

Reorganization energy of electron transfer processes in ionic fluids: A molecular Debye-Hückel approach

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The reorganization energy of electron transfer processes in ionic fluids is studied under the linear response approximation using a molecule Debye-Hückel theory. Reorganization energies of some model reactants of electron transfer reactions in molten salts are obtained from molecular simulations and a molecule Debye-Hückel approach. Good agreements between simulation results and the results from our theoretical calculations using the same model Hamiltonian are found. Applications of our theory to electron transfer reactions in room temperature ionic liquids further demonstrate that our theoretical approach presents a reliable and accurate methodology for the estimation of reorganization energies of electron transfer reactions in ionic fluids. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794790>]

I. INTRODUCTION

As one of the most fundamental reactions in nature, electron transfer reactions are ubiquitous. Marcus theory provides a remarkably accurate description for such reactions.^{1,2} According to the Marcus picture² of electron transfer reactions, a simple relationship between the reaction rate and some fundamental quantities of the system reads

$$k_{\text{et}} = \frac{4\pi^2 V^2}{h(4\pi\lambda RT)^{1/2}} e^{-(\Delta G^0 + \lambda)^2/4\lambda RT}, \quad (1)$$

where the reorganization energy λ is one of the fundamental quantities which relates the coupling between the reactant/product with its dielectric environment besides the coupling matrix element V between the donor and acceptor electronic states. For polar solvents, λ can be related to the electronic state of reactant/product and the dielectric spectra of a polar solvent, which is experimental accessible.³ This correlation has been demonstrated using numerous experimental results for electron transfer reactions in polar solvents.^{2,4} But for electron transfer reactions in electrolyte solutions or any ionic fluids, the traditional calculation of the reorganization energy is based upon the conventional Debye-Hückel theory of electrolyte solutions,^{5,6} which is only valid for infinite dilute solutions. Thus any reliable theoretical understanding of electron transfer reactions in ionic fluids requires an accurate estimate of the reorganization energy theoretically, which is not yet available in contrast to the well-studied polar solvent case.

From molecular simulations, the essential assumption in the Marcus theory on the quadratic dependence of energy fluctuations along the reaction coordinate had been confirmed in polar solvents.⁷⁻⁹ From these simulations the reorganization energy can be obtained. Similar methodology has been applied to model electron transfer reactions in ionic fluids^{10,11} and the parabolic behavior of free energy dependence on the reaction coordinate has been confirmed.

On the other hand, accurate theoretical calculations of the reorganization energy in an ionic fluid are still lacking.

Recently we have developed a molecular Debye-Hückel (MDH) theory of ionic fluids^{12,13} inspired by the dispersion relation of a dielectric function from electrodynamics¹⁴ and the dressed ion theory.^{15,16} In this theory, the solvation energy of a solute in an ionic fluid can be obtained using the first few Debye screening lengths and related combination coefficients, which can be determined from the dielectric function of the neat ionic fluid. As the reorganization energy calculation of electron transfer reactions is essentially solvation energy calculations of the reactant/product at two frequencies,^{6,17} our theory provides a natural methodology to calculate the reorganization energies of electron transfer reactions in ionic fluids beyond the conventional Debye-Hückel approach. The objective of this study is to extend our theory to the reorganization energy calculations and to test this methodology against results from simulations using the same model Hamiltonian.

This paper is organized as follows: In Sec. II, an electron transfer (ET) process is discussed under the linear response assumption, from which practical ways to compute the reorganization energy from simulations and our MDH theory are discussed. Applications of our theory to ET in molten salts are presented in Sec. III. Applications to ET in room temperature ionic liquids are discussed in Sec. IV and some concluding remarks are given in Sec. V.

II. REORGANIZATION ENERGY FROM THE MOLECULE DEBYE-HÜCKEL THEORY

In order to show how the reorganization energy of an electron transfer reaction in ionic fluids can be obtained from our molecular Debye-Hückel theory,¹³ theoretical development of the Marcus free energy parabolas from the linear response theory will be presented. Consider an electron transfer reaction in a homogeneous ionic fluid, where the reactant is tagged as a solute. A diatomic molecule, which has charges q_1^R and q_2^R at two sites S_1 and S_2 , could be used as a simple model for the reactant under the donor-accepter picture.¹⁸ After electron transfer the charges at the two sites

are q_1^P and q_2^P , and the charge neutrality condition leads to $q_1^R + q_2^R = q_1^P + q_2^P$.

A. Transition state and free energy profile of an ET reaction

Before we discuss the reaction rate of an ET reaction, it is necessary to define the microscopic interaction between various particles first. If the pair interaction $u(r_{ij})$ between particles i and j of the solvent is split into a long ranged Coulomb interaction $\frac{q_i q_j}{r_{ij}}$ and a short ranged interaction $u^s(r_{ij})$, i.e.,

$$u(r_{ij}) = \frac{q_i q_j}{r_{ij}} + u^s(r_{ij}), \quad (2)$$

the total energy $E(\mathbf{R}^N; M)$ for the reactant ($M = R$) or the product ($M = P$) system reads

$$E(\mathbf{R}^N; M) = \frac{q_1^M q_2^M}{r_{12}} + u^s(r_{12}) + q_1^M \sum_i \frac{q_i}{r_{1i}} + q_2^M \sum_i \frac{q_i}{r_{2i}} + \sum_i u^s(r_{1i}) + \sum_i u^s(r_{2i}) + \sum_{i>j} u(r_{ij}), \quad (3)$$

where subscripts 1, 2 denote two sites of the reactant or product, i and j denote solvent particles, and $\mathbf{R}^N = \{\mathbf{r}_i, i = 1, N\}$ represents configurations of the solvent. It is also assumed that the short ranged interactions between the reactant and solvents are the same as the one between the product and solvent particles for simplicity.

It would be convenient to introduce an induced potential Φ_o ($o = 1, 2$) due to solvent particles at the site o of the reactant or product

$$\Phi_o(\mathbf{R}^N) = \sum_i \frac{q_i}{r_{oi}}. \quad (4)$$

The vertical energy gap can be used as a reaction coordinate,¹⁹

$$\Delta E(\mathbf{R}^N) = E(\mathbf{R}^N; P) - E(\mathbf{R}^N; R) = \delta E_i + X(\mathbf{R}^N), \quad (5)$$

with the quantities δE_i and X defined as

$$\begin{aligned} \Delta q &= q_1^P - q_1^R = -(q_2^P - q_2^R), \\ \delta E_i &= \frac{\Delta q(q_2^R - q_1^R) - (\Delta q)^2}{r_{12}}, \\ X(\mathbf{R}^N) &= \Delta q(\Phi_1(\mathbf{R}^N) - \Phi_2(\mathbf{R}^N)). \end{aligned} \quad (6)$$

δE_i is the energy difference for the solute molecule in the gas phase. $X(\mathbf{R}^N)$ is the vertical energy gap due to solvent-solute interactions, which depend on the solvent configurations. For brevity we will use $X = X(\mathbf{R}^N)$ as a reaction coordinate in this study without explicitly showing the solvent configuration dependence. Note that the charge parameter q could change by one for an element reaction, we will take $\Delta q = 1$ without loss of generality throughout this study.

Now with the Hamiltonian of the system defined above, one can use the reaction coordinate X to study the ET reaction. An ET reaction in a solution is known to be a thermal fluctuation activated process which is governed by the Frank-Condon principle. According to this principle, *an ET reaction*

happens only for solvent configurations where the total energies of the reactant and product state are the same.^{1,2} For the simple model considered in this study, this condition reads

$$X = -\delta E_i, \quad (7)$$

which defines the transition state. When the solvent relaxation dynamics is fast, the transition state theory could be used to evaluate the rate of an ET reaction, i.e., the rate constant k_{et} for the system going from a reactant state to a product state is proportional to the equilibrium probability that the system in a reactant state with configurations satisfies the transition state criterion Eq. (7). Denote $p(x; M)$ as the distribution function of the reaction coordinate X at the reactant state ($M = R$) or the product state ($M = P$), the rate of an ET reaction $R \rightarrow P$ can be written as²

$$k_{et} = \kappa p(-\delta E_i; R), \quad (8)$$

with $\kappa = 2\pi V^2/h$ for nonadiabatic reactions.

The main idea in the theory of a thermal ET reaction is to construct the free energy curves for the reactant and product states, and the cross point of those two curves would naturally satisfy Eq. (7) and defines the transition state. Define a constrained free energy $A(x; M)$ as a function of the reaction coordinate X to take a particular value x

$$A(x; M) = -\beta^{-1} \ln \left[\Lambda^{-3N} \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; M)} \delta(X - x) \right], \quad (9)$$

where $\beta = 1/(k_B T)$, T is the temperature, and Λ is the thermal wavelength. As shown in Fig. 1, this free energy function represents the energy fluctuations due to the thermal motions of the solvent in the reactant or product electronic state.

