THE JOURNAL OF CHEMICAL PHYSICS **129**, 214503 (2008)

Reaction coordinates for electron transfer reactions

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(Received 3 July 2008; accepted 22 October 2008; published online 4 December 2008)

The polarization fluctuation and energy gap formulations of the reaction coordinate for outer sphere electron transfer are linearly related to the constant energy constraint Lagrangian multiplier m in Marcus' theory of electron transfer. The quadratic dependence of the free energies of the reactant and product intermediates on m and $m+1$, respectively, leads to similar dependence of the free energies on the reaction coordinates and to the same dependence of the activation energy on the reorganization energy and the standard reaction free energy. Within the approximations of a continuum model of the solvent and linear response of the longitudinal polarization to the electric field in Marcus' theory, both formulations of the reaction coordinate are expected to lead to the same results. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3026365]

I. INTRODUCTION

The Marcus–Hush theory of outer-sphere electron transfer (ET) reactions in solution predicts parabolic free energies for reactant and product pairs as functions of an appropriate reaction coordinate.[1,2] The free energies are potentials of mean force, which have been repeatedly verified in computer simulations of ET reactions[3,4] when the reaction coordinate is defined as the difference in the interaction energies of the donor-acceptor pair with the surrounding solvent. Other definitions of the reaction coordinate have also been used.[5–7]

Sumi and Marcus[8] discussed the dynamics of ET reactions in terms of a reaction-diffusion equation that includes contributions from intramolecular vibrations and solvent polarization to the free energy profiles. In extending their work to reversible reactions,[10–12] we defined the reaction coordinate $x(t)$ for the outer-sphere contribution to ET by[10]

$$x(t)^2 = \frac{4\pi}{c}\int |\boldsymbol{P}^{\mathrm{or}}(t,\boldsymbol{r}) - \boldsymbol{P}_1^{\mathrm{or,eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}, \tag{1}$$

where $c=1/\varepsilon_\infty - 1/\varepsilon$ in which ε_∞ and ε are the high frequency optical and static dielectric constants, respectively, $\boldsymbol{P}_1^{\mathrm{or}}(t,\boldsymbol{r})$ is the orientation polarization of the solvent at position $\boldsymbol{r}$ at time t which takes the equilibrium values of $\boldsymbol{P}_1^{\mathrm{or,eq}}(\boldsymbol{r})$ and $\boldsymbol{P}_2^{\mathrm{or,eq}}(\boldsymbol{r})$, respectively, for the reactant and product pairs before and after ET. Although Sumi and Marcus did not explicitly define the reaction coordinate in this way, the adopted reaction coordinate is consistent with the Marcus forms for the outer-sphere free energy curves of the initial and final states, which are similar to the potential energies of two shifted harmonic oscillators,

$$V_1(x) = x^2/2, \tag{2}$$

$$V_2(x) = (x-x_0)^2/2 + \Delta G^0. \tag{3}$$

Here $x_0^2/2=\lambda_0$ is the solvent reorganization energy defined below and ΔG^0 is the standard reaction free energy for ET between the reactant and product intermediates X^* and X. In Eqs. (2) and (3) the vibrational contributions to the reactant and product free energies are omitted for convenience as being irrelevant to the present discussion.

The definition of the reaction coordinate given in Eq. (1) was used by us[9–11] and others[12,13] but it is was not clear how Eqs. (1)–(3) are logically related to each other and how they follow from the Marcus theory of ET. It is the purpose of this article to establish this relationship in detail while pointing out the approximations involved and also the connection to an alternate definition of the reaction coordinate.

II. DERIVATION OF THE FREE ENERGY CURVES AND POLARIZATION FLUCTUATION REACTION COORDINATE FROM THE MARCUS THEORY OF OUTER ELECTRON TRANSFER

A key ingredient in the Marcus theory of ET is that the solvent polarization fluctuates from its equilibrium value during the course of ET, which following the Franck–Condon principle, takes place at constant energy. ET between an A-B pair proceeds through the intermediates X^* and X, at a fixed distance R, which have the same energy and same nonequilibrium solvent configuration,

$$A + B \rightarrow X^* \rightarrow X \rightarrow C + D. \tag{4}$$

There are many possible intermediates and configurations that satisfy these conditions, which led Marcus to determine the optimal free energies F^* and F of X^* and X, respectively, by a variational argument in which the constant energy constraint is incorporated by introducing a Lagrangian multiplier m. Starting from a free energy functional [Eq. (15) of Ref. 1(b)], Marcus showed that[1(b),11]

$$F^*(m) = \frac{1}{8\pi\varepsilon}\int \boldsymbol{E}_c^{*2} d\boldsymbol{r} + m^2\lambda_0, \tag{5}$$

