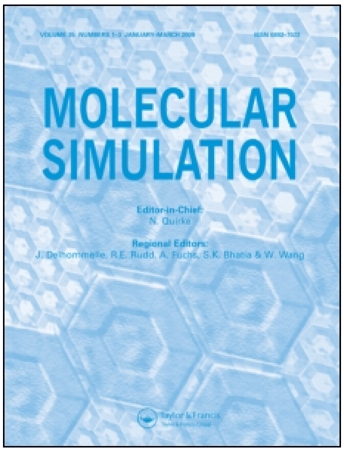

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THE FREE ENERGY PROFILES FOR THE ELECTRON TRANSFER REACTIONS CALCULATED FROM THE INTEGRAL EQUATION METHOD OF LIQUIDS

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A microscopic description of the free energy profile for the electron transfer reaction is presented based on the extended reference interaction site method (ex-RISM) in the statistical mechanical theory of molecular liquids. We employed the scheme proposed by Marcus to characterize the non-equilibrium solvent polarizations at the intermediate states of the reaction. The method is applied to two models of electron exchange reactions where the redox pairs have valence charges of 1/2+/1/2- and 2+/3+, and to a model of a charge separation reaction. Due to the non-linear nature of the hypernetted chain (HNC) closure to solve the RISM equation, our method can shed light on the non-linearity of the free energy profiles.

KEY WORDS: Electron transfer reactions, free energy profiles, RISM, HNC.

1 INTRODUCTION

The space-time density fluctuations in polar liquids and their coupling with a variety of chemical processes have attracted increasing attention from various fields in physical chemistry and biophysics [1–3]. The photo-induced electronic excitation of a solute, if accompanied by an appreciable change in dipole moment, coupled to solvent fluctuation is the simplest and well studied amongst such phenomena [1]. Electronic excitation occurs virtually instantaneously compared to the rate of solvent fluctuation in such a case, and the successive dynamics of the solvent to accomodate the new solute electronic state controls the relaxation process to equilibrium. This dynamics can be probed as the dynamic stokes shift in the time resolved fluorescence measurement. The time dependent solvent reorganization or the solvation dynamics has been the subject of intense investigation through irreversible statistical mechanics [4,5] and the molecular dynamics simulation [6–8].

The other important chemical process which probes the solvent fluctuation is the thermal electron transfer (ET) reaction [2]. In the presence of an immersed solute, a polar solvent around the solute continuously fluctuates due to the translational and orientational motion of its constituent molecules. The concept of a free energy profile governing these fluctuations as a function of solvent coordinates plays a central role in the theory of ET. It is therefore crucial to determine the free energy profile for the theoretical study of the ET reaction. Marcus was the first to realize such a free energy profile in his seminal papers [9 – 12]. The fundamental idea is that the actual non-equilibrium solvent polarization at the intermediate state of the reaction is equivalent to the equilibrium one with a hypothetical charge distribution appropriately defined [11]. Therefore, if one can identify such hypothetical charge distribution, the activation free energy or the diabatic free energy profile can be calculated only in terms of equilibrium properties [12]. Marcus theory has been validated in numerous experimental ET studies [13]. However, the most serious drawback in Marcus theory is the use of the continuum picture for the solvent. It is well established that a continuum model, when applied to a molecular system, leads to an ambiguous interpretation of the molecular parameters introduced as boundary conditions. Nonetheless, the basic idea in Marcus theory for obtaining the free energy profile can still be incorporated in a modified theory where the continuum model can be replaced by a microscopic model. In this article, we present a new approach to obtain the free energy profile based on Marcus' idea and an integral equation theory of molecular liquids [14].

When liquids are viewed as a collection of molecules (or atoms) unlike a continuum model, the molecular (atomic) density fluctuates in space as well as in time. A thermal average of the spatial density $\langle \rho(r) \rangle$ of molecules (atoms) is constant in uniform liquids, and it characterizes the macroscopic state of the liquid system. The second moment of the spatial density fluctuation, or the spatial density correlation, $\langle \rho(r)\rho(r') \rangle$, characterizes the microscopic state of the liquid. It is essentially this quantity that should be incorporated in a microscopic version of Marcus theory. An integral equation developed for molecular liquids, referred to as the reference interaction site method [15] (RISM) and its extended version [16,17] (ex-RISM) gives the density correlation function between a pair of atoms in liquid as a functional of intermolecular interactions which are represented by a sum of interactions between a pair of sites. The theory has been successfully applied to a variety of problems related to the structure and thermodynamic properties of liquids and liquid mixtures. Recent applications and developments of the theory include studies for the electronic structure of solvated molecules [18] and the dynamic structure factor in liquids [19].

Recently, validity of the two assumptions regarding the free energy profile, parabolic and solute independence of the force constants, has been examined by several authors. These assumptions have been predicted from the continuum dielectric models and commonly adopted in many of the early works. Kakitani *et al.* [20] discussed the non-linearity of solvation related to ET in polar solvents, and Carter and Hynes [21] performed molecular dynamics simulations of the charge separation and the charge recombination reactions to observe such non-linear effects. More recently, Ando *et al.* [22] discussed these problems and they observed no such nonlinear effects. Due to the non-linear nature of the hypernetted chain (HNC) closure to solve the RISM equation, our method can shed light on the non-linearity of free energy profiles. We discuss these problems based on the obtained free energy profiles.

The organization of the paper is as follows. In the following section, we present the method of calculating the free energy profile based on Marcus' idea and ex-RISM. In section III, the applicability of the new method is demonstrated by applying it to some typical problems related to ET reactions. We conclude the paper in section IV.