The probability density for X can be written as

$$\begin{aligned} p(x; M) &= \langle \delta(X - x) \rangle_M \\ &= \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; M)} \delta(X - x) / \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; M)}, \end{aligned} \quad (10)$$

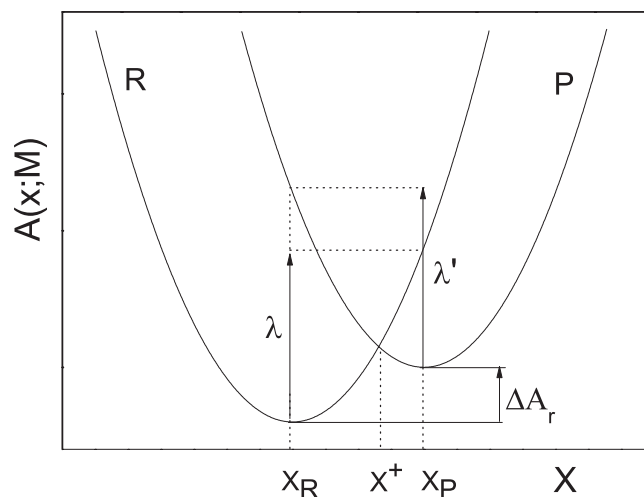


FIG. 1. Schematic Marcus free energy curves $A(x; M)$ for a reactant ($M = R$) and a product ($M = P$).

where $\langle \cdot \rangle_M$ is the ensemble average over the equilibrium configurations of the system while it is at the reactant state ($M = R$) or the product state ($M = P$). Using Eq. (9) this probability distribution can be related to the constrained free energy as

$$A(x; M) = -\beta^{-1} \ln[p(x; M)] + A(M), \quad (11)$$

which suggests a practical way to construct the free energy function using the distribution information of X from molecular simulations. The free energy $A(M)$ is defined as

$$A(M) = -\beta^{-1} \ln \left[\Omega^{-3N} \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; M)} \right]. \quad (12)$$

In order to show that the cross point of the two free energy profiles of the reactant and the product state fulfills the condition defined in Eq. (7), the following identity can be used

$$\begin{aligned} p(x; P) &= \langle \delta(X - x) \rangle_P \\ &= \int d\mathbf{R}^N e^{-\beta(E(\mathbf{R}^N; R) + \delta E_i + X)} \delta(X - x) / Q(P) \\ &= e^{-\beta(x + \delta E_i)} (Q(R) / Q(P)) \\ &\quad \times \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; R)} \delta(X - x) / Q(R) \\ &= e^{-\beta(x + \delta E_i - \Delta A_M)} p(x; R), \end{aligned} \quad (13)$$

where $Q(M) = \int d\mathbf{R}^N e^{-\beta E(\mathbf{R}^N; M)}$ is the partition function of the state M , $\Delta A_M \equiv A(P) - A(R)$ is the free energy difference between the reactant and product state. Using Eqs. (11) and (13), it is straightforward to verify that $x^+ = -\delta E_i$ is the cross point for $A(x^+; R) = A(x^+; P)$.

According to the Marcus picture of an electron transfer reaction² one can define the reorganization energy and the activation energy of the reaction given we know the free energy functions of the reactant and the product. Let $x = x_R$ and $x = x_P$ be the location for the minimum of the free energy functions of the reactant and the product, respectively, and $x = x^+$ be the cross point for those two functions. The reaction free energy difference ΔA_r is

$$\Delta A_r = A(x_P, P) - A(x_R, R). \quad (14)$$

The reorganization energy $\lambda(\lambda')$ for the forward process $R \rightarrow P$ (or backward) is defined as

$$\lambda = A(x_P; R) - A(x_R; R), \text{ or } \lambda' = A(x_R; P) - A(x_P; P) \quad (15)$$

and the activation energy $\Delta A(\Delta A')$ for the forward/backward process is

$$\begin{aligned} \Delta A &= A(x^+; R) - A(x_R; R), \text{ or} \\ \Delta A' &= A(x^+; P) - A(x_P; P). \end{aligned} \quad (16)$$

In general these free energy functions are complicated functions of the reaction coordinate, thus there is no simple relationship between the reorganization energies and the activation energies. The remarkable insight from Marcus is that these free energy functions will take simple quadratic form under some very general assumptions about the thermal motions of the solvent.^{1,2}

B. Linear response assumption and its consequence for ET processes

As the stochastic variable X is a summation of numerous small fluctuations due to thermal motions of solvent particles, the central limit theorem states that $p(x; M)$ will follow a Gaussian distribution in the vicinity of its mean value. Using the mean $x_M = \langle X \rangle_M$ and the standard deviation $\sigma_M = \sqrt{\langle (X - x_M)^2 \rangle_M}$, this Gaussian distribution is

$$p(x; M) = \frac{1}{\sqrt{2\pi}\sigma_M} e^{-(x-x_M)^2/(2\sigma_M^2)}, \quad (17)$$

from which we have the free energy function

$$A(x; M) = \beta^{-1} \ln(\sqrt{2\pi}\sigma_M) + \frac{(x - x_M)^2}{2\beta\sigma_M^2} + A(M), \quad (18)$$

which is a quadratic function of x . In this case, the minimum locations of the free energy functions, i.e., x_R and x_P yield the equilibrium state of the reactant and the product. If the fluctuation magnitude of solvent motions $\sigma_f = \sigma_M$ is independent of $M = R$ or P , the reorganization energy for the forward/backward is the same,

$$\begin{aligned} \lambda &= A(x_P; R) - A(x_R; R) = A(x_R; P) - A(x_P; P) \\ &= \frac{(x_P - x_R)^2}{2\beta\sigma_f^2}, \end{aligned} \quad (19)$$

thus both the average and the fluctuations are required to evaluate the reorganization energy. The Marcus free energy difference ΔA_r between the reactant and the product is

$$\Delta A_r = A(x_P; P) - A(x_R; R) = A(P) - A(R) = \Delta A_M, \quad (20)$$

which implies that the Marcus free energy difference equals the free energy difference ΔA_M given the fluctuation in the two states are the same.

It is noted that the assumption that Eq. (17) being valid for all values of x is equivalent to the linear response approximation. If X in Eq. (5) is treated as a perturbation to the reactant system Hamiltonian, then one can find that the average and the fluctuation for X are related to each other using the linear response theory²⁰

$$x_P - x_R = -\beta\sigma_f^2. \quad (21)$$

Thus a combination of Eqs. (19) and (21) yields that the reorganization energy λ can be evaluated from the fluctuation information

$$\lambda = \frac{(x_P - x_R)^2}{2\beta\sigma_f^2} = \frac{\beta\sigma_f^2}{2}, \quad (22)$$

which states that the reorganization energy can be determined from the curvature of the Marcus parabola.¹⁸ If the fluctuation magnitude σ_f is determined from molecular simulations, we will denote the reorganization energy obtained from the above relation as λ_{EXPF} . It should be noted that direct calculations for the fluctuation magnitude σ_f from theoretical methods are not trivial. In general the calculation of energy fluctuations requires 3-particle distribution function $g_{ijk}^{(3)}$, 4-particle distribution function $g_{ijkl}^{(4)}$ as well as 2-particle distribution

function $g_{ij}(r)$.²¹ Since satisfactory n -particle distribution function ($n > 2$) theory in liquids is not well developed as for the 2-particle case, molecular simulations become the dominant method to obtain σ_f from molecular models of a solvent.

On the other hand, using the combination of Eqs. (19) and (21) the reorganization energy could also be evaluated from the average information

$$\lambda = \frac{(x_P - x_R)^2}{2\beta\sigma_f^2} = \frac{x_R - x_P}{2}. \quad (23)$$

As the calculation of x_P or x_R only requires the pair distribution function $g_{ij}(r)$, Eq. (23) implies that *any theoretical or simulation method that yields accurate pair distribution functions can be used to calculate the reorganization energy of electron transfer reactions*. If the reaction coordinate averages x_P and x_R are determined from molecular simulations we will denote the reorganization energy obtained from the above relation as λ_{EXPA} . One should note that λ_{EXPA} and λ_{EXPF} use different information of X from simulations, the difference between these two routes can be used to test the validity of the linear response assumption for the system studied.

At the same time, the free energy difference could be evaluated using a combination of Eqs. (12) and (20) and the cumulant expansion which is exact under the Gaussian distribution assumption,

$$\begin{aligned} \Delta A_r &= A(P) - A(R) = -\beta^{-1} \ln \langle e^{-\beta(X+\delta E_i)} \rangle_R \\ &= \delta E_i + x_R - \frac{\beta\sigma_f^2}{2} = \delta E_i + \frac{x_R + x_P}{2}, \end{aligned} \quad (24)$$

where Eq. (21) has been used in the last equality. The term δE_i is the contribution from the change of the solute structure, while $\frac{x_R+x_P}{2}$ comes from the solute-solvent interaction.