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$$F(m) = \frac{1}{8\pi\varepsilon}\int \boldsymbol{E}_c^2 d\boldsymbol{r} + (m+1)^2\lambda_0, \tag{6}$$

where $\boldsymbol{E}_c^*$ and $\boldsymbol{E}_c$ are the corresponding electric fields due to the intermediates X^* and X in the absence of the solvent (i.e., in a vacuum), $\boldsymbol{E}_c^{*2}$ and $\boldsymbol{E}_c^2$ are the squares of the absolute values, and

$$\lambda_0 = (c/8\pi)\int |(\boldsymbol{E}_c^* - \boldsymbol{E}_c)|^2 d\boldsymbol{r} \tag{7}$$

is the solvent reorganization energy. We note that F^* and F depend quadratically on m and $m+1$, respectively. When $m=0$, F^* $(m=0)$ is the equilibrium free energy of the reactant intermediate X^* at the bottom of its well, and when $m=-1$, F $(m=-1)$ is the corresponding equilibrium free energy of the product intermediate X. The standard free energy for ET from $X^* \rightarrow X$ is

$$\Delta G^0 \equiv F(m=-1) - F^*(m=0)$$
$$= \frac{1}{8\pi\varepsilon}\int (\boldsymbol{E}_c^2 - \boldsymbol{E}_c^{*2}) d\boldsymbol{r} \tag{8}$$

which is independent of m. Setting $m=-1$ in Eq. (5) shows that λ_0 is the free energy of reorganization of the solvent from its equilibrium configuration at the bottom of the reactant well to the corresponding equilibrium configuration at the bottom of the product well while remaining on the reactant free energy surface (before ET). A corresponding argument pertaining to the product well applies on setting $m=0$ in Eq. (6). This highlights the significance and importance of parameter m and suggests that m, or a variable proportional to it, can be considered as a reaction coordinate for an outer-sphere ET reaction. We proceed to show how this can be accomplished by relating m to the solvent polarization fluctuation.

Marcus treated the solvent polarization $\boldsymbol{P}(r)$ as the sum of contributions from electronic (E-type) polarization $\boldsymbol{P}_e(r)$, which responds instantaneously to ET, and atomic and orientation (U-type) polarization $\boldsymbol{P}_u(r)$ which lags behind; the time scales for these polarizations, 10^{-15} versus $10^{-13}-10^{-11}$ s are vastly different. Marcus also showed, assuming linear response of the U-type polarization to the field, that[1(b)]

$$\boldsymbol{P}_u(m,\boldsymbol{r}) = \left(\frac{\alpha_u}{\varepsilon}\right)[\boldsymbol{E}_c^*(\boldsymbol{r}) + m\{\boldsymbol{E}_c^*(\boldsymbol{r}) - \boldsymbol{E}_c(\boldsymbol{r})\}], \tag{9}$$

where the polarizabilities $\alpha_u=(\varepsilon-\varepsilon_\infty)/4\pi$, $\alpha_u/\varepsilon=c\varepsilon_\infty/(4\pi)$, and $c=1/\varepsilon_\infty-1/\varepsilon$ as defined earlier. Although Marcus' free energy functional is nonlinear in the nonequilibrium U-type polarization, his variational treatment optimizes this functional for ET at constant energy and leads to a linear relationship between this polarization and the Lagrangian multiplier m. The nonequilibrium polarization can also be related to fictitious charges on the reactants during electron transfer, but that is not of concern here.[1,6] In the limits $m=0$ and $m=-1$, $\boldsymbol{P}_u(\boldsymbol{m},\boldsymbol{r})$ attains the equilibrium polarizations of the reactant and product pairs, respectively, which we also characterize by subscripts 1 and 2. Defining $P_{u,1}^{\text{eq}}(r) \equiv P_u(m=0,r)$, $P_{u,2}^{\text{eq}}(r) \equiv P_u(m=-1,r)$, it follows from Eq. (9) and the definition of α_u/ε that

$$m[\boldsymbol{E}_c^*(\boldsymbol{r}) - \boldsymbol{E}_c(\boldsymbol{r})] = (4\pi/c\varepsilon_\infty)[\boldsymbol{P}_u(m,\boldsymbol{r}) - \boldsymbol{P}_{u,1}^{\text{eq}}(\boldsymbol{r})], \tag{10}$$

$$(m+1)[\boldsymbol{E}_c^*(\boldsymbol{r}) - \boldsymbol{E}_c(\boldsymbol{r})] = (4\pi/c\varepsilon_\infty)[\boldsymbol{P}_u(m,\boldsymbol{r}) - \boldsymbol{P}_{u,2}^{\text{eq}}(\boldsymbol{r})]. \tag{11}$$

