22] for THF, λ_{av} is estimated 47.5 kJ mol^{-1} according to Eq. (97). We need to emphasize that we take λ_{av} rather than λ_{fw} here since Marcus' semi-classical model for electron transfer rate adopts the average value of reorganization energies. In Ref. [37], SRE for the present system was experimentally estimated 53.0 kJ mol^{-1} by subtracting a value of 0.13 eV [38] from the value of 0.68 eV [37]. Comparing the present estimation with the value given in Ref. [37], we can find the possible explanation for the difference of about 5 kJ mol^{-1} as following: neither the donor nor the acceptor are not spherical, so the polarized charge tends to concentrate on the portion of cavity surface close to the solute free charge, hence the effective radius of the cavity in the realistic environment of polar solvent should be smaller than the crystallographic radius. This consideration will make the λ_{av} value increase slightly. If we use the experimentally estimated value of 53.0 kJ mol^{-1}, Eq. (97) gives a value of 0.36 nm for effective average radius of biphenyl and naphthalene in solution. However, if we use the average radius of BpH and NpH, 0.38 nm, the conventional two-sphere formula shown in Eq. (24) will predict a value of 95 kJ mol^{-1}. From our present arguments, we think that the continuum theory behaves well for nonequilibrium solvation as for equilibrium solvation.

Several theoretical methods can be used to calculate V_{rp}, such as the partitioning method [57,58], the variational principle on the basis of two-state approach [53,59], and Koopmans' theorem [54,60]. In the present work we employ the direct variational principle treatment to the two charge-localized states. If we denote the two charge-localized states η_{r} for the reactant and η_{p} for the product, we have [53,59]

$$V_{\mathrm{rp}} = [H_{\mathrm{rp}} - S_{\mathrm{rp}}(H_{\mathrm{rr}} + H_{\mathrm{pp}})/2](1 - S_{\mathrm{rp}}^2)^{-1} \tag{124}$$

here $S_{\mathrm{rp}} = \langle \eta_{\mathrm{r}} | \eta_{\mathrm{p}} \rangle$ and $H_{ij} = \langle \eta_i | \mathbf{H} | \eta_j \rangle$ $(i,j = \mathrm{r},\mathrm{p})$ with **H** being the electronic Harmiltonian. If we can correctly produce the two charge-localized states η_{r} and η_{p}, V_{rp} can be calculated with the subroutines linked to HONDO package [55]. A key step is to generate an initial orbital guess to induce the UHF-SCF calculation of V_{rp}, since an ordinary SCF can not produce the charge-localized state at nuclear configuration of transition state.

As described before, two sets of molecular orbitals can yield different charge-localized states. From the position of crossing of the two energy curves shown in Fig. 5, we can determine the geometry of the transition state by setting $R_{\mathrm{c}} = 0.53$, and consequently all the internal nuclear coordinates of the transition state can be determined. The two sets of charge-localized molecular orbitals $\{\varphi_i^{\mathrm{r}}\}$ of Bp^{-}–B–Np at $R = 0$ and $\{\varphi_i^{\mathrm{p}}\}$ of Bp–B–Np^{-} at $R = 1$, are taken as initial guesses to induce the UHF-SCF calculations at transition state ($R_{\mathrm{c}} = 0.53$). The standard method coded in HONDO package [55] can yield two charge-localized states and give the value of V_{rp} according to Eq. (124). In this way, we obtain the value of 2.7 kJ mol^{-1} for V_{rp} in THF solvent. This result is slightly larger than the value of 1.69 kJ mol^{-1} estimated from the experimental fitting in the same solvent [37], the value of 2.0 kJ mol^{-1} by partitioning method [57], and the value of 1.30 kJ mol^{-1} by Koopmans' theorem [56]. By means of the Mulliken population analysis, the bridge has found slightly negatively charged. The incomplete charge localization is a possible reason for the overestimation of V_{rp} in the present work, since it will enlarge the overlap S_{rp}. Eq. (124) shows that the overestimation of V_{rp} will be caused for this reason.