The activation energy can be determined from the free energy functions defined by Eq. (18). Since x^+ is defined as the cross point for the two free energy functions of the reactant and the product, $A(x^+; q) = A(x^+; q+1)$, we have

$$A(R) + \frac{(x^+ - x_R)^2}{2\beta\sigma_f^2} = A(P) + \frac{(x^+ - x_P)^2}{2\beta\sigma_f^2}, \quad (25)$$

from which the cross point is

$$x^+ = -\Delta A_r + \frac{x_R + x_P}{2}. \quad (26)$$

According to the definition Eq. (16), the activation energy for the forward reaction can be evaluated in terms of λ and ΔA_r as

$$\Delta A = A(x^+; R) - A(x_R; R) = \frac{(x^+ - x_R)^2}{2\beta\sigma_f^2} = \frac{(\lambda + \Delta A_r)^2}{4\lambda}. \quad (27)$$

Using the relationship between λ , A and the probability distribution $p(x; M)$, the reaction rate constant defined by Eq. (8) could be evaluated in a straightforward manner

$$k_{et} = \frac{\kappa}{\sqrt{4\pi\lambda/\beta}} e^{-\beta\Delta A} = \frac{\kappa}{\sqrt{4\pi\lambda/\beta}} e^{-\frac{\beta(\lambda+\Delta A_r)^2}{4\lambda}}, \quad (28)$$

which is the conventional Marcus reaction rate expression.^{1,2}

The above key results Eqs. (22)–(24), (27), and (28) have been widely used in molecular simulations of electron transfer reactions (for example, see Refs. 7, 9–11, and 22). As for theoretical calculations of the reorganization energy Eq. (23) is more convenient since any linear response models can be directly used when the reactant or product state is used as a reference state.

From practical point of view, the departure from linear response may affect the reorganization energy, such that λ_{EXPF} and λ_{EXPA} lead to different results of the reorganization energy. Zhou and Szabo²³ had presented a good discussion about the nonlinear effect on the reorganization energy, which demonstrated that λ_{EXPA} is superior to λ_{EXPF} . The main results relevant to this study of Zhou and Szabo²³ are summarized in Appendix A, which will be used for the discussion of ET reorganization energies in molten salt.

C. MDH approach to the reorganization energy in ionic fluids

According to the discussion in Secs. II A and II B, any linear response models for a solute in an ionic fluid can be used to calculate the reorganization energy of an electron transfer reaction in an ionic fluid. For example, extended Debye-Hückel theories, which could be derived from rigorous statistical mechanics formulation of an ionic fluid as in the dressed ion theory (DIT)^{15,24} or from the static limit of Maxwell equations using dispersion relations,^{12,13} can be used.

In particular, our molecule MDH¹³ can be used for such calculations. Consider a solute o immersed in an ionic fluid with spherical cations and anions, n_i and q_i are the particle number density and charge of the i th solvent species, respectively. Assume the pair interaction between o and i particle is $u_{oi}(\mathbf{r}) = u_{oi}^s(\mathbf{r}) + \frac{q_o q_i}{\epsilon_s r}$, where $u_{oi}^s(\mathbf{r})$ being a short-ranged potential. The mean potential $\phi_o(\mathbf{r})$ around the solute o in the ionic fluid satisfies the Poisson equation²⁵

$$-\epsilon_s \nabla^2 \phi_o(\mathbf{r}) = 4\pi [\rho_o^b(\mathbf{r}) + \rho_o^{ind}(\mathbf{r})], \quad (29)$$

where ϵ_s is the dielectric constant of the background, $\rho_o^b(\mathbf{r}) = q_o \delta(\mathbf{r})$ is the bare charge density of the solute, $\rho_o^{ind}(\mathbf{r}) = \sum_i n_i q_i h_{oi}(\mathbf{r})$ is the induced charge density around the solute, with $h_{oi}(\mathbf{r}) = g_{oi}(r) - 1$, the correlation function between o and i species.

Introducing a separation of the direct correlation function into a short ranged part and a long ranged part, which is directly related to long ranged Coulomb interaction potential, the above Poisson equation can be transformed into an exact Debye-Hückel-like equation,^{13,15,26}

$$\nabla^2 \phi_o(\mathbf{r}) = -\frac{4\pi}{\epsilon_s} \rho_o^0(\mathbf{r}) + \frac{4\pi}{\epsilon_s} \int d\mathbf{r}' \alpha(|\mathbf{r} - \mathbf{r}'|) \phi_o(\mathbf{r}') d\mathbf{r}', \quad (30)$$

where $\rho_o^0(r) = \rho_o^b(r) + \rho_o^{ind,0}(r) = \rho_o^b(r) + \sum_i n_i q_i h_{i0}^0(\mathbf{r})$ is an effective charge density of the solute, and $h_{i0}^0(\mathbf{r})$ is the short-ranged correlation between the solute and solvent particles. $\alpha(|\mathbf{r} - \mathbf{r}'|) = \beta \sum_i n_i q_i \rho_i^0(r)$ is related to the dielectric function of the system.

Introducing the Fourier transform $f(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) d\mathbf{r}$ of $f(\mathbf{r})$ with $f(\mathbf{r}) = \phi(\mathbf{r}), \rho(\mathbf{r}), h_{ij}(\mathbf{r})$, the Poisson equation in k -space can be obtained as^{13,15}

$$k^2 \epsilon_l(k) \phi_o(\mathbf{k}) = \rho_o^0(\mathbf{k}), \quad (31)$$

where $\epsilon_l(k)$ is the dielectric function of the pure ionic fluid as the solute is infinite dilute. $\rho_o^0(\mathbf{k})$ is the Fourier transform of $\rho_o^0(\mathbf{r})$ and is an effective charge density of the solute.

In the traditional DIT theory,¹⁵ an asymptotic analysis leads to

$$\phi_o(r) \sim \sum_n \frac{q_{\text{eff},on}}{4\pi \epsilon_{\text{eff},n}} \frac{e^{-k_n r}}{r}, \quad (32)$$

where $q_{\text{eff},on} = \rho_o^0(ik_n)$ is an effective charge, and $\epsilon_{\text{eff},n} = \frac{1}{2} [k \frac{d\epsilon_l(k)}{dk}]_{k=ik_n}$ is an effective dielectric constant determined from the bulk property $\epsilon_l(k)$, and ik_n is the root with positive imaginary part. The calculation of the mean potential $\phi_o(r)$, hence thermodynamic properties of the solvation, will need the full short-ranged correlation function $h_{oi}^0(r)$ and the dielectric function of the solvent $\epsilon_l(k)$. Even these information are available the series converges slowly, thus a not very practical theory for solvation.¹³

Our MDH is a further development of DIT, where only the bulk property $\epsilon_l(k)$ of the pure solvent is required as input.¹³ For a general solvation case, a molecule surface S separates the solute (denoted by Ω_1) from the solvent (denoted by Ω_2). Motivated by the asymptotic expansion of the electric potential Eq. (32) and the readiness to extend our approach to an arbitrary shape of a solute it is assumed that the electric potential can be written as

$$\phi_o(\mathbf{r}) = \sum_l C_{ol} \phi_{ol}(\mathbf{r}), \quad (33)$$

where $\phi_{ol}(\mathbf{r})$ is a Yukawa mode with parameter k_l defined via

$$\begin{aligned} \nabla^2 \phi_{ol}(\mathbf{r}) &= -\frac{4\pi}{\epsilon_s} \rho_o^b(\mathbf{r}), \quad \mathbf{r} \in \Omega_1, \\ \nabla^2 \phi_{ol}(\mathbf{r}) &= k_l^2 \phi_{ol}(\mathbf{r}), \quad \mathbf{r} \in \Omega_2. \end{aligned} \quad (34)$$

Equation (33) as well as Eq. (34) is a reformulation of Eq. (30), and is the main results of our MDH theory.¹³ Under this approach, *the solvent is described by a response function which is parameterized by a set of DH-like response modes with Debye parameters $\{k_l\}$ determined from the pure solvent dielectric function $\epsilon_l(k)$.*

Our MDH approach is a nontrivial reduction of Eq. (30). As long as we have a set of $\{C_{ol}\}$ and $\{k_l\}$, one can predict the solvation energy of various solute in the solvent. For the pure solvent case, the coefficient $\{C_{ol}\}$ can be obtained self-consistently using the pure solvent dielectric function $\epsilon_l(k)$. In general the coefficient $\{C_{ol}\}$ could be solute-dependent. If the solute is not very different from the solvent ions, then a reasonable approximation is that C_{ol} is independent of the solute, e.g., $C_{ol} \approx C_l$, which is the pure solvent one as demonstrated from four-component system calculations.¹³ This strategy will be adopted in our calculations of the reorganization energy in this report.²⁷

Consider the solvation of a diatomic solute in an electron transfer process, the electrostatic potential φ_k at the k th site of

the solute is defined as

$$\langle \Phi_k \rangle = \varphi_k \equiv \lim_{\mathbf{r} \rightarrow \mathbf{r}_k} \left[\phi_k(\mathbf{r}) - \sum_{k'} \frac{q_{k'}}{\epsilon_s |\mathbf{r} - \mathbf{r}_{k'}|} \right], \quad (35)$$

the mean potential difference can be evaluated as $x_M = \varphi_1 - \varphi_2$. With x_M , we could evaluate the reorganization energy according to Eq. (23).