2 THEORY

2.1 *Method to Calculate the Diabatic Free Energy Profile*

In order to describe the ET reactions in solutions, it is important to characterize the configurations of the polar solvent (polarizations) at various stages of the reaction appropriately. We first schematically illustrate how the ET reaction proceeds along a reaction coordinate [23].

In Figure 1, the (diabatic) potential energy surfaces for nuclear motion for the whole system of donor, acceptor and surrounding solvent molecules are plotted against a nuclear coordinate. The latter has as many dimensions as degrees of freedom for nuclear motion of the whole system. However, one available abscissa serves as a representative axis of nuclear motion from an initial equilibrium configuration, A, to a final configuration, B. Curve V^R gives the potential energy of the system when the transferring electron is in the donor (the reactant state), while curve V^P is for when the electron is in the acceptor (the product state). The displacement from A to B represents the change in the equilibrium configuration of the surroundings; the

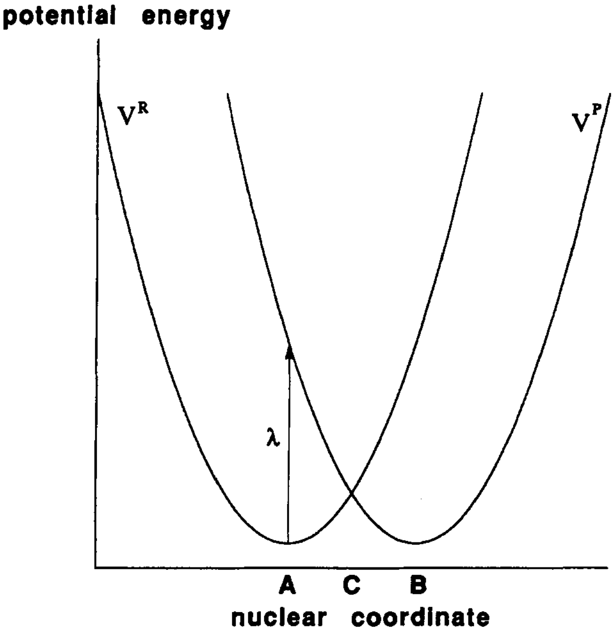

Figure 1 The potential energy surfaces for the reactant, denoted as V^R and the product state, denoted as V^P, of the system.

shifts of nuclear configuration caused by ET. The ET process is a jump from V^R to V^P. The Franck-Condon principle requires the nuclear configuration to be identical immediately before and after ET, that is, ET must be a vertical transition in Figure 1. Conservation of energy requires it to be a horizontal transition. The only possible configuration to meet both requirements is at C where the two curves cross. Therefore, ET can be described as a process of ascending, crossing and then descending the two curves, V^R and V^P.

Before we describe the procedure to characterize the solvent polarizations in the course of ET, we first introduce some notations. The system consists of two reacting particles (in this paper, ions), denoted as A (donor) and B (acceptor), and surrounding solvent molecules. The distance between A and B is fixed. Let e_A and e_B denote the charges of A and B at the reactant state, respectively, which are located at center of each ion, and let R^N denote the coordinates of all the solvent molecules, where N is the total number of the solvent molecules. Let z denote a fraction of the electronic charge transferred from A to B. In other words, $z = 0$ corresponds to $\{e_A, e_B\}$, the charge distribution at the reactant state, where $\{\cdots\}$ denotes the charge distribution of the solute ions, $z = 1$ corresponds to $\{e_A + e, e_B - e\}$, that at the product state, where $-e$ is the charge of an electron, and other values of z correspond to the hypothetical charge distributions $\{e_A + ze, e_B - ze\}$. Let $V_z(R^N)$ denote the potential energy of the system which consists of solute-solvent and solvent-solvent interaction potentials when the solute ions have the charge distribution $\{e_A + ze, e_B - ze\}$. The total potential energy of the system is the sum of $V_z(R^N)$ and $E_{\mathrm{el},z}$, where $E_{\mathrm{el},z}$ is the solute energy term associated with the Coulomb interaction potential and the electronic energies of the solute ions which are independent of solvent motions. The explicit treatment of the z-dependent solute energy terms are unnecessary as shown below, but the difference of the solute energy terms between the reactant and the product states,

$$\begin{aligned} \varepsilon &\equiv E_{\mathrm{el}}^R - E_{\mathrm{el}}^P \\ &= E_{\mathrm{el},0} - E_{\mathrm{el},1} \end{aligned} \tag{1}$$

has to be incorporated when we speak of the relative position (height) of the reactant and the product free energy profiles (see Eq. (10)). In case of an electron exchange reaction, the value of ε is equal to zero by symmetry of the reaction.