6. Summary

From the derivation by the authors, some doubts existing in current theories of nonequilibrium, including the methods, SRE, and spectral shifts, have been clarified. Particular attentions have been paid to the previous virtual work method [16,25,26], but the failure in the modification of Felderhof's equation [18,30,31,34–36] and the misunderstandings on the interaction energy between the polarization field and its source free charge are also clarified in this article. From the derivations given in this work, we feel that the problems in the virtual work approach are simply the inadequate use of the work expression given in Eq. (15). In general, like a great amount of literatures and textbooks, Eq. (15) is invalid. However, if we notice the rarely used Jackson's equation, Eq. (33), we know Eq. (15) is in fact its reduced form. Because the linear response given by Eq. (50) does not remain during the step from the equilibrium state to the nonequilibrium state, the application of Eq. (15) is invalid in the present case. For this reason, as illustrated in Section 2, a series of doubts arose in the theoretical conclusions deduced in the past.

This work reveals that the central defect in the previous theories of nonequilibrium is the postulation of interaction energy between the polarization field and its source charge. Particular attentions should be paid to the zero value for the term $\int \mathbf{E}_{\mathrm{f}} \cdot \mathbf{D}_{\mathrm{p}}\, \mathrm{d}V$, as given in Eq. (78). This leads to an important conclusion that the interaction energy between the polarization field and its source charge no longer possesses the form similar to that between two independent fields. From the present derivation, we feel that the postulations on $G_{\mathrm{f-p}}$ and G_{p} in the past are somewhat arbitrary and lack of physical foundations. These presumptions do not affect the results of the equilibrium solvation, but they will have important influence on the conclusions of the nonequilibrium state, since the a non-zero self energy of the orientatonal component of the solvent polarization will be taken as fixed and brought into the electrostatic free energy of the nonequilibrium state.

It should be mentioned that the zero result of the self-energy of polarization field is exactly derived within the frame of continuous medium theory. However, for the realistic medium, the situation might be different, but it is beyond the ability of the macroscopic continuum model, and the microscopic structures of the individual solvent molecules need to be taken into account. Postulating a non-zero self-energy but making derivations within the framework of continuum model in the past is apparently inappropriate.

The conclusions deduced in the past, for example the identical value of SRE for both the forward and backward processes of ET reaction, are based on the linear response, $\delta D = k\, \delta E$, with k being a constant depending on properties of the solvent. However, our derivations in Section 3.1 show that k is different at equilibrium state and at nonequilibrium state (see Eqs. (48) and (50)). This fact indicates that previous virtual work approach seems not well founded.

Unlike the conventional theory, reformulations in this work reveal that SRE depends on both the direction of ET and the charge distribution ρ_1 of the initial state, but has nothing to do with the charge distribution ρ_2 of the final state (see Eq. (64)). When reduced to the two-sphere model, SRE is case-sensitive. The charge recombination process gives the largest value of SRE.

The failure of the current two-sphere formula for evaluation of SRE of ET can be clarified immediately when it is employed to the Closs–Miller system. The mean radius of 0.59 nm for biphenyl and naphthalene is unacceptable when compared with the structural data, 0.39 nm for biphenyl and 0.37 nm for naphthalene. From our theory, 0.36 nm for the radius of Bp, is slightly smaller than that form the structural data. This deviation can find its explanation if we notice that the polarized charge of solvent tends to distribute on the portion of cavity surface close to the solute charge. This behavior makes the effective radius slightly decrease. As depicted above, the two-sphere formula developed here can only give estimation for Bp radius but not for Np. This feature is somewhat unexpected. However, if we notice that Np is not charged at the initial state, this conclusion becomes understandable. Experiments on this matter are encouraged to validate these new features predicted in the present work.

All the ab initio calculations have been carried out by HONDO/S package [55].

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Appendix A. A proof of Eq. (6)

We consider an arbitrary cavity. As shown in Fig. A1, the interface is denoted S. The solute charge distribution inside

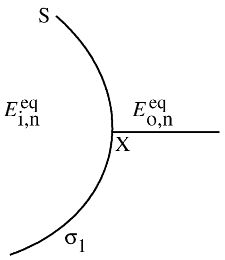

Fig. A1. Electric field inside and outside the interface.

