

Dispersion solute-solvent coupling in electron transfer reactions.

I. Effective potential

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Theories of electron transfer (ET) reactions and optical spectra in condensed phases consider electronic transitions between instantaneous Born-Oppenheimer energies of the intramolecular electronic states which depend on the system nuclear configuration. With the aim of constructing a molecular description of the solvent effect on these phenomena, we consider in the present paper a system composed of a polar polarizable solute immersed in a solvent of polar polarizable molecules. The instantaneous free energies are defined in terms of partial partition functions obtained by averaging over the electronic degrees of freedom of the solute and the solvent. Electronic polarizabilities of the solvent molecules are modelled as quantum Drude oscillators. For the solute, two models are considered: (i) the Drude oscillator and (ii) the two-state solute. The former enables us to derive the solute-solvent dispersion potential with account for the effects of nonlocal polarizability coupling in the solvent and the many-body solute-solvent dispersion contributions. These effects are analyzed using equilibrium theories of nonpolar liquids. The two-state description of the solute involves redistribution of the electron density between the two localized sites. The instantaneous adiabatic (in contrast to diabatic in the Drude oscillator model) free energy can be derived in this case under the only restriction of the quantum character of the solvent electronic excitations. It leads to the ET matrix element renormalized from its vacuum value due to the equilibrium field of the electronic solvent polarization and the instantaneous field of the permanent solvent dipoles. The theory predicts some useful relations which can be applied to treating the solvent effect on transition moments of optical spectra. The equilibrium ET matrix element is found to depend on the orientation of the solute diabatic transition dipole in the solute molecular frame and the spectral shift due to solvation by permanent and induced dipoles. This offers an interesting phenomenon of self-localization of the transferred electron (zero ET matrix element). Finally, the comparison of two derivations performed enables us to write down the diabatic instantaneous free energies which can be used for a molecular formulation of the effect of the solvent and the solute energy gap on ET rates. © 1998 American Institute of Physics. [S0021-9606(98)03315-7]

I. INTRODUCTION

Theoretical treatments of optical spectra and activation barriers of electron transfer (ET) reactions belong to a broad class of problems related to the behavior of liquids with quantum internal degrees of freedom.¹ The main challenge in treating such systems is the necessity to combine the quantum nature of intramolecular internal modes with predominantly classical statistics of the disordered liquid state. The system partition function

$$Z = \text{Tr}_{\text{cl}} \text{Tr}_{\text{el}}(\hat{\rho}) \quad (1)$$

includes thus traces of the density matrix $\hat{\rho} = \exp(-\beta H)$ over the quantum electronic (el) and classical nuclear (cl) coordinates. Here H is the system Hamiltonian and $\beta = 1/(k_B T)$ with k_B Boltzmann's constant and T the temperature. Considerable progress in tackling such problems has been achieved in recent years in the framework of the functional integral description of the quantum subsystem.^{1,2} This formalism reverses the order of traces in Eq. (1) ($\text{Tr}_{\text{cl}} \text{Tr}_{\text{el}} \rightarrow \text{Tr}_{\text{el}} \text{Tr}_{\text{cl}}$) applying the machinery of the liquid state theory to every point of the quantum intramolecular path. The approach becomes especially attractive in the framework

of the diagrammatic expansion,³ when a liquid with internal degrees of freedom becomes equivalent to an effective liquid without internal degrees of freedom and effective parameters (dipole moments, polarizabilities, etc.) to be determined from a self-consistency relation.¹ This method has been successfully applied to treating thermodynamic⁴ and optical⁵ properties of nonpolar liquids. Its main virtues are based on the possibility of switching the order of averaging over the classical nuclear and quantum electronic degrees of freedom when calculating the partition function.

The calculation of the ET probability and the spectral lineshape both involve the dynamic density matrix

$$\hat{\rho}(t) = \exp(iHt)\hat{\rho}(0)\exp(-iHt).$$

Dynamic problems present a serious challenge and dynamics of radiationless transitions can be successfully treated only for simplest model Hamiltonians like that of the spin-boson model.⁶ The physical realization of the spin-boson model closest to ET is that of the molecular polaron: one electron on either of two sites in a molecule coupled to harmonic optical phonons of the lattice.⁷ Though the spin-boson model has been used to model ET reactions,^{6d,8,9} it is rather limited

when applied to ET in liquids.¹⁰ The fundamental distinction between solids (spin-boson model) and liquids is the ability of the liquid molecules to translate resulting in density fluctuations and destruction of translational order. In contrast to fluctuations of harmonic oscillators which are totally enthalpic,¹¹ fluctuations in liquids include an entropic component of rearranging positions of the solvent molecules. The difference between the harmonic (corresponding to long-range interactions of a quasi-macroscopic length) and density (usually more short-ranged) modes is reflected in different temperature dependences of the activation barrier.^{12,13} This feature is not accounted for by harmonic representations of the solvent excitations and more sophisticated models are needed for treating electronic transitions in liquid solvents. This demand meets, however, with essential difficulties of realizing the above mentioned procedure of switching the trace order when applied to $\hat{\rho}(t)$. The way around the problem has actually been long used in the theory of ET reactions and optical spectra and consists in separating the dynamic and static parts of the problem in terms of instantaneous free energy surfaces.¹⁴ In the present paper, we will follow this traditional strategy focusing on deriving the instantaneous free energies in terms of molecular nuclear coordinates of the solvent. The definition of the instantaneous free energies is based on the separation of the characteristic timescales in the system.