As one shall see from Secs. III A–III D, our MDH approach could yield satisfactory results for the reorganization energy when compared to MD simulations using the same molecular model, while the conventional DH theory breaks down.

III. APPLICATIONS TO ET IN A SIMPLE MOLTEN SALT

A. Model description

Consider a mixture of a solute and N_s pairs of salt ions. An atomic solute or a diatomic solute will be used as a model of reactants. The background of a simple molten salt is taken as vacuum and then the dielectric constant $\epsilon_s = 1$ is used. The pair interaction between two particles is $u_{ij}(r) = u_{ij}^s(r) + \frac{q_i q_j}{r}$, where q_i is the charge of the i th particle, and $u_{ij}^s(r)$ is the short-ranged part of the interaction. A simple model of molten salts (NaCl)²⁸ is used for the solvent, where the short ranged part of the solvent-solvent interaction is $u_{ss}^s(r) = E_{ss} (\frac{\sigma_{ss}}{r})^9$ with size parameter $\sigma_{ss} = 2.34 \text{ \AA}$ and energy parameter $E_{ss} = 65.97 \text{ kJ/mol}$. The short-ranged interaction between solvent and solute is a Leonard-Jones potential as $u_{so}^s(r) = 4E_{so} [(\frac{\sigma_{so}}{r})^{12} - (\frac{\sigma_{so}}{r})^6]$, and the short-ranged interaction for two solute sites also takes the Leonard-Jones potential as $u_{oo}^s(r) = 4E_{oo} [(\frac{\sigma_{oo}}{r})^{12} - (\frac{\sigma_{oo}}{r})^6]$. In the dilute limit, the reorganization energy is not sensitive to the short ranged potential $u_{oo}^s(r)$ given σ_{oo} is not too small.

Molecule dynamics simulations are performed using the DL-POLY program.²⁹ NVT ensemble with periodic boundary conditions at temperature $T = 1267 \text{ K}$ and total number density $n = 0.0287/\text{\AA}^3$ are used. Most of the simulations use a cell with total number of particles $N = 512$, from which the thermodynamics has no significant difference compared with a larger cell with $N = 1000$. Time step in the simulations is about 1.5 fs, and a trajectory of 0.9 ns was collected after an equilibrium run of 2 ns. Ewald summation is used to find the induced potential at the charged site of the solute, where particles in the image cells are treated as part of the solvent, which contribute to the induced potential of the solute.

B. Input parameters to the MDH approach

Before solving the linearized PB equation (34), the molecule surface³⁰ and the Debye parameters should be determined.

The molecule surface is defined as a union of hard spheres where the size of such spheres is determined from perturbation theory methods such as Weeks-Chandler-Anderson (WCA) or Barker-Henderson (BH) prescription.^{13,21} Naturally a better strategy is to use some variational method in combination with the short ranged contributions to the solvation energy.³¹ As the electrostatic contribution is not sensitive

to the choice of the effective size, we will use the Barker-Henderson prescription due to its simplicity. From BH prescription, the effective size is

$$\sigma_* = \int_0^{r_c} (1 - e^{-\beta u_{is}^s(r)}) dr, \quad (36)$$

where the truncated parameter r_c is determined by $\beta u_{is}^s(r_c) = 0$. In this study the effective size for the pure solvent is $\sigma_s = 2.8 \text{ \AA}$, and the effective size for the solvent-solute interaction is $\sigma_* = 0.74\sigma_{os}, 0.87\sigma_{os}$ when the energy parameter for the LJ potential is $E_{os} = 0.1, 1.0 \text{ kJ/mol}$, respectively. Using these effective sizes, one could generate the molecule surface using MSMS code from Sanner.³⁰

The Debye parameters $\{k_l\}$ and $\{C_l\}$ for Debye modes could be determined using the dielectric function of the pure solvent, and one can refer to Ref. 13 for more details. In this case, a molecule dynamics simulation is performed using 1372 pairs of NaCl in a cubic cell with length $d = 45.73 \text{ \AA}$ at $T = 1267 \text{ K}$, which is the same thermodynamic state as the solution simulation. The conventional Debye parameter is $k_D = 6.9 \text{ \AA}^{-1}$. Radial distribution functions are collected and used to compute the dielectric function $\epsilon_l(k)$. In order to find the roots of the dielectric function, an empirical function is used,

$$\chi(k) = \frac{a_0 k^2}{k^4 + (a_1 k^2 - a_2) \cos(bk) + a_3 k \sin(bk) + a_2}, \quad (37)$$

with restriction $\chi(0) = 1$. This response function has the same function form as the one from the mean spherical approximation, but the coefficients are determined by fitting the response function $\chi(k) \equiv 1 - \epsilon_0/\epsilon_l(k)$ from simulations. The advantage of such a procedure lies in the fact that this function form already satisfies some of the limiting behaviors of a response function. After the fitting, we could easily find the Debye parameters k_l by solving $\epsilon_l(k = ik_l) = 0$, or equivalently $k^4 + (a_1 k^2 - a_2) \cos(bk) + a_3 k \sin(bk) + a_2 = 0$, from which several pairs of k_l can be obtained. As noted in our previous study,¹³ generally the first few (typically 2 or 4) Debye modes are capable of describing the thermodynamics. In this case we take the first four Debye parameters which appear in complex conjugate pairs as $k_{1,2} = 0.1792 \pm 1.7144i$ and $k_{3,4} = 0.7832 \pm 3.8465i$, and the corresponding four coefficients for the solvent are $C_{1,2} = -0.5959 \mp 1.1599i$ and $C_{3,4} = 1.0959 \mp 0.3950i$, with an effective size of the pure solvent particles being $\sigma_s = 2.8 \text{ \AA}$ from BH prescription. Using those parameters the electrostatic part of the excess internal energy for the pure solvent is estimated as $u_{ele}^{ex} = -\frac{q^2}{2\epsilon_0} \sum_{l=1}^4 \frac{C_l k_l}{1+k_l \sigma_s} = -377.5 \text{ kJ/mol}$, which could be compared with the internal energy $-399.1(\pm 1.0) \text{ kJ/mol}$ directly from simulations.

Using the molecule surface generated from the MSMS code, the boundary element method³²⁻³⁴ is used to solve Eq. (34) with different Debye parameters, from which the induced potential and hence x_M is obtained, and then the reorganization energy could be evaluated from Eq. (23).

C. Results for full reactions

As a test of our MDH approach, we consider a full reaction where the reactant is modeled as a diatomic solute with charges $q_{1,2} = \pm q$ at its two sites, and the distance r_{12} between the two sites is taken as a control parameter. Three evaluations of the reorganization energy, namely, λ_{EXPA} from MD simulations, λ_{DH} from the conventional DH theory and λ_{MDH} from our MDH theory, will be presented. The accuracy of the DH or MDH approach could be tested by comparing with the reorganization energy, λ_{EXPA} , from simulations.

MD simulations are performed with an NVT ensemble of one solute and 255 pairs of NaCl. LJ parameters used in the simulations are $E_{so} = E_{oo} = 1.0 \text{ kJ/mol}$ and $\sigma_{so} = \sigma_{oo} = 4.0 \text{ \AA}$. The effective hard sphere diameter of each site is $\sigma_* = 0.865\sigma_{so} = 3.46 \text{ \AA}$ according to the BH prescription. In this case we focused on the charge separation process with $q \rightarrow q + 1$. For certain values of the control parameter r_{12} , MD simulations are performed both for the reactant state with charge q and the product state with charge $q + 1$. The reaction coordinate $X = \Phi_1 - \Phi_2$ is calculated using Ewald summation for configurations from MD simulations. The block average method³⁵ had been used to analyze the statistical error of x and to make sure the results is converged. The typical numerical uncertainty could be reduced to several kJ/mol when a large number of configuration are used. For example, using a total of 200 000 equilibrium configurations for a system with $r_{12} = 6 \text{ \AA}$ and $q = 1$, the error bar for x_R and $\beta\sigma_f^2$ is about 1 kJ/mol and 6 kJ/mol, respectively.