Setting $m=-1$ in Eq. (10), taking the dot product of the result with itself, and integrating over the solvent coordinates, one finds that the solvent reorganization energy is given by

$$\lambda_0 = \frac{2\pi}{c\varepsilon_\infty^2}\int |\boldsymbol{P}_{u,2}^{\text{eq}}(\boldsymbol{r}) - \boldsymbol{P}_{u,1}^{\text{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}. \tag{12}$$

Likewise by taking the dot product of each side in Eq. (10) with itself, integrating, and using Eq. (12), we see that

$$m^2\lambda_0 = \frac{2\pi}{c\varepsilon_\infty^2}\int |\boldsymbol{P}_u(m,\boldsymbol{r}) - \boldsymbol{P}_{u,1}^{\text{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}. \tag{13}$$

Here the integrand is the absolute square of the deviation of the U-type solvent polarization from its equilibrium value around the reactant pair X^*. By a similar argument, starting from Eq. (11) we find

$$(m+1)^2\lambda_0 = \frac{2\pi}{c\varepsilon_\infty^2}\int |\boldsymbol{P}_u(m,\boldsymbol{r}) - \boldsymbol{P}_{u,2}^{\text{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}, \tag{14}$$

where the integrand is now the absolute square of the deviation of the same solvent polarization from its equilibrium value around the product pair X.

A major advantage of our nonlinear formulation of m over linear formulations[6(b),18] that involve the polarization fluctuation, the bare fields $\boldsymbol{E}_c^*(\boldsymbol{r})$ and $\boldsymbol{E}_c(\boldsymbol{r})$ and the reorganization energy λ_0 is that the bare fields have been eliminated in the nonlinear form and m can be calculated from λ_0 and the polarization fluctuations alone. For example, the bare fields due to a complex molecule may be unknown because the charges themselves may be unknown, and it is an advantage to eliminate these fields and cast the reaction coordinate solely in terms of the polarization fluctuations and the reorganization energy. Moreover our nonlinear form gives two solutions for m in nonequilibrium states. The two symmetrical placed solutions of Eq. (13) for m (except when $m=0$, when the solutions coincide) for a given integrated polarization fluctuation correspond to two states with the same free energy for the reactant pair X^* as expected from the parabolic form of the free energy dependence on the parameter m in Eq. (5). Likewise, Eq. (14) leads to two values of m symmetrically placed around $m=-1$, corresponding to two states with the same free energy of the product pair X as is evident from Eq. (6).

Inserting Eqs. (13) and (14) in Eqs. (5) and (6), respectively, we have

$$F^*(m) = F^*(m=0) + \frac{2\pi}{c\varepsilon_\infty^2}\int |\boldsymbol{P}_u(\boldsymbol{r}) - \boldsymbol{P}_{u,1}^{\text{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r} \tag{15}$$

and

$$F(m) = F(m = -1) + \frac{2\pi}{c\varepsilon_\infty^2} \int |\boldsymbol{P}_u(\boldsymbol{r}) - \boldsymbol{P}_{u,2}^{\mathrm{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}, \qquad (16)$$

which are seen to follow directly from Marcus' theory of electron transfer. Equations (15) and (16) or their equivalent have been given earlier by Lee and Hynes[6(b)] who obtained them by a different route.

Our discussion suggests that the Lagrangian multiplier m introduced by Marcus as a constant energy constraint in the free energy functional for electron transfer is a natural reaction coordinate. We have related it to fluctuations in the solvent polarization. As shown below it defines two other reaction coordinates (the polarization fluctuation and energy gap formulations) that are linearly related m.