Both the solute and solvent subsystems can generally be subdivided into fast electronic and much slower nuclear modes. The Born–Oppenheimer (BO) approximation employs this separation of the characteristic times to define the energies of electronic levels as a function of the nuclear coordinates. In a finite-temperature thermostat, they are calculated by integrating out the electronic degrees of freedom

$$\exp[-\beta E^e] = \text{Tr}_{\text{el}}(\hat{\rho}) \quad (2)$$

retaining hence the order of traces as it is in Eq. (1). The nuclear dynamics along the BO surfaces E^e can then be treated in a stochastic or an equilibrium transition state formalism leading to desired dynamic quantities. The definition of the BO surface E^e becomes, however, a nontrivial problem when applied to ET systems. This is because the trace over the coupled solute and solvent quantum degrees of freedom cannot be taken in a general case. It was Pekar¹⁵ who first suggested that the solute electron can be treated as a slow one compared to the solvent electrons in terms of the adiabatic decoupling scheme. This enables one to consider the motion of the solute electron as that of a small molecular polaron adiabatically “dressed” by the field of the solvent electrons. The basic assumption is that the characteristic frequency $\omega_0 = \Delta J/\hbar$ of transitions between the two localized states at the solute with the adiabatic energy gap ΔJ is much lower than the characteristic frequency of the solvent electronic excitations ω_s

$$\omega_0 \ll \omega_s. \quad (3)$$

The desire to go beyond the adiabatic Pekar approximation was the motivation of recent studies of the role played by the high-frequency solvent polarization.^{8,16,17} These were limited to the continuum description of the solvent and fo-

cused only on the solvent electronic polarization neglecting the solute polarizability and thus nonpolar solvation due to dispersion solute-solvent forces. A nonzero solute polarizability has only recently been incorporated into the dielectric continuum scheme by Kim.¹⁸ In many treatments,^{16,17a,d–f,18} the exact free energy E^e was replaced by the ground state energy $E' = \langle \phi_0 | H | \phi_0 \rangle$ ^{16,17f} with the expectation value taken in the ground state ϕ_0 of an orthonormal basis ϕ_0, \dots, ϕ_n optimized by using the variational principle.^{15,16} This is in fact a zero temperature variational procedure following from the upper Peierls bound:¹⁹

$$E^e \leq -\beta^{-1} \ln \sum_{\phi} \exp(-\beta \langle \phi | H | \phi \rangle) \quad (4)$$

in the $\beta \rightarrow \infty$ limit

$$E^e \leq E'.$$

Caution is, however, necessary in applying this approximation, since it results in a localized symmetry-breaking transition state that does not exist for E^e defined according to Eq. (2).⁸ (The appearance of such false states is in fact a well-known deficiency of simple variational procedures when applied to molecular polaron and exciton problems.^{7b,20}) Even such a simplified treatment does not achieve the goal of obtaining an *exact* solution for an arbitrary ω_0/ω_s ratio. It exists only for two limiting cases: (i) the Pekar approximation (3)²¹ (sudden approximation in Stratt’s classification¹) and (ii) the opposite limit of slow solvent electrons $\omega_0 \gg \omega_s$ (self-consistent approximation of Kim and Hynes¹⁶). An approximate ground state energy interpolating between the two known limits was suggested by Kim and Hynes.^{16d} The free energies E^e for an arbitrary ω_0/ω_s ratio can be obtained by means of Chebyshev–Markov inequalities^{7b} or by using variational calculations.^{7b,20,22} Note also that the condensed phase BO scheme (2) differs in one important point from the classical BO approximation developed for isolated molecules. The average over the electronic subsystem is performed for a quantum ensemble at finite temperature of the thermal bath^{8,17b,22} including thus a possibility of thermal excitations both of the solvent and the solute. A similar procedure is employed in the one-impurity Anderson model.²³ The BO surfaces in condensed phases thus become (partial) *free* energies instead of energies as in the gas phase.

Now we will be a bit more specific about the system Hamiltonian in Eq. (2). Under very general assumptions H can be split into the solute H_0^e , solvent H_s , and solute-solvent H_{0s} parts

$$H = H_0^e + H_s + H_{0s}. \quad (5)$$

Here and throughout below “0” and “s” indicate the solute and solvent, respectively. ET systems are usually viewed as a complex of donor and acceptor moieties weakly coupled in a donor-acceptor complex (DAC). The solute Hamiltonian H_0^e is thus given by the sum of the Hamiltonians $H_0^{(i)}$ corresponding to the electron localized at the donor ($i=1$) and acceptor ($i=2$) and a hopping Hamiltonian $H_0^{(12)}$

$$H_0^e = \sum_{i=1}^2 H_0^{(i)} + H_0^{(12)}.$$

The hopping Hamiltonian introduces a new timescale of the tunneling rate (hopping frequency) $|V_{12}|/\hbar$ between the two localized states, where V_{12} is the ET matrix element. Therefore, three timescales

$$|V_{12}|/\hbar, \omega_0, \omega_s$$

characterize the electronic subsystem. Only if the characteristic frequency²⁴ of the solvent nuclear motions ω_n is larger than the tunneling rate can we use the whole solute Hamiltonian H_0^e in Eq. (2). The ET rate is controlled in this case by the nuclear dynamics over the BO surface E^e .²⁵ In the opposite case $|V_{12}|/\hbar \ll \omega_n$, the ET rate is controlled by the tunneling rate at the intersection point of the two diabatic BO surfaces

$$\exp[-\beta E_i] = \text{Tr}_e(\exp[-\beta H_i]), \quad (6)$$

where the diabatic Hamiltonians H_i

$$H_i = H_0^{(i)} + H_s + H_{0s}^{(i)} \quad (7)$$

are defined by substituting $H_0^{(i)}$ instead of H_0^e in Eq. (5).