The solvent polarizations at the transition state or at other intermediate states of the reaction are non-equilibrium polarizations for the actual charge distribution of the solute ions, $\{e_A, e_B\}$. The scheme in Marcus theory to characterize the non-equilibrium solvent polarization is as follows [24]; the hypothetical charge distribution, $\{e_A + ze, e_B - ze\}$, is that with which the actual non-equilibrium solvent polarization would be in equilibrium. As an instructive example, we take the ferric-ferrous ET reaction in water. This system can be viewed as consisting of two Fe^{3+} ions, an electron and surrounding water molecules. The charge distribution of the reactant state is $\{Fe^{2+}, Fe^{3+}\}$, and that of the product state is $\{Fe^{3+}, Fe^{2+}\}$. In both cases, the electron is bound to one of the two Fe^{3+} ions. Most of the times in the reactant state, the solvent will exist in the stable configurations corresponding to $\{Fe^{2+}, Fe^{3+}\}$. Infrequently, however, a solvent configuration which makes the two redox sites degenerate can occur because of the fluctuation of the solvent configurations. When this solvent configuration appears, the electron will resonate between the two ions and it can then transfer. That is, this infrequent solvent configuration corresponds to the transition state of ET (point C of Fig. 1). Of course, there are many solvent configurations that make the two redox sites degenerate. Following Marcus theory, these non-equilibrium solvent configurations at the transition state can be characterized as the equilibrium ones for the hypothetical charge distribution $\{Fe^{2.5+}, Fe^{2.5+}\}$. Other non-equilibrium solvent configurations at the intermediate states can be characterized as the equilibrium ones for the hypothetical charge distributions $\{Fe^{2+z}, Fe^{3-z}\}$ with appropriately chosen z. The actual charge distribution in the reactant state is $\{Fe^{2+}, Fe^{3+}\}$, and the hypothetical charge distributions are only to characterize non-equilibrium solvent configurations in the course of the reaction.

The fraction z can be regarded as a solvent reaction coordinate because it characterizes, not the actual charge distribution of the solute ions, but the non-equilibrium solvent configurations. We define here a more convenient reaction coordinate. This new reaction coordinate is defined by [25],

$$\Delta E = e(V_B - V_A), \tag{2}$$

where V_A (or V_B) denotes the electric potential that the solvent molecules produce at the site of the ion A (or B), and e is the unit charge. A specific value of ΔE defines the system along the reaction coordinate. Let ΔE_0 represent the bottom (the stable state) of the profile, *i.e.* ΔE_0 is the value of ΔE produced by the stable configurations of the solvent, and let ΔE^* represent the crossing point (the transition state) of the two surfaces. Intermediate values of ΔE represent the states between the stable state and the transition state. The schematic interpretation of ΔE is illustrated in Figure 2. The reaction coordinate ΔE characterizes the tendency of the solvent polarization as a whole around the solute ions, and this polarization can be illustrated by an arrow located between the solute ions. This arrow can be regarded as a hypothetical dipole that produces ΔE. The fluctuations of the solvent configurations can be illustrated as the Brownian-like librational motion of that arrow. Unlike the reaction coordinate used in Figure 1, which has as many dimensions as degrees of freedom of the system, ΔE (or z) is a scalar coordinate; other degrees of freedom are averaged out. The surface along that scalar coordinate becomes free energy curve (profile). In this paper, we are not concerned about the overlap of the electronic orbitals between the reacting ions, therefore, the free energy profile which will be obtained is a diabatic one.

The method for obtaining the diabatic free energy profile for the reactant state is summarized in Figure 3. What we want to calculate is the non-equilibrium solvation free energy, ΔF^R in Figure 3, and we derive an alternative (indirect) way of calculating this quantity. The configurations of the solvent (polarizations) are characterized by specific values of ΔE which are illustrated by arrows as in Figure 2. One arrow in Figure 3 represents ΔE_0, produced by the equilibrium solvent configurations corresponding to $\{e_A, e_B\}$, while the other represents ΔE_z, calculated from the equilibrium solvent configurations corresponding to the hypothetical charge distribution

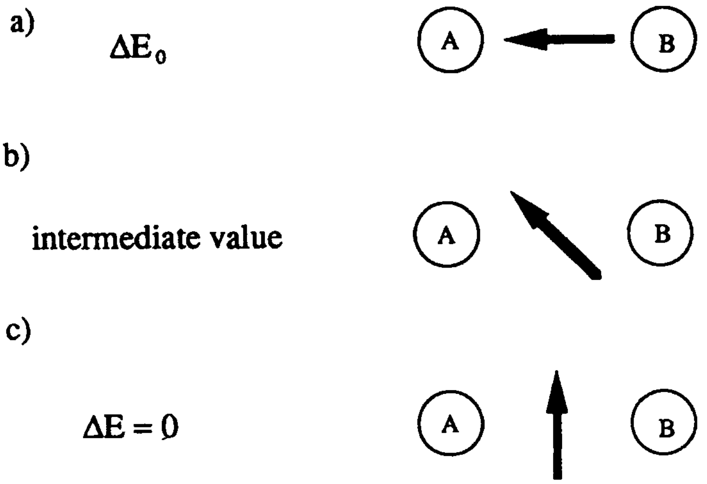

Figure 2 Schematical interpretation of ΔE defined by Eq. (2). The arrow in (a) represents a set of equilibrium solvent configurations. The arrow in (c) represents a set of solvent configurations at the transition state of an electron exchange reaction. The arrow in (b) represents a set of solvent configurations at the intermediate state between the stable state and the transition state.

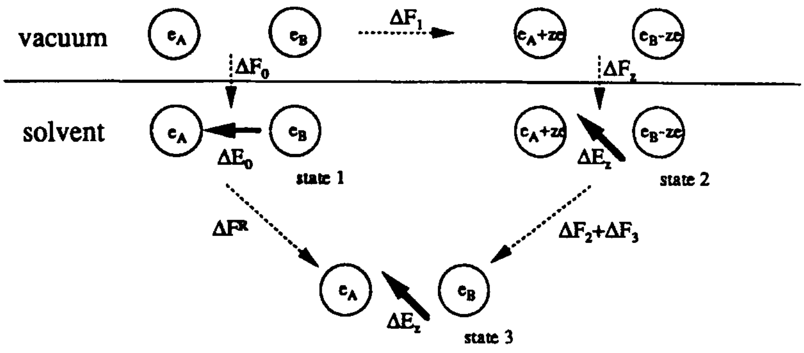

Figure 3 Diagrammatic illustration of the method to calculate ΔF^R.