the cavity is ρ_1, and the medium is of a dielectric constant of ε_S. We assume that the distribution of polarized surface charge on S is σ_1. We denote the electric fields of equilibrium state $E_{o,n}^{eq}$ outside the surface and $E_{i,n}^{eq}$ inside the surface with n being the normal direction of the interface. We have

$$\varepsilon_s E_{o,n}^{eq} = E_{i,n}^{eq} \tag{A.1}$$

$$E_{o,n}^{eq} - E_{i,n}^{eq} = 4\pi\sigma_1 \tag{A.2}$$

At the point X on S, we divide the total electric field into two parts: $E_{i,n}^{X}$ ($E_{o,n}^{X}$) due to the polarized surface charge at X, and $E_{i,n}^{Y}$ ($E_{o,n}^{Y}$) by other charge distribution, including both solute charge and polarized charge. Hence

$$E_{o,n}^{eq} = E_{o,n}^{X} + E_{o,n}^{Y}, \quad E_{i,n}^{eq} = E_{i,n}^{X} + E_{i,n}^{Y} \tag{A.3}$$

In addition, we notice the following properties of the electric field on the interface, i.e. (see Fig. A1)

$$E_{i,n}^{Y} = E_{o,n}^{Y} = E_{n}^{Y}, \quad E_{i,n}^{X} = -E_{o,n}^{X} \tag{A.4}$$

Combining Eqs. (A.2)–(A.4) gives

$$E_{o,n}^{eq} = 2\pi\sigma_1 + E_n^Y, \quad E_{i,n}^{eq} = -2\pi\sigma_1 + E_n^Y \tag{A.5}$$

Substituting Eq. (A.5) into Eq. (A.1) yields

$$2\pi\sigma_1 \frac{\varepsilon_s + 1}{\varepsilon_s - 1} + E_n^Y = 0 \tag{A.6}$$

Expressing E_n^Y in the form of integral, Eq. (A.6) becomes

$$2\pi\sigma_1(\mathbf{r}) \frac{\varepsilon_s + 1}{\varepsilon_s - 1} + \int_{S-X} \frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}}{|\mathbf{r}-\mathbf{r}'|^3} \sigma_1(\mathbf{r}')\mathrm{d}S' + \int_{V'} \frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}}{|\mathbf{r}-\mathbf{r}'|^3} \rho_1(\mathbf{r}')\mathrm{d}V' = 0 \tag{A.7}$$

The surface integration is over all the interface but the point X is excluded. Eq. (A.7) is just what is used in D-PCM method by Cossi and Barone [61]

In the equilibrium state in the medium of ε_S, the polarized surface charge can be divided into two parts: the orientational $\sigma_{or,1}$ and electronic $\sigma_{op,1}$. The following relationships are well known

$$\frac{\sigma_1}{\chi} = \frac{\sigma_{or,1}}{\chi_{or}}, \quad 4\pi\chi = \varepsilon_s - 1 \quad \text{and} \quad 4\pi\chi_{or} = \varepsilon_s - \varepsilon_{op} \tag{A.8}$$

Hence, we have

$$\sigma_{or,1} = \frac{\chi_{or}}{\chi}\sigma_1 = \frac{\chi - \chi_{op}}{\chi}\sigma_1 = \frac{\varepsilon_s - \varepsilon_{op}}{\varepsilon_s - 1}\sigma_1 \tag{A.9}$$

We suppose the dielectric constant is suddenly changed from ε_S to ε_{op}, the polarized charge becomes to σ_1^{op} such that $\sigma_1^{op} = \sigma_{or,1} + \sigma_{or,1-op} + \sigma_{\rho 1-op}$ and Eq. (5) holds. Similar to Eqs. (A.1)–(A.6), we have

$$\varepsilon_{op} E_{o,n}^{op} - E_{i,n}^{op} = 4\pi\sigma_{or,1} \tag{A.10}$$

$$E_{o,n}^{op} - E_{1,n}^{op} = 4\pi\sigma_1^{op} \tag{A.11}$$

$$E_{o,n}^{op} = E_{o,n}^{op,X} + E_{o,n}^{op,Y}, \quad E_{i,n}^{op} = E_{i,n}^{op,X} + E_{i,n}^{op,Y} \tag{A.12}$$

$$E_{i,n}^{op,Y} = E_{o,n}^{op,Y} = E_{n}^{op,Y}, \quad E_{i,n}^{op,X} = -E_{o,n}^{op,X} \tag{A.13}$$

$$E_{o,n}^{op} = 2\pi\sigma_1^{op} + E_n^{op,Y}, \quad E_{i,n}^{op} = -2\pi\sigma_1^{op} + E_n^{op,Y} \tag{A.14}$$

$$2\pi\left[\sigma_1^{op}\frac{\varepsilon_{op}+1}{\varepsilon_{op}-1} - \sigma_{or,1}\frac{2}{\varepsilon_{op}-1}\right] + E_n^{op,Y} = 0 \tag{A.15}$$