The motivation for the present paper is to calculate the instantaneous BO free energies E^e (2) and E_i (6)²⁶ not restricted to the continuum solvent model, as in previous studies,^{8,16–18} and suitable for nuclear averaging in the framework of liquid state theories. A molecular theory of ET activation based on this development will be presented in a forthcoming paper.²⁷ Our aim is also to show how nonequilibrium functionals of collective solvent coordinates (e.g., solvent polarization) commonly used in ET and allied applications^{16–18} appear as a result of a rigorous adiabatic elimination of the electronic degrees of freedom. Our treatment of instantaneous free energies E^e goes beyond the Pekar approximation and is valid for an arbitrary ratio ω_0/ω_s under the assumption of quantum excitations of solvent electrons. Since our particular interest is to understand the effect of the solute-solvent dispersion coupling on the ET energy gap law, we chiefly focus here on the derivation of the dispersion potential in Sec. II employing two models of solute polarizability: quantum Drude oscillator and two-state models. In particular, we analyze the effect of nonlocal interactions between induced solvent dipoles and the role of many-particle solute-solvent response on the interaction potential. The virtues and shortcomings of the two models are analyzed in Sec. III where the effective interaction potential is written down. Section IV concludes with the comparison of our derivation to other results and discussion focusing on the solvent renormalization of the ET matrix element and its consequences for optical spectroscopy.

II. INSTANTANEOUS FREE ENERGIES

We will assume that intramolecular electronic transitions proceed between two localized electronic states within the DAC. The charge distribution within the DAC varying in the course of ET will be represented by its initial m_{01} and final m_{02} dipole moments, the higher multipoles will be disregarded. The BO free energies will be calculated for the sys-

tem of a polar polarizable solute in a polar polarizable solvent. Two models of polarizable molecules are most frequently used in condensed phase theories: (i) the Drude oscillator model^{5,4,28} and (ii) the two-state model.^{29a,30} The former is simpler and is easily adjustable to use in liquid state calculations.^{5,4} The latter is more realistic and can be extended to a larger basis set.^{18,29b} To derive the BO instantaneous free energies we employ below both models for the solute and restrict ourselves to the Drude oscillator model for the solvent polarizability.

A. Drude oscillator model

Since the Drude oscillator model does not allow charge redistribution between the two localized states at the DAC, we will consider in this subsection only diabatic instantaneous energies E_i given by Eq. (6). State dependent dipole moments \mathbf{m}_{0i} and polarizabilities α_{0i} ($i=1$ for the initial and $i=2$ for the final state, respectively) are assigned to the DAC, whereas the solvent molecules are assumed to bear dipole moments \mathbf{m}_j and polarizabilities α_j . Since we assume below the anisotropic form for the solute polarizability, α_{0i} and α_j are given as the rank-two tensors. For polarizable molecules, the solute and the solvent dipole moments are sums of permanent (\mathbf{m}_{0i} and \mathbf{m}) and induced (\mathbf{p}_0 and \mathbf{p}) components. The solute-solvent part of the diabatic Hamiltonians (7) reads

$$H_{0s}^{(i)} = U_{0s}^{\text{rep}} - \sum_j (\mathbf{m}_{0i} + \mathbf{p}_0) \cdot \mathbf{T}_{0j} \cdot (\mathbf{m}_j + \mathbf{p}_j), \quad (8)$$

where \mathbf{T} is the dipole-dipole interaction tensor, U_{0s}^{rep} is the solute-solvent repulsion potential, and the sum runs over the N solvent molecules. To proceed further, we need a model describing intramolecular charge fluctuations resulting in induced dipole moments. In the quantum Drude oscillator model the solute and the solvent Hamiltonians read

$$H_0^{(i)} = I_i + \frac{1}{2} \omega_0^{-2} \dot{\mathbf{p}}_0 \cdot \alpha_{0i}^{-1} \cdot \dot{\mathbf{p}}_0 + \frac{1}{2} \mathbf{p}_0 \cdot \alpha_{0i}^{-1} \cdot \mathbf{p}_0 \quad (9)$$

and

$$H_s = U_s^{\text{rep}} + \frac{1}{2} \sum_j (\omega_s^{-2} \dot{\mathbf{p}}_j \cdot \alpha_j^{-1} \cdot \dot{\mathbf{p}}_j + \mathbf{p}_j \cdot \alpha_j^{-1} \cdot \mathbf{p}_j) - \frac{1}{2} \sum_{j,k} (\mathbf{m}_j + \mathbf{p}_j) \cdot \tilde{\mathbf{T}}_{jk} \cdot (\mathbf{m}_k + \mathbf{p}_k), \quad (10)$$

where $\tilde{\mathbf{T}}_{jk} = \mathbf{T}_{jk}(1 - \delta_{jk})$. In Eqs. (9) and (10) I_i are the vacuum energies of the electron in the i th state and U_s^{rep} is the solvent-solvent repulsion potential.

Equations (7)–(10) form the system diabatic Hamiltonian H_i . Here the Drude oscillator model introduces the simplification of equidistant ($\hbar\omega_0$ and $\hbar\omega_s$) electronic levels in the solute and solvent molecules. The second order quantum perturbation theory commonly used in deriving intermolecular potentials³¹ does not contain this restriction. However, we have chosen the Drude model based upon its two significant virtues: (i) the finite temperature averaging (6) is feasible in the quantum harmonic bath formalism used below

and (ii) an accurate definition of the interaction potential for a general form of solute and solvent polarizabilities is possible.