$\{e_A + ze, e_B - ze\}$. The non-equilibrium solvation free energy ΔF^R can be understood as the reversible work needed to change the orientation of the arrow in the schematic description. ΔF_1 is the energy required to change the charge distribution from $\{e_A, e_B\}$ to $\{e_A + ze, e_B - ze\}$, *i.e.* from the actual to the hypothetical charge distribution, in vacuum. ΔF_0 and ΔF_z are the equilibrium solvation free energies of the actual and the hypothetical ions, respecitvely. To move the system from state 2 to state 3 in Figure 3, the charge ze must be moved from one site to the other against the electric field produced by the solute and the solvent. During this process, the solvent configuration should be fixed. The reversible work needed to do so can be divided into two parts, the reversible work against the electric field from the solute, ΔF_2, and that against the electric field produced by the solvent, ΔF_3. By symmetry,

$$\Delta F_1 = -\Delta F_2, \tag{3}$$

thus, we do not have to explicitly treat the z-dependent solute energy terms. Since the solvent configurations are fixed during the process of changing state 2 into state 3 in Figure 3, ΔF_3 can be calculated from the following equation,

$$\Delta F_3 = z\Delta E_z, \tag{4}$$

by the definition of ΔE (see Eq. (2)). Free energy is a state function, and so we can calculate ΔF^R from the following closed equation,

$$\Delta F_0 + \Delta F^R = \Delta F_1 + \Delta F_z + (\Delta F_2 + \Delta F_3). \tag{5}$$

From Eqs. (3), (4), and (5), we obtain ΔF^R as,

$$\Delta F^R(\Delta E_z) = \Delta F_z - \Delta F_0 + z\Delta E_z. \tag{6}$$

The diabetic free energy profile for the reactant state can be calculated as a function of ΔE_z from this equation. The profile for the product state can be obtained by a similar procedure. In this case, however, the reference charge distribution of the solute ions is $\{e_A + e, e_B - e\}$, that is, $z = 1$, and the corresponding expression for the free energy profile is,

$$\Delta F^P(\Delta E_z) = \Delta F_z - \Delta F_1 + (z-1)\Delta E_z. \tag{7}$$

If we regard the total (including solute energy terms) free energies of the reactant and the product states at the reaction coordinate ΔE as follows (see Fig. 3),

$$F^R(\Delta E) = E_{\mathrm{el},0} + \Delta F_0 + \Delta F^R(\Delta E), \tag{8}$$

$$F^P(\Delta E) = E_{\mathrm{el},1} + \Delta F_1 + \Delta F^P(\Delta E), \tag{9}$$

with Eqs. (1), (6) and (7), we obtain the well known relation between the free energy profiles and the reaction coordinate [20,26],

$$F^R(\Delta E) - F^P(\Delta E) = \Delta E + \varepsilon. \tag{10}$$

Note that our reaction coordinate (see Eq. (2)) is different in definition from that conventionally employed in the literature, the vertical energy gap [20,26], but from this relation, it is seen that two reaction coordinates are equivalent. From Eq. (10), we obtain the value of the reaction coordinate at the transition state as $\Delta E^* = -\varepsilon$.

2.2 *Realization of Eq. (6) Based on the Extended RISM Theory*

Hereafter, we focus on the calculation of the reactant free energy profile, Eq. (6). The calculation of the product one is similar, or it can be obtained from Eq. (10) after the calculation of the reactant profile. If we identify the solvation free energy ΔF_z as follows,

$$\Delta F_z = -k_B T \ln[\mathrm{Tr}\{\exp(-\beta V_z(R^N))\,\delta(\Delta E(R^N) - \Delta E_z)\}], \tag{11}$$

where "Tr" denotes the state sum over the configuration space spanned by R^N, with Eq. (6), we immediately recover the expression derived by Kuharski *et al.* [25] with non-Boltzmann sampling technique.

Next, we describe how to realize the calculation of Eq. (6) based on ex-RISM [16,17] with the HNC closure. The theory provides the correlation functions between sites of solute or solvent molecules as a functional of intermolecular interactions which are represented by a sum of interaction between a pair of sites. To calculate ΔE in Eq. (2) with ex-RISM, we use the following equation,

$$V_A = 4\pi\rho\sum_s \int r^2 dr \frac{g_{As}^{\mathrm{uv}}(r)e_s}{r}, \tag{12}$$

where g_{As}^{uv} is the solute(u)-solvent(v) radial distribution function for the sites A and s, where s refers to the sites of the solvent, and e_s denotes the partial charge of the site s. The equation for V_B is given by replacing A in Eq. (12) with B. Then ΔE_z can be calculated from Eqs. (2) and (12) with the solute charge distribution $\{e_A + ze, e_B - ze\}$. The equilibrium solvation free energy ΔF_z at infinite dilution can be calculated in terms of the correlation functions as [27,28],

$$\beta\Delta\mu_{\mathrm{solv}} = 4\pi\rho\sum_{\alpha,s}\int r^2 dr\left[\frac{1}{2}h_{\alpha s}^{\mathrm{uv}2}(r) - c_{\alpha s}^{\mathrm{uv}}(r) - \frac{1}{2}h_{\alpha s}^{\mathrm{uv}}(r)\,c_{\alpha s}^{\mathrm{uv}}(r)\right], \tag{13}$$