Eq. (A.15) can be expressed in the form of integral, i.e.

$$2\pi\left[\sigma_1^{op}(\mathbf{r})\frac{\varepsilon_{op}+1}{\varepsilon_{op}-1} - \sigma_{or,1}(\mathbf{r})\frac{2}{\varepsilon_{op}-1}\right] + \int_{S-X} \frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}}{|\mathbf{r}-\mathbf{r}'|^3} \sigma_1^{op}(\mathbf{r}')\mathrm{d}S' + \int_{V'} \frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}}{|\mathbf{r}-\mathbf{r}'|^3} \rho_1(\mathbf{r}')\mathrm{d}V' = 0 \tag{A.16}$$

Making use of Eq. (A.9), the first term in Eq. (A.16) becomes

$$2\pi\left(\sigma_1^{op}\frac{\varepsilon_{op}+1}{\varepsilon_{op}-1} - \sigma_{or,1}\frac{2}{\varepsilon_{op}-1}\right) = 2\pi\left[(\sigma_1^{op} - \sigma_1)\frac{\varepsilon_{op}+1}{\varepsilon_{op}-1} + \sigma_1\frac{\varepsilon+1}{\varepsilon-1}\right] \tag{A.17}$$

Combining Eqs. (A.7), (A.16) and (A.17) gives

$$\int_{S-X} \frac{(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}}{|\mathbf{r}-\mathbf{r}'|^3}[\sigma_1^{op}(\mathbf{r}') - \sigma_1(\mathbf{r}')]\mathrm{d}S' + 2\pi[\sigma_1^{op}(\mathbf{r}) - \sigma_1(\mathbf{r})]\frac{\varepsilon_{op}+1}{\varepsilon_{op}-1} = 0 \tag{A.18}$$

Eq. (A.18) holds true for any interface S unless $\sigma_1^{op}(\mathbf{r}) = \sigma_1(\mathbf{r})$. This means that the sudden change of dielectric constant does not change the polarized charge since $\sigma_{or,1}$ and ρ_1 remain unchanged. Based on this conclusion, we have

$$\varphi_1^{\mathrm{eq}}(\rho_1,\varepsilon_{\mathrm{s}})=\varphi_1^{\mathrm{eq}}(\rho_1+\sigma_{\mathrm{or},1},\varepsilon_{\mathrm{op}}) \tag{A.19}$$

Appendix B. Field superposition approach to Eq. (42)

For the simplicity of the derivation, we make our derivation in terms of charge-potential notation. Here we employ the field superposition principle for our purpose. As shown in Eq. (1), the nonequilibrium state $[\rho_2, \Phi_2^{\mathrm{non}}]$ can be taken as a superposition of the two independent fields $[\rho_1, \Phi_1^{\mathrm{eq}}]$ and $[\Delta\rho,\Delta\Phi_{\mathrm{op}}]$ which, respectively, relate to the equilibrium in the realistic medium of ε_{S} and the pseudoequilibrium in the hypothetical medium of $\varepsilon_{\mathrm{op}}$. Making the energy decomposition similar to Eq. (71), these two independent fields have their individual self-energies as

$$G_{\mathrm{s}}=\frac{1}{2}\int \rho_1\Phi_1^{\mathrm{eq}}\,\mathrm{d}V \tag{B.1}$$

$$G_{\mathrm{op}}=\frac{1}{2}\int\limits_V \Delta\rho\Delta\Phi_{\mathrm{op}}\,\mathrm{d}V \tag{B.2}$$

The interaction energy between these two fields is thus given by

$$G_{\mathrm{s-op}}=\frac{1}{2}\int\limits_V(\rho_2\Delta\Phi_{\mathrm{op}}+\Delta\rho\Phi_1^{\mathrm{eq}})\mathrm{d}V \tag{B.3}$$

Up to this stage, the expression of the electrostatic free energy of the nonequilibrium state is rather straightforward. By summing over the three parts of energy contributions given in Eqs. (B.1)–(B.3) and noticing Eqs. (2) and (8), we can obtain the same expression as given by Eq. (42).

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