With the Hamiltonians H_i in hand we can calculate the free energies E_i . We will take the trace in Eq. (2) by applying the path integral approach within the imaginary time interval.^{2,5} Accordingly, Eq. (2) can be rewritten as

$$\exp[-\beta E_i] = \int \exp(-\hbar^{-1} S_i[\mathbf{p}_0, \mathbf{p}_j]) \mathcal{D}\mathbf{p}_0 \mathcal{D}\mathbf{p}, \quad (11)$$

where

$$S_i[\mathbf{p}_0, \mathbf{p}_j] = \int_0^{\beta\hbar} H_i[\mathbf{p}_0(\tau), \mathbf{p}_j(\tau)] d\tau.$$

The integral over trajectories $\mathbf{p}_{0,j}(\tau)$

$$\mathcal{D}\mathbf{p}_0 \mathcal{D}\mathbf{p} = \prod_{n=-\infty}^{\infty} d\mathbf{p}_{0n} \prod_j d\mathbf{p}_{jn},$$

can be replaced by that over the the Fourier components of the quantum oscillator coordinates

$$\mathbf{p}_{jn} = \int_0^{\beta\hbar} \mathbf{p}_j(\tau) \exp(i\omega_n \tau) d\tau,$$

$$\mathbf{p}_j(\tau) = (\beta\hbar)^{-1} \sum_n \mathbf{p}_{jn} \exp(-i\omega_n \tau),$$

where the frequencies $\omega_n = 2\pi n/\beta\hbar$ correspond to periodic boundary conditions $\mathbf{p}_j(0) = \mathbf{p}_j(\beta\hbar)$ of a boson field.

The action $S_i[\mathbf{p}_0, \mathbf{p}_j]$ is Gaussian in \mathbf{p}_{0n} and \mathbf{p}_{jn} and the integral (11) can thus be computed exactly.³² The effective energy becomes a rather cumbersome expression which we simplify by disregarding the solute-solvent induction interactions involving more than three particles and replacing the bare solvent polarizability α_j by its ‘‘dressed’’ value α_j^∞ renormalized due to the field of the surrounding induced dipoles. The diabatic energies E_i attain the form^{32,33}

$$\begin{aligned} E_i = & I_i + U^{\text{rep}} - \sum_j \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot \mathbf{m}_j - \frac{1}{2} \sum_{jk} \mathbf{m}_j \cdot \tilde{\mathbf{T}}_{jk} \cdot \mathbf{m}_k \\ & - \frac{1}{2} \sum_{jk} \mathbf{m}_j \cdot \mathbf{T}_{j0} \cdot \alpha_{0i} \cdot \mathbf{T}_{0k} \cdot \mathbf{m}_k \\ & - \frac{1}{2} \sum_j \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot \alpha_j^\infty \cdot \mathbf{T}_{j0} \cdot \mathbf{m}_{0i} \\ & - (2\beta)^{-1} \text{Tr} \sum_{nj} (\ln \boldsymbol{\pi}^{(n)})_{jj}. \end{aligned} \quad (12)$$

In Eq. (12), $U^{\text{rep}} = U_{0s}^{\text{rep}} + U_s^{\text{rep}}$, the trace in the last summand is taken over the Cartesian components of the dipole tensors, and

$$\boldsymbol{\pi}_{jk}^{(n)} = \delta_{jk} \mathbf{1} - \alpha_j^{(n)} \cdot \tilde{\mathbf{T}}_{jk} - \alpha_j^{(n)} \cdot \mathbf{T}_{j0} \cdot \alpha_{0i}^{(n)} \cdot \mathbf{T}_{0k},$$

where $\alpha_{0i}^{(n)} = \alpha_{0i} \omega_0^2 / (\omega_0^2 + \omega_n^2)$ and $\alpha_j^{(n)} = \alpha_j \omega_s^2 / (\omega_s^2 + \omega_n^2)$ are the polarizabilities of unperturbed Drude oscillators evaluated at the imaginary frequency $i\omega_n$.

The effective solvent polarizability α^∞ is enhanced compared to its vacuum value α due to the field of the surround-

ing induced dipoles of the solvent. Following the argumentation of the theory of nonpolar liquids,^{4,5,30a} α^∞ can be represented in the form

$$\alpha_{\alpha\beta}^\infty = [\boldsymbol{\alpha} \cdot (\mathbf{1} - 2a^\infty(\alpha^\infty) \boldsymbol{\alpha})^{-1}]_{\alpha\beta}, \quad (13)$$

where $a^\infty(\alpha^\infty)$ denotes the response function of the induced solvent field gauging its solvation power. It is obtained from the internal energy $-(3\alpha^\infty/\beta)a^\infty(\alpha^\infty)$ of induced solvent dipoles depending on $\alpha^\infty = (1/3) \text{Tr}(\boldsymbol{\alpha}^\infty)$. Equation (13) is thus a self-consistent relation with respect to α^∞ .