We define the polarization reaction coordinate $x = -(2\lambda_0)^{1/2}\, m$, where the square of m is explicitly related to the solvent polarization by Eq. (13) when it follows that

$$x^2 = \frac{4\pi}{c\varepsilon_\infty^2} \int |\boldsymbol{P}_u(m,\boldsymbol{r}) - \boldsymbol{P}_{u,1}^{\mathrm{eq}}(\boldsymbol{r})|^2 d\boldsymbol{r}. \qquad (17)$$

Assuming $\varepsilon_\infty \approx 1$, Eq. (17) leads to Eq. (1), if we identify the U-type solvent polarization $\boldsymbol{P}_u(m,\boldsymbol{r})$ with the solvent orientation polarization $\boldsymbol{P}^{\mathrm{or}}(r)$ when $\boldsymbol{P}_{u,1}^{\mathrm{eq}}(\boldsymbol{r}) \equiv \boldsymbol{P}_1^{\mathrm{or,eq}}(\boldsymbol{r})$. Equation (15) can also be written as

$$F^*(x) = F^*(x=0) + x^2/2, \qquad (18)$$

which is a quadratic function of the reaction coordinate x identified as the negative of the Lagrangian multiplier m multiplied by the square root of twice the reorganization energy. The corresponding equation for the free energy of the product intermediate is obtained by shifting the origin of the reaction coordinate from reactant to product, which is equivalent to considering the deviation of the solvent polarization from its equilibrium value around the product pair X. Defining $x_0 = (2\lambda_0)^{1/2}$, i.e., taking the positive square root of the definition of x_0^2 given earlier in Sec. I, we see that $(x - x_0)^2/2 = \lambda_0(m+1)^2$, which provides the analog of Eq. (17) on substitution in Eq. (14). It follows from Eq. (6) that the free energy of the product pair X is

$$F(x) = F(x = x_0) + (x - x_0)^2/2. \qquad (19)$$

Equation (13) provides two values of m with the same reactant free energy centered about $m=0$, and Eq. (14) gives the two values for m centered around $m=-1$ for the product well. The nonlinear form thus gives both values of x and $x - x_0$ associated with the parabolic free energy wells.

Subtracting $F^*(x=0)$ from Eqs. (18) and (19) shifts the free energy curves vertically, and we arrive at Eqs. (2) and (3) if we define

$$V_1(x) \equiv F^*(x) - F^*(x=0),$$

$$V_2(x) \equiv F(x) - F^*(x=0), \quad \text{and}$$

$$\Delta G^0 \equiv F(x = x_0) - F^*(x=0).$$

Note that the Lagrangian multiplier ensures that the energies of the reactant and products intermediates are equal at a given m, although the energies themselves may change with m.

The intersection of the reactant and product free energies defines the transition state, when the reaction coordinate

$$x^\# = (x_0^2 + 2\Delta G^0)/(2x_0) = (\lambda_0 + \Delta G^0)/(2\lambda_0)^{1/2}, \qquad (20)$$

and $m^\# \equiv -x^\#/(2\lambda_0)^{1/2} = -(\lambda_0 + \Delta G^0)/2\lambda_0$. The "activation energy" for the ET reaction

$$\begin{aligned} E_A &\equiv F^*(x^\#) - F^*(x=0) \\ &= V_1(x^\#) = x^{\#2}/2 = (\lambda_0 + \Delta G^0)^2/(4\lambda_0) \end{aligned} \qquad (21)$$

is well known and is derived here using our definition of the reaction coordinate. For an isotopic exchange reaction, $\Delta G^0 = 0$, $x^\# = (\lambda_0/2)^{1/2}$, $m^\# = -1/2$, and $E_A = \lambda_0/4$ which again is well known.[1] The reorganization energy is necessarily positive and the activation energy is zero for electron transfer reactions with negative ΔG^0 when $\lambda_0 = -\Delta G^0$. At this point the reaction rate reaches a maximum before decreasing as ΔG^0 becomes more negative. This is the Marcus inversion region.[1,14,15]

Except for the assumptions that the solvent is a dielectric continuum with linear response of the longitudinal polarization to an electric field, the reaction coordinate x is model independent. In particular, it does not assume that ET occurs between spherical ions of given radii (a_1 and a_2) and charges (e_1^*, e_2^*) before and (e_1, e_2) after electron transfer although it can be applied to such systems. In this case one finds on evaluating the integral in Eq. (7) that

$$\lambda_0 = c(\Delta e)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right], \qquad (22)$$

as first shown by Marcus.[1] Here $\Delta e = e_2 - e_2^* = e_1^* - e_1$. The standard free energy [Eq. (8)] is also easily calculated to be

$$\Delta G^0 \equiv \frac{e_1 e_2 - e_1^* e_2^*}{\varepsilon R} + \frac{1}{\varepsilon}\left(\frac{e_1^2 - e_1^{*2}}{2a_1} + \frac{e_2^2 - e_2^{*2}}{2a_2} \right). \qquad (23)$$