The results for the reorganization energy λ as a function of the bond length r_{12} for the solute with the charge fixed as $q = 0$ is shown in Fig. 2. For $r_{12} < 2\sigma_* = 6.92 \text{ \AA}$ where the spheres from the two sites are overlapping, the solvation energy is obtained from direct calculations using the boundary element methods. For $r_{12} > 6.92 \text{ \AA}$ where spheres from the two sites are not overlapping, an approximate analytical solution, Eq. (B9), is available as shown in Appendix B, and is used to evaluate the reorganization energy. This analytical approximation is accurate when comparisons with numerically exact results from boundary element method is made. As one can see, the conventional DH theory breaks down, which underestimates the reorganization energy by 40%–60%; while our MDH is in very good agreement with the simulation results, which has a difference smaller than 7%.

The effect from various sizes of the charge on the solute with $r_{12} = 6 \text{ \AA}$ is shown in Fig. 3. The reorganization energy λ_{EXPA} from MD is a function of the charge q , e.g., λ_{EXPA} for different q could have a maximum difference of 11%, which reflect the non-linear response effect. The reorganization energy from MDH or DH predict is independent of q , and could not capture the weak charge dependence. Despite of such deficiency, the results from our MDH theory are in good agreement with MD results within 6%; while the DH theory underestimates the results by almost 50%. From these observations, it is clear that our MDH theory can be used to evaluate the reorganization energies of electron transfer reaction in ionic fluids.

The validity of the linear response approximation, Eq. (21), could be tested by comparing $x_R - x_P$ and $\beta\sigma_M^2$.

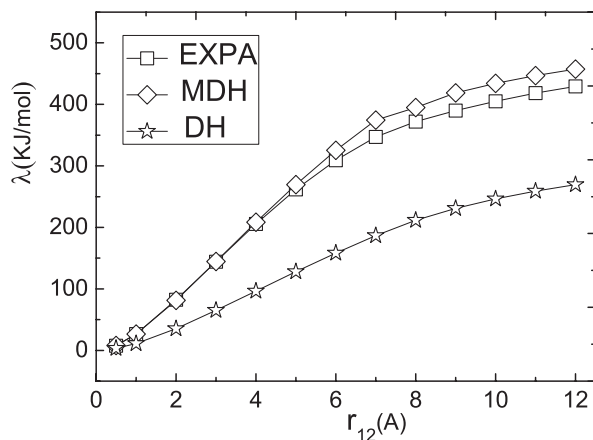


FIG. 2. Dependence of reorganization energies λ on the site distance r_{12} of a diatomic solute with charge $q = 0$. Results from average information of MD simulations (EXPA) (square), our MDH theory (diamond), and DH theory (star) are presented with symbols. The lines are guides to the eye.

For the parameters used in Figs. 2 and 3, it is noted that $x_R - x_P$ differs from $\beta\sigma_M^2$ ($M = R, P$) by 10%, while $\beta\sigma_R^2$ differs from $\beta\sigma_P^2$ by 20%. Using x_M and $\beta\sigma_M^2$ ($M = R, P$) for the reactant and product, one can also calculate λ_M defined via Eq. (A4) which had taken the nonlinear response effect into account. We find that λ_{EXPA} differs from λ_R by 4%, while λ_{EXPF} differs from λ_R by 10%. Such comparisons demonstrate that the linear response assumption is satisfactory for full reactions, and both λ_{EXPA} and λ_{EXPF} from simulations could be used to estimate the reorganization energy.

D. Results for half reactions

The extension of our treatment to half reactions is straightforward. In fact, Lynden-Bell already gave a good discussion about using the reaction coordinate $X = \Delta q\Phi_0$ to evaluate the reorganization energy from simulations, where Φ_0 is the induced electric potential due to the solvent at an atomic solute. Readers could refer to Ref. 11 for more details.

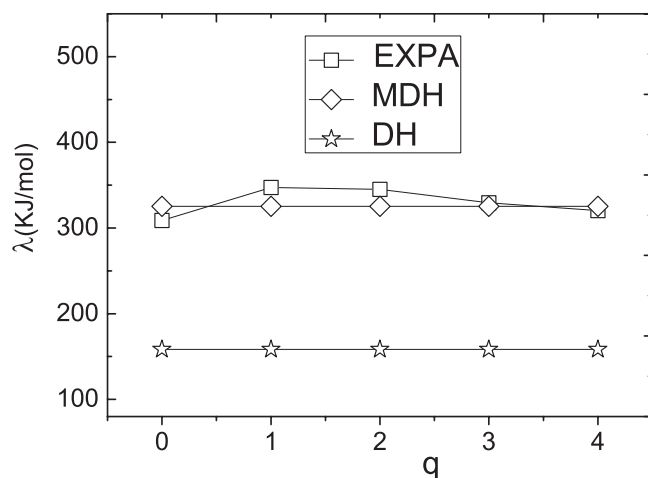


FIG. 3. Dependence of reorganization energies λ on the charge q of a diatomic solute with site distance $r_{12} = 6$ Å. Results from average information of MD simulations (EXPA) (square), our MDH theory (diamond), and DH theory (star) are presented with symbols. The lines are guides to the eye.

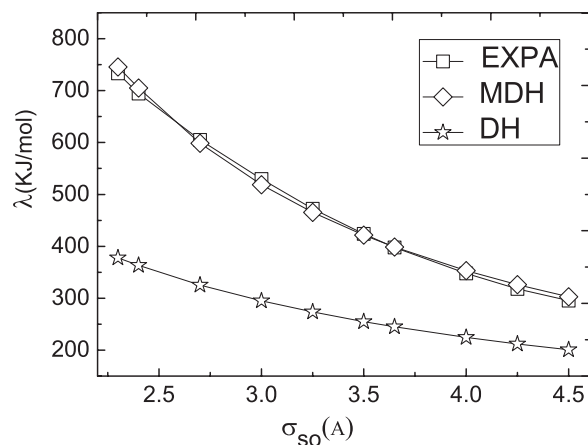


FIG. 4. Dependence of reorganization energies λ on the solvent-solute diameter σ_{so} . Results from average information of MD simulations (EXPA) (square), our MDH theory (diamond), and DH theory (star) are presented with symbols. The lines are guides to the eye.

In this study, we also use this reaction coordinate to study half reactions, where λ_{EXPA} will be used as the benchmark for the comparison with theoretical predictions.

For a half reaction, a reactant is modeled as an atomic ion. MD simulations are performed using an NVT ensemble with a pair of solute with charges $\pm q$ in 255 pairs of NaCl, where the LJ parameters used in the simulations are $E_{so} = E_{oo} = 0.1$ kJ/mol and $\sigma_{oo} = 4.5$ Å. As the solute is spherical in this case, the reaction coordinate could be evaluated analytically,¹³ $x_M = -\frac{q_M}{\epsilon_s} \sum_l \frac{C_l k_l}{1+k_l \sigma_s}$, where σ_s is the effective size from the solute-solvent interaction. In this study, we focus on the half reaction $O^q \rightarrow O^{q+1} + e^-$ with $\Delta q = 1$.

By fixing the solute charge at $q = 0$, the dependence of the reorganization energy λ on the solvent-solute LJ interaction parameter σ_{so} is shown in Fig. 4. Again, the DH theory breaks down and underestimates the reorganization energy by about 30%–50%, while the difference between our MDH theory and MD results is only 3%.

By fixing the LJ parameter at $\sigma_{so} = 3.5$ Å, the dependence of the reorganization energy λ on the solute charge q is shown in Fig. 5. In this case, λ_{EXPA} for various q could differ by 16%, which is a little bit larger than the 11% difference in full reactions. Our MDH theory is very accurate for small q , i.e., the difference between λ_{MDH} and λ_{EXPA} is smaller than 2% for $q = 0, 1$. However, it becomes less satisfactory for large q , which overestimates the reorganization energy by 16% for $q = 2, 3, 4$. The DH theory breaks down for both small and large q , which underestimates the reorganization energy by 40% for $q = 0, 1$ and by 30% for $q = 2, 3, 4$.

The validity of the linear response assumption could also be tested for half reactions, where it is found that the linear response works much worse in half reactions than in full reactions. For the parameters used in Fig. 4, it is noted that $x_R - x_P$ could differ from $\beta\sigma_M^2$ by 20% while $\beta\sigma_R^2$ differs from $\beta\sigma_P^2$ by 20%–30%. We have also calculated the reorganization energy λ_M for the reactant and product state. It is noted that λ_{EXPA} differs from λ_R by 5%, however, λ_{EXPF} differs from λ_R by 20%–30%.