Now we embark on a detailed analysis of the dispersion potential [the last summand in Eq. (12)]. The treatment of dispersions is complicated by their nonpairwise character originating from (i) the nonadditive polarization coupling between the induced solvent dipoles and (ii) the many-body solute-solvent interactions. The first feature results in a non-local character of the effective pairwise solute-solvent potential. The second point arises from the series expansion of the logarithm in Eq. (12) and involves products of the loop solute-solvent-solute excitations. We analyze both effects below and first split the last summand in Eq. (12) into the solvent-solvent, U_s^{disp} , and solute-solvent, $U_{0s,i}^{\text{disp}}$, parts

$$(2\beta)^{-1} \text{Tr} \sum_{nj} (\ln \boldsymbol{\pi}^{(n)})_{jj} = U_s^{\text{disp}} + U_{0s,i}^{\text{disp}}$$

with

$$U_s^{\text{disp}} = (2\beta)^{-1} \text{Tr} \sum_{n,j} (\ln(\mathbf{1} - \boldsymbol{\alpha}^{(n)} \cdot \tilde{\mathbf{T}}))_{jj},$$

$$\begin{aligned} U_{0s,i}^{\text{disp}} = & (2\beta)^{-1} \text{Tr} \sum_{n,j,k} (\ln(\mathbf{1} - (\mathbf{1} - \boldsymbol{\alpha}^{(n)} \cdot \tilde{\mathbf{T}})_{jk}^{-1} \boldsymbol{\alpha}_k^{(n)} \cdot \mathbf{T}_{k0} \\ & \cdot \boldsymbol{\alpha}_{0i}^{(n)} \cdot \mathbf{T}_{0j})). \end{aligned} \quad (14)$$

The inverse matrix

$$\begin{aligned} (\mathbf{1} - \boldsymbol{\alpha}^{(n)} \cdot \tilde{\mathbf{T}})_{jk}^{-1} = & \delta_{jk} \mathbf{1} + \boldsymbol{\alpha}_j^{(n)} \cdot \tilde{\mathbf{T}}_{jk} \\ & + \sum_m \boldsymbol{\alpha}_j^{(n)} \cdot \tilde{\mathbf{T}}_{jm} \cdot \boldsymbol{\alpha}_m^{(n)} \cdot \tilde{\mathbf{T}}_{mk} + \dots \end{aligned}$$

generates under the logarithm in $U_{0s,i}^{\text{disp}}$ an infinite tensor series usually considered in the theory of nonpolar fluids. The diagrammatic analysis of such series has been performed by Wertheim³³ and we will follow here that procedure. The structure of expansion graphs remains the same for every summand over n in Eq. (14).⁵ We can therefore calculate each n -component separately. Let us consider the first expansion term of the solute-solvent dispersion potential in Eq. (14)

$$F_n(12) = \text{Tr}(\boldsymbol{\alpha}_{0i} \cdot \mathbf{T}_{01} \cdot [(\mathbf{1} - \boldsymbol{\alpha}^{(n)} \cdot \tilde{\mathbf{T}})^{-1} \cdot \boldsymbol{\alpha}^{(n)}]_{12} \cdot \mathbf{T}_{20}),$$

where

$$[(\mathbf{1} - \boldsymbol{\alpha}^{(n)} \cdot \tilde{\mathbf{T}})^{-1} \cdot \boldsymbol{\alpha}^{(n)}]_{12} = \delta_{12} \boldsymbol{\alpha}_1^{(n)} + \boldsymbol{\alpha}_1^{(n)} \cdot \tilde{\mathbf{T}}_{12} \cdot \boldsymbol{\alpha}_2^{(n)} + \sum_k \boldsymbol{\alpha}_1^{(n)} \cdot \tilde{\mathbf{T}}_{1k} \cdot \boldsymbol{\alpha}_k^{(n)} \cdot \tilde{\mathbf{T}}_{k2} \cdot \boldsymbol{\alpha}_2^{(n)} + \dots$$

In the diagrammatic formalism, $F_n(12)$ can be represented as a sum of graphs composed of a white circle referring to the solute and some black circles representing solvent sites, each bearing the vacuum polarizability $\boldsymbol{\alpha}_j^{(n)}$. The white circle and the black circles are connected by \mathbf{T} -bonds. The loop diagrams starting and ending at the same black circle can be included into renormalized vertices replacing the vacuum polarizability $\boldsymbol{\alpha}_j^{(n)}$ by the graph $\mathcal{B}_n(j)$ representing $\boldsymbol{\alpha}_j^{(n)}$ in the field of the solvent induced dipoles acting on the j th molecule. The remaining diagrams, according to Wertheim,³³ are the chains of irreducible graphs without bridge points and with the factor \mathcal{B}_n associated with each black point. As a result, $F_n(12)$ is given by

$$F_n(12) = \text{Tr}(\boldsymbol{\alpha}_{0i}^{(n)} \cdot \mathbf{T}_{01} \cdot \hat{\mathcal{A}}_n(12) \cdot \mathbf{T}_{20}), \quad (15)$$

where

$$\hat{\mathcal{A}}_n(12) = \mathcal{B}_n(1) \delta_{12} + \mathcal{A}_n(12). \quad (16)$$