The second term in Eq. (23) is $W_{\mathrm{iso}} - W_{\mathrm{iso}}^*$; the difference between the energies of the product and reactant ions at an infinite distance apart ($R = \infty$).

Marcus also defined another standard free energy

$$\Delta F^0(\boldsymbol{m}) = (F^*(\boldsymbol{m}) - W_{\mathrm{iso}}^*) - T\Delta S_e + (W_{\mathrm{iso}} - F(m)), \qquad (24)$$

where $-T\Delta S_e$ is the free energy of electron transfer from X^* to X which occurs at constant energy. Each term in Eq. (23) corresponds to a step in the mechanism of ET presented in Eq. (4). ΔF^0 is clearly a function of *m which is here the same for both the reactant and product free energy surfaces* in this expression. The relationship to ΔG^0 follows from Eqs. (5) and (6) for the difference $F^*(m) - F(m)$, when

$$\Delta F^0(m) = -\Delta G^0 + (W_{\mathrm{iso}} - W_{\mathrm{iso}}^*) - T\Delta S_e - (2m+1)\lambda_0. \qquad (25)$$

The $-T\Delta S_e$ term is quite small and negligible. Using Eq. (23) in Eq. (25), one finds[1]

$$\Delta F^0(m) = \frac{e_1^* e_2^* - e_1 e_2}{\varepsilon R} - (2m+1)\lambda_0. \tag{26}$$

For an isotopic exchange reaction the numerator of the first term is zero, $m=-1/2$ at the transition state and $\Delta F^0(m^\#)=0$.

To study the dynamics of electron transfer reactions, the definition of the reaction coordinate is extended to include the time variable by considering the U-type polarization states to be a function of time so that the parameter m is itself a function of time. Identifying the U-type polarization in Eqs. (10) and (11) with the orientation polarization leads to

$$\boldsymbol{P}^{\rm or}(t,\boldsymbol{r}) = [P_1^{\rm or,eq}(\boldsymbol{r}) + m(t)(P_1^{\rm or,eq}(\boldsymbol{r}) - P_2^{\rm or,eq}(\boldsymbol{r})\}], \tag{27}$$

where $P_1^{\rm or,eq}(\boldsymbol{r})=(\alpha_u/\varepsilon)E_c^*$. Defining $x(t)=-(2\lambda_0)^{1/2}m(t)$ we have from Eq. (13),

$$x(t)^2 = \frac{2\pi}{c\varepsilon_\infty^2}\int |\boldsymbol{P}^{\rm or}(t,\boldsymbol{r}) - \boldsymbol{P}_1^{\rm eq,or}(\boldsymbol{r})|^2 d\boldsymbol{r}. \tag{28}$$

This is analogous to Eq. (17) but has the time variable explicitly represented in the equation. It has been discussed elsewhere how the time correlation function of this reaction coordinate is related to the time correlation function for solvent dynamics.[6,10(a)] This applies also to the time correlation function of $m(t)$ since $x(t)$ and $m(t)$ are linearly related.

III. ENERGY-GAP REACTION COORDINATE FOR ELECTRON TRANSFER

Another form of the reaction coordinate for ET reactions seen frequently in the literature[5,6(b),7,12(b),16,17] is the interaction-energy gap

$$y \equiv \int d\boldsymbol{r}\boldsymbol{P}(r)\cdot[\boldsymbol{E}_c^*(r) - \boldsymbol{E}_c(\boldsymbol{r})]$$

$$= y_e + \int d\boldsymbol{r}\boldsymbol{P}_u(m,r)\cdot[\boldsymbol{E}_c^*(r) - \boldsymbol{E}_c(r)], \tag{29}$$

which is related to the instantaneous change in solvation energy on electron transfer from reactant to product. Here $\boldsymbol{P}(r)$ is the total polarization, y_e the contribution to y from the electronic polarization, and the remainder is the energy gap first introduced by Zusman.[5] The second term is twice the difference between the interaction energies of the polarized solvent with the product (X) and reactant (X^*) ion pairs and can be calculated directly in a computer simulations.[3,4] There have been many theoretical discussions that lead to Eq. (29). Lee and Hynes' discussion, Tachiya's discussion, and that of Zhu and Stell start from a nonequilibrium free energy functional slightly different from the Marcus functional.[18] We continue our discussion of Eq. (29) by retaining the Marcus' energy constraint, which leads to Eq. (9).