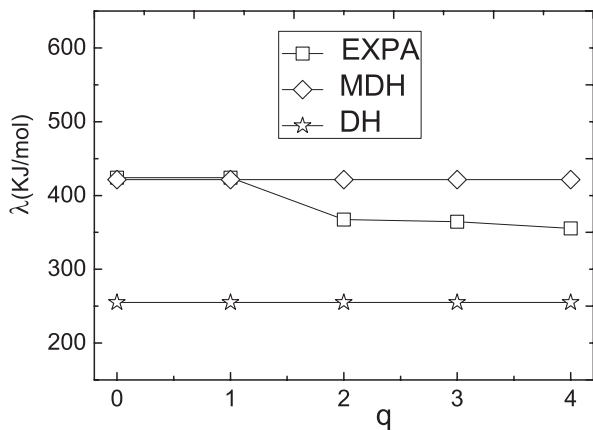


FIG. 5. Dependence of reorganization energies λ on the reactant charge q . Results from average information of MD simulations (EXPA) (square), our MDH theory (diamond), and DH theory (star) are presented with symbols. The lines are guides to the eye.

In this half reaction, one may wonder why the linear response works much worse than in full reactions. In fact, this is not unexpected by noting the charge distribution difference in full and half reactions. For a full reaction, the net charge of a diatomic solute keeps the same in the reactant and product state, where only a dipole and high order multipole changes; while for half reaction, the net charge of single ion does change in the initial and final state. Note that the net charge could have much larger effect to the solute-solvent interaction compared to a dipole, one can expect that the reactant and product state for a half reaction could have much larger difference than that of the full reaction, and then the linear response would work much worse for half reactions.

By comparing the reorganization energy from our theoretical prediction and MD simulations of full reactions as well as of half reactions, the λ_{EXPA} route provides better estimates than the λ_{EXPF} route for the evaluation of the reorganization energy when the linear response is not satisfied. Our MDH theory can provide satisfactory reorganization energies when comparing with the results from MD simulations, while the conventional DH theory breaks down for this molten salt system.

IV. APPLICATION TO ET IN ROOM TEMPERATURE IONIC LIQUIDS

In addition to ET in simple molten salts, the validation of our approach is also tested for ET in two room temperature ionic liquids (RTILs).

As the cations and/or anions for RTILs could be complex molecular ions, a coarse-grained approach is introduced so that one can apply the MDH theory directly without extending the MDH theory to molecular solvents.³⁶ To this end, a complex ion in a RTIL is coarse-grained as a spherical ion with a net charge at the center, and the background is a continuum with an effective dielectric constant ϵ_s , which accounts for the dielectric effect of complex ions, so that the Coulomb interaction between two coarse-grained ions reads

$$v_{ij}^{CG}(r) = \frac{q_i q_j}{\epsilon_s r}. \quad (38)$$

At the coarse-grained level, the effective sizes of the ions and the effective dielectric constant will be extracted from the equilibrium configurations of the original RTIL system. Using the configurations of a RTIL from MD simulations, the radial distribution functions (RDFs) $g_{ij}^{CG}(r)$ ($i, j = +, -$) of the coarse-grained cations and anions can be obtained. For this coarse-grained approach, the electrostatic energy of the RTIL system could be evaluated as

$$\begin{aligned} E_{ele}^{CG} &= \frac{\rho}{2} \int_0^\infty \sum_{i,j=+,-} x_i x_j v_{ij}(r) g_{ij}^{CG}(r) 4\pi r^2 dr \\ &= \frac{\pi \rho}{2\epsilon_s} \int_0^\infty (g_{++}^{CG}(r) + g_{--}^{CG}(r) - 2g_{+-}^{CG}(r)) r^2 dr, \quad (39) \end{aligned}$$

where $x_\pm = 1/2$ is the mole fraction of the cation and anion, and ρ is the total number density. Thus, ϵ_s can be determined by equating the above electrostatic energy to the electrostatic energy E_{ele}^{MD} directly from MD simulations of the RTIL with full atomic description.

Introducing a function $f_s(r)$:

$$f_s(r) = \rho(g_{++}^{CG}(r) + g_{--}^{CG}(r) - 2g_{+-}^{CG}(r))/4, \quad (40)$$

the location r_1 of its first peak can be a reasonable estimation of the effective hard sphere size σ_s for the RTIL. Such a strategy is motivated by the fact that for a restricted primitive model, the first peak of the above function yields the size of the hard sphere. Similarly, we also introduced the coarse-grained RDF $g_{oi}^{CG}(r)$ between a solute particle o and a solvent ion i , and the induced charge density around the solute could be evaluated as

$$\rho_o^{ind}(r) = \rho \sum_i q_i x_i g_{oi}^{CG}(r) = \rho(g_{o+}^{CG}(r) - g_{o-}^{CG}(r))/2, \quad (41)$$

from which the first peak position r_{o1} is taken as an estimation of the effective solvent-solute diameter σ_* .

Hence, a RTIL system can be mapped into a restrictive primitive model with effective ion sizes and effective dielectric constant at a coarse-grained level, and then the application of our MDH approach is straightforward. The following results indicate that our MDH approach can be used to evaluate the reorganization energies of electron transfer reactions in RTILs at least for two model systems studied.

The first RTIL system, a diatomic solute as a model reactant of a full reaction in 1-ethyl-3-methylimidazolium hexafluorophosphate (emipf6), was studied by Shim and Kim.¹⁰ MD simulations were performed for pure emipf6 using the same force field as Shim and Kim¹⁰ and the coarse-grained RDFs are obtained from these simulations, from which the dielectric function $\epsilon_l(k)$ and the effective size of the solvent could be evaluated. The effective dielectric constant for the coarse-grained model is calculated to be $\epsilon_s = 1.01$, which is almost the same as in vacuum. From the dielectric function, it is found that the first four Debye parameters are $k_{1,2} = 0.0555 \pm 0.9544i$ and $k_{3,4} = 0.2959 \pm 2.0677i$. From the first peak position of the function $f_s(r)$, an effective size 5.1 Å for the emipf6 solvent leads to the linear combination coefficients $C_{1,2} = -0.5987 \mp 1.2934i$ and $C_{3,4} = 1.0987 \mp 0.2175i$. The effective size 4.2 Å for the solute-solvent interaction is

taken from the first peak of the induced charge density around the solute. Numerical calculations using the boundary element method lead to a reorganization energy 39.7 kcal/mol, which could be compared with the averaged reorganization energy 40.8 kcal/mol determined by Shim and Kim¹⁰ using MD simulations. In this case, the DH theory gives a reorganization energy 12.2 Kcal/mol, which is too low.

The second RTIL system, a spherical solute as the reactant of a half reaction in dimethylimidazolium hexafluorophosphate (dmimpf6), was studied by Lynden-Bell.¹¹ For this system, coarse-grained RDFs from simulations using the same force field as Lynden-Bell are used to calculate $\epsilon_l(k)$ and the effective size for the solvent. The effective dielectric constant for the coarse-grained model is $\epsilon_s = 1.48$. The first four Debye parameters are $k_{1,2} = 0.0676 \pm 0.9717i$ and $k_{3,4} = 0.3704 \pm 1.9677i$. An effective size 5.0 Å for the dmimpf6 solvent evaluated from the first peak of the function $f_s(r)$ leads to $C_{1,2} = -0.4511 \mp 1.3458i$ and $C_{3,4} = 0.9511 \pm 0.0298i$. An effective size 3.0 Å for the solute-solvent interaction is obtained from the first peak of the induced charge density around the solute. The reorganization energy evaluated from our MDH approach is 280 kJ/mol, which is comparable with 275 kJ/mol (or 285 kJ/mol) for the half reaction with charge $1 \rightarrow 0$ (or $0 \rightarrow 1$) from Lyden Bell's simulations, while the DH approach gives 144 kJ/mol, which again is too low.

One should note that the efficiency of the mapping from an ionic liquid to a primitive model depends on the short ranged interaction between ions of the ionic liquid. For ionic liquids with ions close to spheres such as emipf6 and dmimpf6, this approximation would work reasonably well. As one can image, charged ellipsoid mixtures or more detailed molecular models would be a better approximation for ionic liquid with long side chains. However, such kind of extensions deserves further studies.

V. CONCLUDING REMARKS

The reorganization energy of electron transfer processes in ionic fluids is studied under the linear response approximation using a molecule Debye-Hückel theory. Reorganization energies of some model reactants of electron transfer reactions in molten salts are obtained from molecular simulations and a molecule Debye-Hückel approach. Good agreements between simulation results and the results from our theoretical calculations using the same model Hamiltonian are found. Applications of our theory to electron transfer reactions in room temperature ionic liquids further demonstrate that our theoretical approach presents a reliable and accurate methodology for the estimation of reorganization energies of electron transfer reactions in ionic fluids. We believe that this study represents the first attempt to calculate the reorganization energy of electron transfer reactions in ionic fluids beyond the conventional Debye-Hückel theory, thus greatly expands our ability to accurately estimate the electron transfer rate in ionic fluids.