The first term in (16) accounts for the one-particle solvent excitations whereas the second term is caused by the correlations between the induced dipoles of different molecules. The tensor $\hat{\mathcal{A}}_n(12)$ depends on the configurations of all the solvent molecules representing the many-body character of the solute-solvent coupling [recall that the nuclear averaging is left out of Eq. (6)]. In order to reduce the problem to an effectively pairwise potential, we replace the response function $\hat{\mathcal{A}}_n(12)$ by its value averaged over the nuclear configurations of all $N-2$ solvent molecules excluding the probe particles 1 and 2: $\hat{\mathbf{A}}_n(12) = \langle \hat{\mathcal{A}}_n(12) \rangle_{j \neq 1,2}$. This yields³³

$$\hat{\mathbf{A}}_n(12) = \boldsymbol{\alpha}_1^{(n)\infty} \delta_{12} + \rho \boldsymbol{\alpha}_1^{(n)\infty} \cdot \mathbf{H}_n(12) \cdot \boldsymbol{\alpha}_2^{(n)\infty}, \quad (17)$$

where ρ is the solvent number density and the correlation second-rank tensor $\mathbf{H}_n(12)$ can be written as

$$\mathbf{H}_n(12) = h_n^A(r_{12}) \mathbf{1} + h_n^D(r_{12}) \mathbf{D}_{12}, \quad (18)$$

where $\hat{\mathbf{r}}_{jk} = \mathbf{r}_{jk}/r_{jk}$ and

$$\mathbf{D}_{jk} = 3\hat{\mathbf{r}}_{jk}\hat{\mathbf{r}}_{jk} - \mathbf{1}. \quad (19)$$

Now, in order to obtain the effective pairwise solute-solvent dispersion potential, we will integrate over the center-of-mass positions and orientations of one of the two probe particles. This results in

$$U_{0s,i}^{\text{disp}} = (2\beta)^{-1} \text{Tr} \sum_{n,j} \ln \left[\mathbf{1} - \boldsymbol{\alpha}_{0i}^{(n)} \cdot \mathbf{T}_{0j} \cdot \int \hat{\mathbf{A}}_n(j2) \cdot \mathbf{T}_{20} d2 \right]. \quad (20)$$

In Appendix A we show that the inclusion of the nonlocal correlation effects represented by $\mathbf{H}_n(12)$ in (17) results in the appearance of the Kirkwood g -factor of the induced solvent dipoles $g_{K,n}^\infty$ multiplying $\boldsymbol{\alpha}^{(n)\infty}$ so that

$$U_{0s,i}^{\text{disp}} = (2\beta)^{-1} \sum_{n,j} \ln [\mathbf{1} - g_{K,n}^\infty \boldsymbol{\alpha}_j^{(n)\infty} \cdot \mathbf{T}_{j0} \cdot \boldsymbol{\alpha}_{0i}^{(n)} \cdot \mathbf{T}_{0j}]. \quad (21)$$

The simplification (21) is achieved by replacing the nonlocal polarizability interactions by an effective pairwise potential. The dispersion potential (21) includes thus only the products of pairwise interactions when the logarithm is expanded in a series. If we take only the first non-vanishing term in the expansion, we get [$g_{K,n}^\infty$ is replaced by $g_K^\infty = g_{K,0}^\infty$]

$$U_{0s,i}^{\text{disp}} = - \frac{g_K^\infty}{2\beta} \sum_{n,j} \frac{\omega_0^2 \omega_s^2}{(\omega_0^2 + \omega_n^2)(\omega_s^2 + \omega_n^2)} \text{Tr}(\boldsymbol{\alpha}_j^\infty \cdot \mathbf{T}_{j0} \cdot \boldsymbol{\alpha}_{0i} \cdot \mathbf{T}_{0j}). \quad (22)$$

The sum over n can be computed using residue calculus^{4d}

$$\beta^{-1} \sum_n \frac{\omega_0^2 \omega_s^2}{(\omega_0^2 + \omega_n^2)(\omega_s^2 + \omega_n^2)} = \frac{\hbar \omega_0 \omega_s}{2(\omega_s^2 - \omega_0^2)} [\omega_s \coth(\beta \hbar \omega_0/2) - \omega_0 \coth(\beta \hbar \omega_s/2)]. \quad (23)$$

Under the conditions of quantum excitation frequencies

$$\beta \hbar \omega_0 \gg 2 \quad \text{and} \quad \beta \hbar \omega_s \gg 2 \quad (24)$$

and isotropic solute and solvent polarizabilities $\alpha_{\alpha\beta}^\infty = \alpha^\infty \delta_{\alpha\beta}$, $\alpha_{0,\alpha\beta} = \alpha_0 \delta_{\alpha\beta}$ Eqs. (22) and (23) reduce to the well-known London form³¹

$$U_{0s,i}^{\text{disp}} = - \frac{3\alpha_{0i} g_K^\infty \alpha^\infty}{2} \frac{\hbar \omega_0 \omega_s}{\omega_0 + \omega_s} \sum_j \frac{1}{r_{0j}^6} \quad (25)$$

which still differs from its gas-phase analog by the replacement of α by $g_K^\infty \alpha^\infty$.

In the potential (25) the dependence on temperature is eliminated due to the conditions (24) excluding occupation of the solute and solvent electronic states by thermal excitations of the thermostat. Throughout below we will assume a quantum excitation energy $\hbar \omega_s$ for the solvent molecules implying the second inequality (24) to be valid. The first inequality in (24) can however be violated under the ET resonance condition. Therefore, the solute-solvent dispersion coupling should be taken in the form

$$U_{0s,i}^{\text{disp}} = \frac{g_K^\infty \hbar \omega_0 \omega_s}{4(\omega_s^2 - \omega_0^2)} \left[\omega_s \coth \frac{\beta \hbar \omega_0}{2} - \omega_0 \right] \times \sum_j \text{Tr}(\boldsymbol{\alpha}_j^\infty \cdot \mathbf{T}_{j0} \cdot \boldsymbol{\alpha}_{0i} \cdot \mathbf{T}_{0j}). \quad (26)$$

When $\beta \hbar \omega_0 < 2$, the solute is excited by the thermostat thermal motion and the dispersion potential becomes proportional to T

$$U_{0s,i}^{\text{disp}} = (g_K^{\infty} k_B T/2) \sum_j \text{Tr}(\alpha_j^{\infty} \cdot \mathbf{T}_{j0} \cdot \alpha_{0i} \cdot \mathbf{T}_{0j}). \quad (27)$$

The possibility that the dispersion potential is proportional to T in the classical limit of high temperatures has been mentioned already by Linder.³⁴ We, however, have not found analogs of the more general Eqs. (23) and (26) in the textbooks on intermolecular interactions.^{31,35} An expression analogous to Eq. (23) for the symmetrical case $\omega_s = \omega_0$ appeared in the study by Cao and Berne³⁶ of Lennard–Jones (LJ) clusters. They however used only its quantum limit (25).