where $h_{\alpha s}^{\mathrm{uv}}$ and $c_{\alpha s}^{\mathrm{uv}}$ are the total and direct correlation functions between the site α of the solute and the site s of the solvent, respectively, and ρ is the bulk density of the solvent. Note that the solvation free energy calculated via Eq. (13) is the excess free energy when the reference state is taken as the pure solvent, but the terms associated with pure solvent cancel out because these are two solvation free energy terms in Eq. (6), ΔF_z and ΔF_0. Thus, in this sense, Eq. (13) corresponds to,

$$\Delta F_z = -k_B T \ln[\mathrm{Tr}\{\exp(-\beta V_z(R^N))\}]. \tag{14}$$

The difference in the calculation of $\Delta F_z - \Delta F_0$ in Eq. (6) between via Eq. (11) and via Eq. (13) (equivalently via Eq. (14)) is usually small [20]. Then, the diabatic free energy profile for the reactant state can be calculated based on ex-RISM from Eqs. (2), (6), (12) and (13).

3 APPLICATIONS

3.1 An Electron Exchange Reaction Studied by Zichi et al. [29]

In this part of the section, we analyze an simplest model of an electron exchange reaction which was previously studied by Zichi *et al.* [29] and compare our results with theirs. The model we consider here is the ET reaction,

$$\mathrm{A}^{-1/2}\mathrm{B}^{1/2} \rightarrow \mathrm{A}^{1/2}\mathrm{B}^{-1/2}, \tag{15}$$

for a solute pair AB, with A = B, in diatomic solvent molecules which have structure similar to that of CH_3Cl if the CH_3 group is regarded as an united atom. Separation between A and B is fixed at 3.0 Å. The solvent molecules have a fixed atomic separation of 2 Å with partial charges such that the dipole moment is 2.4 D. The number density and the temperature of the solvent are 0.012 molecules $Å^{-3}$ and 250 K, respectively. All the sites of the solute and the solvent interact via Coulomb and Lennard-Jones (LJ) interaction. The LJ parameters $\sigma = 3.5$ Å and $\varepsilon/k_B = 200$ K are identical for all the sites of both the solute and the solvent.

The diabatic free energy profile obtained by our method is plotted in Figure 4 along with that obtained from the simulation. (By symmetry of the reaction, it is sufficient to calculate only the reactant profile). From Figure 4, we can see that the profile obtained by ex-RISM agrees well with that obtained from the simulation. (Note that our reaction coordinate ΔE is different in definition from that of Zichi *et al.* [29], but is equivalent as mentioned in part A of section II). The most notable feature of Figure 4 is that it is essentially parabolic with respect to the reaction coordinate ΔE in accord with Marcus' prediction, and we examine the so-called Marcus relation for the exchange reaction,

$$\Delta F^* = \frac{\lambda}{4}, \tag{16}$$

where ΔF^* is the activation free energy and λ is the reorganization energy. From Eq. (10) with $\varepsilon = 0, \lambda$ can be calculated as (See Fig. 1),

$$\lambda = |\Delta E_0|. \tag{17}$$

Equation (16) is examined for various spacings between reacting ions. The results are listed in Table 1. As can be seen, Eq. (16) is well satisfied in this reaction.

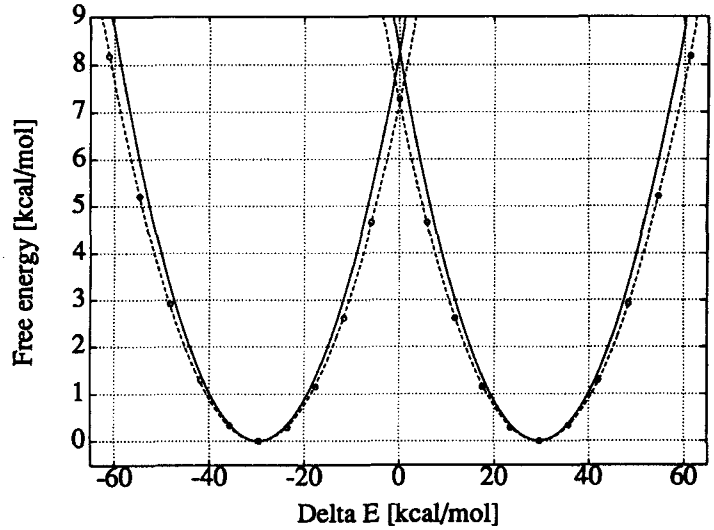

Figure 4 Diabatic free energy profiles: o, the result of the ex-RISM calculation; dashed line, parabola fitting curve for o's; solid line, simulation result by Zichi *et al.* Though the profile in their literature is of adiabatic, we modified it so that it looks like diabatic.

Table 1 Examination of the Marcus' relation $\Delta F^* = \lambda/4$.

separation distance *r(Å)*	*activation free energy*[a] ΔF^**(kcal/mol)*	*(reorganization energy)*[b]*/4* $\lambda/4$*(kcal/mol)*
3.0	7.275	7.391
4.0	10.39	10.53
5.0	13.27	13.42
6.0	15.77	15.91
7.0	17.79	17.92
8.0	19.32	19.43
9.0	20.33	20.43

[a] calculated via Eq. (6) with $z = 0.5$. ($\Delta E_{0.5} = 0.0$).
[b] calculated via Eq. (17).