Naturally there are many possible directions that the current work can be improved. One immediate possibility is to further development of our molecule Debye-Hückel approach to molecular ionic fluids so that a mapping of molecular ionic

fluids to a primitive model can be avoided. Another possible extension is to the reorganization energy calculations for electron transfer processes in an electric cell where simulation results have appeared recently.^{37,38}

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APPENDIX A: THE NONLINEAR RESPONSE EFFECT TO THE REORGANIZATION ENERGY

The discussion of ET reaction in Sec. II B is based on the assumption of a perfect linear response, from which we have two evaluation routes of the reorganization energy, namely λ_{EXPA} defined via Eq. (23) and λ_{EXPF} defined via Eq. (22) from molecular simulations. However, it is not clear how accurate these two evaluations are, and which could be a better choice when the nonlinear response effect is not negligible. As one shall see from the following discussion, Eq. (23) is superior to Eq. (22) especially when the departure from the linear response is significant.

To this end, we turn to the results from Zhou and Szabo,²³ where a very detailed discussion about the nonlinear response effect on ET reactions was presented. It is noted that the concept of the reorganization energy λ , reaction energy ΔA , and the Marcus reaction rate formula defined in Eq. (28) are still valid, and the only price we need to pay is to introduce a state-dependent reorganization energy, e.g., the reorganization energy for the reactant and the product could be different. In the following we will summarize the main results from Zhou and Szabo,²³ which are used in the discussion of our simulation results for λ_{EXPA} and λ_{EXPF} .

As indicated by Eq. (8), the key to the reaction rate is to find the probability distribution $p(x^+; M)$ at the transition state. As x^+ generally is far way from the mean value of x_M , it is very time consuming to extract the information of $p(x^+; M)$ from direct simulations. An alternative method is to use the free energy perturbation method with Eq. (13). A charging parameter ζ is used by Zhou and Szabo²³ to construct the free energy curve for both the reactant and product state. Let $H_\zeta = \zeta X$ denote the solute-solvent interaction energy difference between the reactant state with charge q_R and a state with charge $q_\zeta = q_R + \zeta$, thus $\zeta = 0$ and $\zeta = 1$ correspond to the reactant and product states, respectively. One can simulate a series of intermediate state with the charging parameter varying between 0 and 1, and these distributions could be pieced together to generate $p(x; M)$ over a wide range which covers x^+ .

For a state with charge parameter ζ , there is a contribution $\Delta A_{\zeta 0}$ to the free energy difference, which could be evaluated as

$$\Delta A_{\zeta 0} = \int_0^\zeta d\zeta' x_{\zeta'}, \quad (\text{A1})$$

where $x_\zeta = \langle X \rangle_\zeta$, is the mean energy gap for a certain value of parameter ζ . As noted by Zhou and Szabo,²³ this free energy difference could be used to evaluate the reorganization energy of the system, where the reorganization energy λ_M for the state M ($M = R, P$) is given by

$$\begin{aligned}\lambda_P &= x_0 - \Delta A_{10}, \\ \lambda_R &= \Delta A_{10} - x_1.\end{aligned}\quad (\text{A2})$$

Especially, Zhou and Szabo²³ had developed a simplified method which could construct $p(x; M)$ with the information from only the reactant and product state simulations, where a nonlinear interpolation up to third order is used to evaluate x_ζ with the mean information x_M and fluctuation σ_M^2 . The free energy difference ΔA_{10} could be calculated explicitly as

$$\Delta A_{10} = \frac{x_R + x_P}{2} - \frac{\beta\sigma_R^2 - \beta\sigma_P^2}{12}.\quad (\text{A3})$$

A combination of Eqs. (A1)–(A3) leads to the following reorganization energy expression:

$$\begin{aligned}\lambda_P &= \frac{x_R - x_P}{2} + \frac{\beta\sigma_R^2 - \beta\sigma_P^2}{12}, \\ \lambda_R &= \frac{x_R - x_P}{2} - \frac{\beta\sigma_R^2 - \beta\sigma_P^2}{12}.\end{aligned}\quad (\text{A4})$$

As the derivation of the above equation does not depend on the validity of the linear response over the whole range, Eq. (A4) could be a very useful reference to test the efficiency and accuracy of λ_{EXPF} and λ_{EXPA} defined by Eqs. (22) and (23). It is noted that the result $\lambda_{EXPA} = (x_R - x_P)/2$ equals to the averaged value for λ_R and λ_P , which means λ_{EXPA} always lies between λ_R and λ_P ; however, $\lambda_{EXPF} = \beta\sigma_M^2$ has no such advantage. Furthermore, one can find that the mean value x_M and the fluctuation σ_M^2 have different weight in Eq. (A4), where the weight of $\beta\sigma_M^2$ is 6 times smaller than that of x_M . Generally, the departure from linear response in ionic fluid is not too drastic, e.g. as shown in Sec. III, where $(x_R - x_P)$ differs $\beta\sigma_M^2$ about 10%–20%, so $(x_R - x_P)$ and $\beta\sigma_M^2$ are roughly the same as indicated by the fluctuation-dissipation relation Eq. (21). This observation implies that the reorganization energy is much less sensitive to the change of $\beta\sigma_M^2$. As the difference between λ_{EXPA} and λ_M could be much smaller compared to the difference between λ_{EXPF} and λ_M , λ_{EXPA} route is superior to λ_{EXPF} route. Therefore, the λ_{EXPA} route provides a reasonable estimation for the reorganization energies for both the reactant and product state even in systems with moderate nonlinear effect.

APPENDIX B: REORGANIZATION ENERGY OF AN ET OF TWO SPHERICAL IONS IN AN IONIC FLUID

Consider the electrostatic problem for two spherical ions immersed in an ionic fluid. In general an ionic fluid could be described as a mixture of polar species and ionic species. Since the purpose of this appendix is to study the electrostatic interaction between two ions rather than to build a model for the dielectric response of an ionic fluid, we just introduce the conventional description for ionic fluids. In the simplest continuum approach, the dielectric response of an ionic fluid

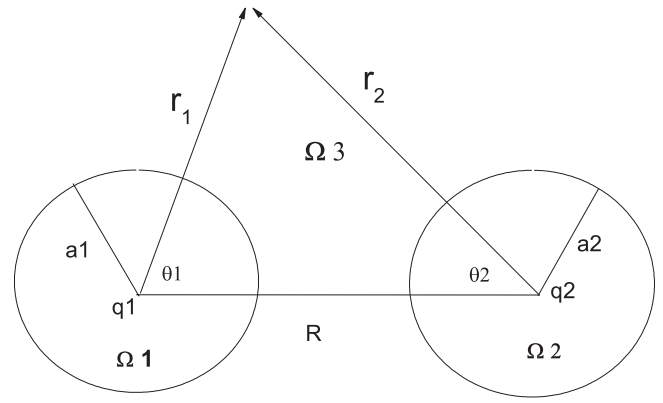


FIG. 6. A schematic diagram for two spherical ions ($i = 1, 2$) with charge q_i and radius a_i in an ionic fluid. R is the center-to-center distance, (r_1, θ_1) and (r_2, θ_2) are the coordinate systems from spheres 1 and 2, respectively.³⁹

could be parameterized with only two parameters, i.e., the partial screen effect of the polar molecules is described by a dielectric constant ϵ_1 as in the Born model, and the perfect screen effect of ion species is characterized by the Debye screening length κ as in the conventional DH theory.