The natural question arising in connection with the truncation (22) of Eq. (21) is the contribution of higher-order terms. The whole expansion of the logarithm in Eq. (21) is calculated in Appendix A. The ratio of the second and the first order expansion terms in Eq. (21) is shown there to be $\approx 3\alpha_0\alpha/(4r_{0j}^6)$. This can be evaluated by using an approximation $\alpha_0 = \sigma_0^3/16$, $\alpha = \sigma^3/16$ [σ_0 and σ are the solute and solvent hard sphere (HS) diameters] and $r_{0j} = (\sigma_0 + \sigma)/2$. The ratio thus becomes $3\sigma_0^3\sigma^3/[16(\sigma + \sigma_0)^6]$. Even for the solute and solvent of equal size, the second term in the expansion (21) is just 3/1024 of the first one. The ratio decreases quickly with increasing size asymmetry and we can safely use the truncation (22) disregarding the higher order terms in (21). Our present analysis thus shows that both the nonpairwise effects (due to the solvent-solvent polarization coupling, Appendix A) and the many-body solute-solvent forces (Appendix B) have only a very minor effect on the dispersion interaction potential. This result is in agreement with the analogous conclusion drawn by Cao and Berne from simulations of LJ clusters.³⁶

B. Two-state solute model

We now calculate the adiabatic instantaneous energy E^e given by Eq. (2) for the two-state model of the solute. This approach has several important virtues: (i) it explicitly involves the charge redistribution between the two localized states in the DAC, (ii) explicit form for the solute polarizability, and (iii) the time separation requirements discussed in the Introduction are revealed in a transparent way from the derivation. The vacuum solute Hamiltonian can be represented in terms of the fermionic creation $\psi^+(\mathbf{r})$ and annihilation $\psi(\mathbf{r})$ operators of the transferred electron at the point \mathbf{r}

$$H_0^e = \int \psi^+(\mathbf{r}) \left[\sum_{i=1}^2 H_0^{(i)} + H_0^{(12)} \right] \psi(\mathbf{r}) d\mathbf{r}.$$

In the vacuum two-state solute basis $\phi_1(\mathbf{r})$, $\phi_2(\mathbf{r})$, $H_0^{(i)}\phi_i(\mathbf{r}) = I_i\phi_i(\mathbf{r})$, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ we have $\psi^+(\mathbf{r}) = a_1^+\phi_1^*(\mathbf{r}) + a_2^+\phi_2^*(\mathbf{r})$ and H_0^e reads

$$H_0^e = I_1 a_1^+ a_1 + I_2 a_2^+ a_2 + V_{12}(a_2^+ a_1 + a_1^+ a_2), \quad (28)$$

where a_i^+ and a_i refer to the i th state. The solute-solvent interaction Hamiltonian by the same token takes the form

$$H_{0s} = U_{0s}^{\text{rep}} - \sum_{i,k=1}^2 a_i^+ a_k \sum_j \mathbf{m}_0^{jk} \cdot \mathbf{T}_{0j} \cdot (\mathbf{m}_j + \mathbf{p}_j),$$

where $\mathbf{m}_0^{ik} = \langle \phi_i | \hat{\mathbf{m}}_0 | \phi_k \rangle$ is the matrix element of the solute dipole operator $\hat{\mathbf{m}}_0$. Note that the diagonal terms \mathbf{m}_0^{ii} are \mathbf{m}_0 in our notation above. The sum of H_0^e and H_{0s} is

$$H_0^e + H_{0s} = U_{0s}^{\text{rep}} + \sum_{i=1}^2 \tilde{I}_i[\{\mathbf{m}_j, \mathbf{p}_j\}] a_i^+ a_i + \tilde{V}_{12}[\{\mathbf{m}_j, \mathbf{p}_j\}] \times (a_2^+ a_1 + a_1^+ a_2), \quad (29)$$

where, under the assumption $\mathbf{m}_0^{ik} = \mathbf{m}_0^{ki}$,

$$\tilde{I}_i[\{\mathbf{m}_j, \mathbf{p}_j\}] = I_i - \sum_j \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot (\mathbf{m}_j + \mathbf{p}_j),$$

$$\tilde{V}_{12}[\{\mathbf{m}_j, \mathbf{p}_j\}] = V_{12} - \sum_j \mathbf{m}_0^{12} \cdot \mathbf{T}_{0j} \cdot (\mathbf{m}_j + \mathbf{p}_j).$$