3.2 *Aqueous Ferric-Ferrous Electron Transfer*

A system we consider in this part of the section consists of the Fe^{2+}/Fe^{3+} redox pair in water. The solvent in this system is the SPC (simple point charge) water model with alternation suggested by Pettitt and Rossky [30], at temperature of $T = 298$ K and an experimental number density at 1 atm of $\rho = 0.03334$ molecules $Å^{-3}$. Interaction potentials between solute ions and the SPC water are taken from Kuharski *et al.* [25]

We examine the system with the separation between two ions (Fe^{2+}/Fe^{3+}) fixed at 6.075 Å. Coordination numbers for each ion and distance between ion and oxygen in the first solvation shell are listed in Table 2 where experimental and simulation results are compared. It is experimentally well-known that both ferric and ferrous ions are 6-fold coordinated by water ligands in aqueous solution, that the ion-oxygen distance for $Fe^{3+}(H_2O)_6$ is approximately 2.0 Å, and that the distance for $Fe^{2+}(H_2O)_6$ is approximately 0.12 Å longer [31]. These facts are well reproduced by simulation [25]. From Table 2, one can see that the ex-RISM calculation

Table 2 Coordination numbers and Ion-Oxygen ligand bond length for ferric and ferrous ions.

Coordination number for Fe^{2+} 5.2
for Fe^{3+} 7.3

Ion-Oxygen ligand bond length

Ion	[a]*Single ion experiment*	[b]*Two ion simulation*	[c]*Two ion ex-RISM*	[b]*Transition state simulation*	[c]*Transition state ex-RISM*
Fe^{2+}	2.10 Å	2.15 Å	2.02 Å		
Fe^{3+}	1.98 Å	2.02 Å	1.90 Å		
($Fe^{2.5+}$)				2.08 Å	1.94 Å

[a] EXAFS measurements, Ref. 31.
[b] Two ions, Fe^{2+} and Fe^{3+}, with interionic separation fixed at 5.5 Å, Ref. 25.
[c] This work from the radial distribution function with interionic separation fixed at 6.075 Å.

gives satisfactory ion-oxygen bond length, but that it cannot reproduce correct coordination numbers. This is because of an inherent shortcoming in ex-RISM when it is applied to a system which has 'large' charges such as in ferric and ferrous ions; ex-RISM cannot reproduce quantitatively correct radial distribution functions for such a site with large charge [32].

We plotted the diabatic free energy profile for this system in Figure 5. As can be seen, the obtained profile is roughly but not well approximated by parabola, and the Marcus relation is not well satisfied in this reaction; (reorganization energy)/4 gives 46.0 kcal/mol, while the activation free energy is equal to 44.4 kcal/mol. Quantitative agreement with the simulation result is poor (see Fig. 2 of Ref. 25). The primary reason for the discrepancy between the result of ex-RISM and that of the simulation is, as mentioned above, the inability of ex-RISM to reproduce the correct radial distribution functions because all the quantities to construct the free energy profile based on ex-RISM are related to these correlation functions (see part B of section II). One possible path [32] for improving the result is to adopt a 'complex' model for the solute; to include the water molecules in the first solvation shell as the constituent of a 'complex' solute. This idea of a 'complex' molecule, however, neglects the fluctuations of the complex molecule itself, and that fluctuations have to be analyzed by other methods because the contribution from the molecules in the first solvation shell to the activation free energy can be significant. Another path [32] for improving the result is to improve the ex-RISM formalism; to improve the closure relations to solve the RISM equation. One possibility of improving the closures is to employ those suggested by density functional theory [33]. Further study to improve the closure relations is needed.

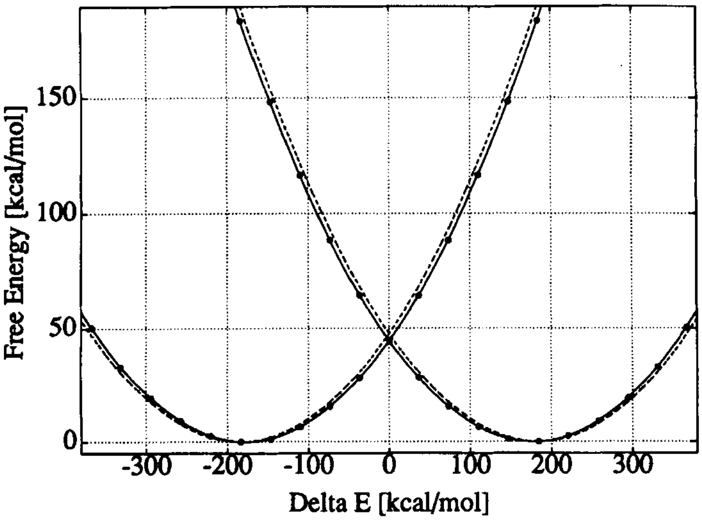

Figure 5 Diabatic free energy profile for the Fe^{2+}/Fe^{3+} exchange reaction: o, the result of the ex-RISM calculation; dashed line, parabola fitting curve; solid line; 4th order polynomial fitting curve.

3.3 Charge Separation Reaction

In this part of the section, we apply our method to a charge separation reaction which was previously studied by Carter and Hynes [21]. The specific reaction we analyze here is,

$$A^0B^0 \rightarrow A^1B^{-1}, \tag{18}$$

for a solute pair AB, with A = B, in diatomic solvent molecules which are the same as that we employed in part A of this section. The solute at the reactant state is a neutral pair (NP) AB, and that at the product state is an ion pair (IP) A^+B^-, and separation between A and B is fixed at 3.0 Å. The number density and the temperature of the solvent are 0.012 molecules $Å^{-3}$ and 250 K respectively. All the sites of the solute and the solvent interact via Coulomb and Lennard-Jones (LJ) interaction. The LJ parameters $\sigma = 3.5$ Å and $\varepsilon/k_B = 200$ K are identical for all the sites of both the solute and the solvent.