In order to find the potentials at the center of the two ions, a similar strategy as in Ref. 39 for the linearized Poisson-Boltzmann equation is used. The charge and the radius of the i th ion ($i = 1, 2$) is denoted by q_i and a_i , respectively. As shown in Fig. 6, the space inside in spherical ion i is denoted by Ω_i ($i = 1, 2$) and the space outside the spheres is denoted as Ω_3 . Under the linearized Poisson-Boltzmann approach, the electric potentials are given by the following equations:

$$\begin{aligned}\nabla^2 \phi_i(\mathbf{r}) &= -\frac{4\pi q_i \delta(\mathbf{r} - \mathbf{r}_{i0})}{\epsilon_0}, \quad \mathbf{r} \in \Omega_i (i = 1, 2) \\ \nabla^2 \psi(\mathbf{r}) &= \kappa^2 \psi(\mathbf{r}), \quad \mathbf{r} \in \Omega_3,\end{aligned}\quad (\text{B1})$$

where ϵ_0 is the dielectric constant of the solute ions. The dielectric constant outside the solutes is ϵ_1 , from which we can introduce the relative dielectric constant as $\epsilon_r = \epsilon_1/\epsilon_0$. The general solution for the above equations reads⁴⁰

$$\phi_i(\mathbf{r}_i) = \frac{q_i}{\epsilon_0 r_i} + \sum_{n=0}^{\infty} A_n^i r^n P_n(\cos \theta_i), \quad (i = 1, 2) \quad (\text{B2})$$

and

$$\psi(\mathbf{r}) = \sum_{n=0}^{\infty} D_n^1 k_n(\kappa r_1) P_n(\cos \theta_1) + \sum_{n=0}^{\infty} D_n^2 k_n(\kappa r_2) P_n(\cos \theta_2), \quad (\text{B3})$$

where the unknown coefficients A_n^i and D_n^i can be determined by applying the boundary conditions of the potential on the surfaces of the spheres at $r_i = a_i$

$$\begin{aligned}\psi|_{r_i=a_i} &= \phi_i|_{r_i=a_i}, \\ \epsilon_1 \frac{\partial \psi}{\partial r_i} \Big|_{r_i=a_i} &= \epsilon_0 \frac{\partial \phi_i}{\partial r_i} \Big|_{r_i=a_i}.\end{aligned}\quad (\text{B4})$$

These boundary conditions could be simplified by using the addition theorem⁴¹

$$k_n(\kappa r_2)P_n(\cos \theta_2) = \sum_{m=0}^{\infty} B_{nm} i_n(\kappa r_1) P_m(\cos \theta_1), \quad (\text{B5})$$

with $B_{nm} = \sum_{v=0}^{\min\{m,n\}} A_{nm}^v k_{n+m-2v}(\kappa R)$, and $A_{nm}^v = \frac{\Gamma(n-v+1/2)\Gamma(m-v+1/2)\Gamma(v+1/2)(n+m-v)!(n+m-2v+1/2)}{\pi\Gamma(m+n-v+3/2)(n-v)!(m-v)!v!}$, where $i_n(x)$ and $k_n(x)$ are the modified spherical Bessel functions of the first and third kind, respectively. Then one can find the following linear equations from the boundary condition:

$$\begin{aligned} \sum_{n=0}^{\infty} D_n^1(2j+1)B_{nj} i_j(\kappa a_1) + D_j^2 k_j(\kappa a_1) &= \frac{q_1}{\epsilon_0 a_1} \delta_{0j} + A_n^1 a_1^n, \\ \sum_{n=0}^{\infty} D_n^2(2j+1)B_{nj} i_j(\kappa a_2) + D_j^1 k_j(\kappa a_2) &= \frac{q_2}{\epsilon_0 a_2} \delta_{0j} + A_n^2 a_2^n, \\ \epsilon_r \sum_{n=0}^{\infty} D_n^1(2j+1)B_{nj} \kappa i_j'(\kappa a_1) + \epsilon_r D_j^2 \kappa k_j'(\kappa a_1) &= \frac{-q_1}{\epsilon_0 a_1^2} \delta_{0j} + A_n^1 n a_1^{n-1}, \\ \epsilon_r \sum_{n=0}^{\infty} D_n^2(2j+1)B_{nj} \kappa i_j'(\kappa a_2) + \epsilon_r D_j^1 \kappa k_j'(\kappa a_2) &= \frac{-q_2}{\epsilon_0 a_2^2} \delta_{0j} + A_n^2 n a_2^{n-1}, \end{aligned} \quad (\text{B6})$$

with $i_j'(x) = \frac{di_j(x)}{dx}$ and $k_j'(x) = \frac{dk_j(x)}{dx}$. Solving the above linear equations, one can find the coefficient A_n^i and D_n^i .

Note that the element of A_n^i and D_n^i with larger index generally have smaller contribution as $A_0^i \gg A_1^i \gg A_2^i \gg \dots$, one can truncate the Eq. (B6) to a system with a few elements, which leads to a perturbation solution to the original problem. To the lowest order, one can take $A_n^i = 0$ and $D_n^i = 0$ for $n \geq 1$ and only keep the zero index elements A_0^i, D_0^i , from which the zeroth order equation reads

$$\begin{aligned} D_0^1 k_0(\kappa R) i_0(\kappa a_1) + D_0^2 k_0(\kappa a_1) &= \frac{q_1}{\epsilon_0 a_1} + A_0^1, \\ D_0^2 k_0(\kappa R) i_0(\kappa a_2) + D_0^1 k_0(\kappa a_2) &= \frac{q_2}{\epsilon_0 a_2} + A_0^2, \\ -\epsilon_r D_0^1 k_0(\kappa R) \kappa i_1(\kappa a_1) - \epsilon_r D_0^2 \kappa k_1(\kappa a_1) &= \frac{-q_1}{\epsilon_0 a_1^2}, \\ -\epsilon_r D_0^2 k_0(\kappa R) \kappa i_1(\kappa a_2) - \epsilon_r D_0^1 \kappa k_1(\kappa a_2) &= \frac{-q_2}{\epsilon_0 a_2^2}. \end{aligned} \quad (\text{B7})$$

where $B_{00} = k_0(\kappa R)$, $i_0'(x) = -i_1(x)$ and $k_0'(x) = -k_1(x)$ has been used. This equation could be solved analytically.

The element A_0^i is of special interest since it is closely related to the reaction field. According to the definition, A_0^i is the potential induced by other ions in the solution (which also include the charged site $j \neq i$). Note the site j has an

electrical potential $\frac{q_j}{\epsilon_0 R}$ at site i , the reaction field at site i due to solvent particles is $\varphi_i = A_0^i - \frac{q_j}{\epsilon_0 R}$, which could be used to evaluate the potential difference $x_M = \varphi_1 - \varphi_2$, and hence the reorganization energy λ according to Eq. (23). For $q_1 = -q_2 = e$ and $dq = \pm e$, the reorganization energy λ could be evaluated as

$$\lambda = \frac{e}{2} \left(-A_0^1 + A_0^2 - \frac{2e}{\epsilon_0 R} \right). \quad (\text{B8})$$

For the simple diatomic model of an electron transfer reaction with $q_1 = -q_2 = e$ and $a_1 = a_2 = a$, it is noted that $A_0^1 = -A_0^2$ and $D_0^1 = -D_0^2$ due to the charge symmetry, the reorganization energy has a simple form

$$\lambda = \frac{e^2}{\epsilon_0} \left\{ \frac{-k_0(\kappa a) + k_0(\kappa R) i_0(\kappa a)}{\epsilon_r \kappa a^2 [k_1(\kappa a) - k_0(\kappa R) i_1(\kappa a)]} + \frac{1}{a} - \frac{1}{R} \right\}. \quad (\text{B9})$$

It is interesting to note that λ could have an even simpler asymptotic form in the weak coupling limit $\kappa a_i \ll 1$. Note that $k_0(x) = \frac{e^{-x}}{x}$, $k_1(x) = \frac{e^{-x}(1+x)}{x^2}$, $i_0(x) = \frac{\sinh(x)}{x}$ and $i_1(x) = \frac{x \cosh(x) - \sinh(x)}{x^2}$, one can find the asymptotic solution for $A_0^{1,2}$ from Eq. (B7) in the large separation limit $R \gg a_i$, and the final result for the reorganization energy reads

$$\begin{aligned} \lambda = \frac{e^2}{2} \left\{ \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_1} \right) \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{2}{R} \right) \right. \\ \left. + \frac{1}{\epsilon_1} \left(\frac{\kappa}{1 + \kappa a_1} + \frac{\kappa}{1 + \kappa a_2} \right) \right. \\ \left. + \frac{1}{\epsilon_1 R} \left[\frac{e^{-\kappa(R-a_1)}}{1 + \kappa a_1} + \frac{e^{-\kappa(R-a_2)}}{1 + \kappa a_2} - 2 \right] \right\}, \quad (\text{B10}) \end{aligned}$$

which reflects solvent contributions from dipole, ion and dipole-ion cross effect. In the low coupling limit $\kappa \rightarrow 0$, Eq. (B10) reduce to the familiar Marcus result as $\lambda = \frac{e^2}{2} \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_1} \right) \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{2}{R} \right)$; while in the molten salt case where no dipole species are involved so that $\epsilon_1 = \epsilon_0$, we have $\lambda = \frac{e^2}{2\epsilon_0} \left\{ \frac{\kappa}{1 + \kappa a_1} + \frac{\kappa}{1 + \kappa a_2} + \frac{1}{R} \left[\frac{e^{-\kappa(R-a_1)}}{1 + \kappa a_1} + \frac{e^{-\kappa(R-a_2)}}{1 + \kappa a_2} - 2 \right] \right\}$.

According to Eq. (B8), one can find the corresponding reorganization energy λ_l for a single Yukawa mode with Debye parameter κ_l . When we apply the MDH approach to the diatomic model of an electron transfer reaction, the total reorganization energy could be evaluated by a linear combination of individual Yukawa modes, i.e., $\lambda = \sum_l C_l \lambda_l$.

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