The difference $E_c^*(\boldsymbol{r})-E_c(\boldsymbol{r})$ is not a solvent property, but its relation to the solvent orientation polarization is given by Eq. (9). It follows from, Eqs. (9) and (29), that

$$y = y_0^* + m\varepsilon_\infty 2\lambda_0 = y_0^* - x\varepsilon_\infty(2\lambda_0)^{1/2}, \tag{30}$$

where $y_0^*=y_e+(c\varepsilon_\infty/4\pi)\int d\boldsymbol{r}\boldsymbol{E}_c^*(r)\cdot[\boldsymbol{E}_c^*(r)-\boldsymbol{E}_c(r)]$. The reaction coordinates y and x are linearly related and $y=y_0^*$, when $m=x=0$. Defining $Y\equiv(y-y_0^*)/\varepsilon_\infty=m2\lambda_0$, we see that $m=Y/2\lambda_0$ and $(1+m)=(Y+2\lambda_0)/2\lambda_0$. Inserting this in Eqs. (5) and (6) we obtain

$$F^*(Y) = F^*(m=0) + \frac{Y^2}{4\lambda_0}, \tag{31}$$

$$F(Y) = F(m=-1) + \frac{(Y+2\lambda_0)^2}{4\lambda_0}. \tag{32}$$

Subtracting $F^*(n=0)$ from both sides and defining V_1 and V_2 as before we have

$$V_1(Y) = Y^2/4\lambda_0, \tag{33}$$

$$V_2(Y) = (Y+2\lambda_0)^2/4\lambda_0 + \Delta G^0, \tag{34}$$

where $\Delta G^0\equiv F(m=-1)-F^*(m=0)$. Equations (33) and (34) are equivalent to the expressions for the free energies of reactant and product intermediates given elsewhere.[5,7,12(b)] We see they are also equivalent to Eqs. (2) and (3) derived here using the reaction coordinate x to which Y is linearly related. The reaction coordinates x and Y fluctuate with time since the solvent orientation polarization $\boldsymbol{P}^{\rm or}(\boldsymbol{r},\boldsymbol{t})$ is time dependent. This can be used to relate the solvation dynamics with the time correlation function of the reaction coordinates.

CONCLUSION

We have shown how the polarization fluctuation and the energy gap formulations of the reaction coordinate follow naturally from Marcus's theory of outer electron transfer without any further modification or extension. They both lead to a quadratic dependence of the free energies of the reactant and product intermediates on the respective reaction coordinates. Both reaction coordinates are linearly related to the Lagrangian multiplier m in Marcus' theory of outer sphere electron transfer, so that m also plays the role of a natural reaction coordinate.

ACKNOWLEDGMENTS

J.C.R. acknowledges support from the Chemistry Division of the National Science Foundation under Grant No. CHE 0549187, discussions with Gerhard Hummer, and the hospitality of Dave Thirumalai and Michael Fisher at the Institute of Physical Science and Technology, University of Maryland, College Park, MD at the time this work was done.

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[18] A linear form for m follows from taking the spatial integral of the dot product of Eq. (10) with $[\mathbf{E}_c^*(\mathbf{r})-\mathbf{E}_c(\mathbf{r})]$, rearranging and using Eq. (7) for the reorganization energy when one finds $m=(1/2\lambda_0\varepsilon_\infty)\int[\mathbf{P}_u(m,\mathbf{r})-\mathbf{P}_{u,1}^{\mathrm{eq}}(\mathbf{r})]\cdot[\mathbf{E}_c^*(\mathbf{r})-\mathbf{E}_c(\mathbf{r})]d\mathbf{r}$. This is essentially Lee and Hynes Eq. (2.14) for the solvation coordinate given in Ref. 6(b). If Eq. (10) is used again to eliminate $[\mathbf{E}_c^*(\mathbf{r})-\mathbf{E}_c(\mathbf{r})]$ we arrive at Eq. (13) which is nonlinear.