The diabatic free energy profiles obtained by our method is plotted in Figure 6 [34]. By symmetry of the system we consider, the NP profile is symmetrical with regard to the minimum point of the profile. Now we discuss the problems related to the parabolic free energy profiles and the solute independence of force constants. As is obvious from Eq. (10), the force constants of the NP and the IP profiles have to be the same if the profiles are exactly parabolic. But it is possible that the free energy profiles are non-parabolic, and that this causes the difference in the force constants. To elucidate these problems, we first attempted to fit the NP profile by parabola and then calculated the IP profile using Eq. (10). From the plotted profiles in Figure 6, we can see that the IP profile can not be well approximated by the curve so obtained. We therefore attempted to fit the NP profile

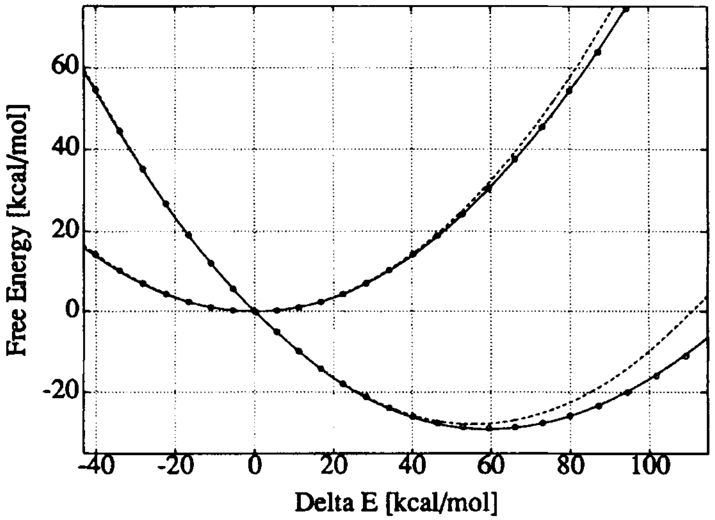

Figure 6 The diabatic free energy profiles for the NP and the IP states: o, ex-RISM results; dashed line, 2nd order fitting curve; solid line, 4th order polynomial fitting curve.

Table 3 The force constants for the NP and IP free energy profiles.

	force constants[a] *for*	
	NP	*IP*
2nd order fitting	0.018	0.018
4th order fitting	0.018	0.016
(*cf.* Carter and Hynes)[b]	0.017	0.028

[a] Force constants (in $[\mathrm{kcal/mol}]^{-1}$) are calculated from the second derivative coefficients at the minimum points of the profiles.

[b] The result of Ref. 21.

by 4th order polynomials, and then calculated the IP profile using Eq. (10), which is also plotted in Figure 6. It is seen from Figure 6 that 4th polynomial fitting curves give better results. Our resultant profiles do not agree with those of Carter and Hynes [21], but are quantitatively in good agreement with the results of King and Warshel [35]. The force constants of two profiles are summarized in Table 3. The resultant force constants are in contrast to the data of Carter and Hynes; they reported that the force constant for the IP profile is 1.6 times larger than that for the NP profile. From Table 3, it is seen that the difference of the force constants is not so large, which is in agreement with the result of King and Warshel. The motivation that Carter and Hynes performed the simulation is to check the validity of the hypothesis proposed by Kakitani and Mataga [20] which says that dielectric saturation of the first solvation shell causes the curvature of the free energy profile for the IP to be much larger than that for the NP. On the other hand, from the more detailed analysis of the same system that Carter and Hynes had studied, King and Warshel [35] concluded that the saturation effect in the first solvation shell seems to be almost completely compensated by underpolarization of the next solvation shells. Thus, the dielectric saturation effect does not alter the force constants of the free energy profiles appreciably. Our results support the conclusion given by King and Warshel, and one can not expect the large difference of the force constants corresponding to the NP and the IP states due to the dielectric saturation effect.

4 CONCLUDING REMARKS

We presented a method to obtain the free energy profile for ET reactions based on ex-RISM. Due to the non-linear nature of the HNC closure to solve the RISM equation, our method can shed light on the non-linearity of the free energy profiles. The approach supplemented with ex-RISM to obtain the free energy profile can be applied not only to such simple solute as spherical ions, which we treated in this paper, but to molecules with complex geometry. Such calculations for the diabatic free energy profile of the intramolecular ET reactions for more complex molecules are currently underway in our group.

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References

[1] "Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena; Proceedings of Yamada Conference XXIX", N. Mataga, eds, Elsevier Science Publication and Yamada Science Foundation, (1992).

[2] H. Heitele, "Dynamic Solvent Effects on Electron-Transfer Reactions", *Angew. Chem. Int. Ed. Engle.*, **32**, 359 (1993).

[3] "Electron Transfer: A Critical Link between Subdisciplines in Chemistry", in *Chem. Rev.*, **92**, 365 (1992).

[4] B. Bagchi and A. Chandra, "Collective orientational relaxation in dense dipolar liquids", *Adv. Chem. Phys.*, **80**, 1 (1991).

[5] F. Raineri, H. Resat, B. Perng, F. Hirata and H. L. Friedman, "A molecular theory of solvation dynamics", *J. Chem. Phys.*, **100**, 1477 (1994).

[6] M. Maroncelli and G. R. Fleming, "Computer simulation of the dynamics of solvation of aqueous solution", *J. Chem. Phys.*, **89**, 5044 (1988).

[7] M. Maroncelli, "Computer simulations of solvation dynamics in acetonitrile", *J. Chem. Phys.*, **94**, 2084 (1991).

[8] T. Fonseca and B. M. Ladanyi, "Breakdown of Linear Response for Solvation Dynamics in Methanol", *J. Phys. Chem.*, **95**, 2116 (1991).

[9] R. A. Marcus, "On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I", *J. Chem. Phys.*, **24**, 966 (1956).

[10] R. A. Marcus, "Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. I", *J. Chem. Phys.*, **24**, 979 (1956).

[11] R. A. Marcus, "Exchange Reactions and Electron Transfer Reactions including Isotopic Exchange", *Discussions Faraday Soc.*, **29**, 21 (1960).

[12] R. A. Marcus, "Free Energy of Nonequilibrium Polarization Systems. II. Homogeneous and Electrode Systems", *J. Chem. Phys.*, **38**, 1858 (1963).

[13] R. A. Marcus and N. Sutin, "Electron transfers in chemistry and biology", *Biochim. Biophys. Acta*, **811**, 265 (1985).

[14] S. Chong, S. Mirua, G. Basu and F. Hirata, "Molecular Theory for the Nonequilibrium Free Energy Profile in Electron Transfer Reaction", *J. Phys. Chem.* (in press)

[15] D. Chandler and H. C. Andersen, "Optimized Cluster Expansions for Classical Fluids. II. Theory of Molecular Liquids", *J. Chem. Phys.*, **57**, 1930 (1972).

[16] F. Hirata and P. J. Rossky, "An extended RISM equation for molecular polar fluids", *Chem. Phys. Lett.*, **83**, 329 (1981).

[17] F. Hirata, P. J. Rossky and B. M. Pettitt, "The interionic potential of mean force in a molecular polar solvent from an extended RISM equation", *J. Chem. Phys.*, **78**, 4133 (1983).

[18] S. Ten-no, F. Hirata and S. Kato, "Reference interaction site model self-consistent field study for solvation effect on carbonyl compounds in aqueous solution", *J. Chem. Phys.*, **100**, 7443 (1994).

[19] F. Hirata, "Interaction-site representation of the Smoluchowski-Vlasov equation: The space-time correlation functions in a molecular liquid", *J. Chem. Phys.*, **96**, 4619 (1992).

[20] A. Yoshimori, T. Kakitani, Y. Enomoto and N. Mataga, "Shapes of the Electron-Transfer Rate vs. Energy Gap Relations in Polar Solutions", *J. Chem. Phys.*, **93**, 8316 (1989).

[21] E. A. Carter and J. T. Hynes, "Solute-Dependent Solvent Force Constants for Ion Pairs and Neutral Paris in a Polar Solvent", *J. Chem. Phys.*, **93**, 2184 (1989).

[22] K. Ando and S. Kato, "Dielectric relaxation dynamics of water and methanol solutions associated with the ionization of N, N-dimethylaniline: Theoretical analyses", *J. Chem. Phys.*, **92**, 7241 (1990).

[23] D. DeVault, *Quantum-mechanical tunneling in biological systems*, 2nd ed., Cambridge University Press, 1984.

[24] J. T. Hynes, "Outer-Sphere Electron-Transfer Reactions and Frequency-Dependent Friction", *J. Phys Chem.*, **90**, 3701 (1986).

[25] R. A. Kuharski, J. S. Bader, D. Chandler, M. Sprik, M. L. Klein and R. W. Impey, "Molecular model for aqueous ferrous-ferric electron transfer", *J. Chem. Phys.*, **89**, 3248 (1988).

[26] M. Tachiya, "Relation between the Electron-Transfer and the Free Energy Change of Reaction", *J. Phys. Chem.*, **93**, 7050 (1989).

[27] S. J. Singer and D. Chandler, "Free energy functions in the extended RISM approximation", *Mol. Phys.*, **55**, 621 (1985).

[28] D. A. Zichi and P. J. Rossky, "Molecular conformational equilibria in liquids", *J. Chem. Phys.*, **84**, 1712 (1986).

[29] D. A. Zichi, G. Ciccotti, J. T. Hynes and M. Ferrario, "Molecular Dynamics Simulation of Electron-Transfer Reactions in Solution", *J. Phys Chem.*, **93**, 6261 (1989).

[30] B. M. Pettitt and P. J. Rossky, "Integral equation prediction of liquid state structure for waterlike intermolecular potentials", *J. Chem. Phys.*, **77**, 1451 (1982).

[31] B. S. Brunschwig, C. Creutz, D.H. Macartney, T.-K. Sham and N. Sutin, "The Role of Inner-sphere Configuration Changes in Electron-exchange Reactions of Metal Complexes", *Faraday Discuss. Chem. Soc.*, **74**, 113 (1982).

[32] R.A. Kuharski and D. Chandler, "Solvation of Multiply Charged ions: Predictions Using the Reference Interaction Site Method with Hypernetted Chain Closure", *J. Phys. Chem.*, **91**, 2978 (1987).

[33] D. Chandler, J. D. McCoy and S. J. Singer, "Density functional theory of nonuniform polyatomic systems", *J. Chem. Phys.*, **85**, 5977 (1986).

[34] We calculated the free energy profile neglecting ε in Eq. (10). Neglecting this term does not change the shape of the each profile, but only the relative height of two profiles.

[35] G. King and A. Warshel, "Investigation of the free energy functions for electron transfer reactions", *J. Chem. Phys.*, **93**, 8682 (1990).