Now the instantaneous free energies E^e can be obtained by integrating over the electronic degrees of freedom. We perform this as above in the form of a Euclidean path integral. One correction of Eq. (2) is, however, first necessary. Since we adopted the description of the two-level system in terms of creation and annihilation operators, we need also to determine the chemical potential μ^e of the two-level system in order to ensure correct statistics of the finite-temperature quantum system. The value of μ^e is derived from the condition that only one electron can occupy the two levels of the solute

$$\langle \hat{N} \rangle = \text{Tr}_{\text{el}}(\hat{N} \exp[-\beta(H_0^e - \mu^e \hat{N})]) = 1, \quad (30)$$

where $\hat{N} = a_1^+ a_1 + a_2^+ a_2$. E^e can be obtained from the functional integral over the solvent and solute quantum degrees of freedom in the holomorphic representation.³⁷ The functional integral over the solute electronic subsystem results in the grand-partition function.^{7c} The canonical partition function can then be obtained by differentiating over the fugacity $z = \exp(\beta\mu^e)$. We thus get

$$\begin{aligned} \exp[-\beta E^e] &= \frac{\partial}{\partial z} \text{Tr}_{\text{el}}(\exp[-\beta(H - \mu^e \hat{N})])|_{z=0} \\ &= \frac{\partial}{\partial z} \int \exp(\hbar^{-1} S_{0s}[a_i^*, a_i, \mathbf{p}_j] \\ &\quad - \hbar^{-1} S_s[\mathbf{p}_{jn}]) \mathcal{D}\mathbf{p} \mathcal{M}|_{z=0}. \end{aligned} \quad (31)$$

In Eq. (31) the measure

$$\mathcal{M} = \prod_{k=1}^2 \prod_{\beta\hbar \geq \tau \geq 0} \frac{da_k^*(\tau) da_k(\tau)}{2\pi i}$$

defines functional integration over the Grassmann field amplitudes³⁸ $a_i^*(\tau)$ and $a_i(\tau)$ with aperiodic boundary conditions $a_i(0) = -a_i(\beta\hbar)$.³⁷ The action $S_{0s}[a_i^*, a_i, \mathbf{p}_j]$ is defined as

$$S_{0s}[a_i^*, a_i, \mathbf{p}_j] = \int_0^{\beta\hbar} \sum_i [\hbar a_i^*(\tau) \partial_\tau a_i(\tau) + (\mu^e - \tilde{T}_i[\{\mathbf{m}_j, \mathbf{p}_j(\tau)\}]) a_i^*(\tau) a_i(\tau)] d\tau - \int_0^{\beta\hbar} \tilde{V}_{12}[\{\mathbf{m}_j, \mathbf{p}_j(\tau)\}] (a_1^*(\tau) a_2(\tau) + a_2^*(\tau) a_1(\tau)) d\tau$$

The quantum Drude oscillator model is retained for the solvent induced dipoles and the action $S_s[\mathbf{p}_{jn}]$ is

$$\beta\hbar S_s[\mathbf{p}_{jn}] = \frac{1}{2} \sum_{j,k,n} \mathbf{p}_{jn} \cdot (\alpha_j^{(n)-1} \delta_{jk} - \tilde{\mathbf{T}}_{jk}) \cdot \mathbf{p}_{kn}^*$$

The integration over the Gaussian fields \mathbf{p}_{jn} yields the action in terms of only the fermionic amplitudes a_i^* and a_i that contains convolution terms of the form

$$\int_0^{\beta\hbar} \int_0^{\beta\hbar} a_i^*(\tau) a_k(\tau) \mathbf{G}(\tau - \tau') a_m^*(\tau') a_n(\tau') d\tau d\tau', \quad (32)$$

where for the isotropic solvent polarizability $\alpha_{j,\alpha\beta}^{(n)} = \alpha^{(n)} \delta_{\alpha\beta}$ we have

$$\mathbf{G}(\tau - \tau') = \sum_n \alpha^{(n)} (\mathbf{1} - \alpha^{(n)} \tilde{\mathbf{T}})^{-1} \exp[i\omega_n(\tau - \tau')]. \quad (33)$$

The zeroth order in $\alpha^{(n)} \tilde{\mathbf{T}}$ term in (33) leads to the usual Green's function of a quantum harmonic bath

$$\mathbf{G}_0(\tau - \tau') = \mathbf{1} \sum_n \alpha^{(n)} \exp[i\omega_n(\tau - \tau')] = \mathbf{1} \frac{\alpha\beta\hbar\omega_s \cosh \omega_s(|\tau - \tau'| - \beta\hbar/2)}{2 \sinh(\beta\hbar\omega_s/2)}$$

$\mathbf{G}(\tau - \tau')$ determines the retardation of the solvation of the solute electronic states by the solvent electrons in the case of comparable time scales of the electronic subsystems $\omega_0/\omega_s \sim 1$. This retardation is eliminated in terms of the Pekar approximation (3) when the two time scales differ substantially. The Grassmann amplitudes $a_i^*(\tau)$ and $a_i(\tau)$ evolve on the characteristic timescale $\hbar/|\Delta I|$. When the transferred electron is much more sluggish than the solvent electrons $|\Delta I|/\hbar \ll \omega_s$, the problem can be simplified by replacing $\mathbf{G}(\tau - \tau')$ by a delta function

$$\mathbf{G}(\tau - \tau') = \beta\hbar \alpha (\mathbf{1} - \alpha \tilde{\mathbf{T}})^{-1} \delta(\tau - \tau'). \quad (34)$$

This removes the correlation terms resulting in a two-level description of the solute electronic subsystem in an adiabatic field of the solvent electrons. The effective action takes the form

$$S^{\text{eff}}[a_i^*, a_i] = \sum_{i=1}^2 \int_0^{\beta\hbar} [\hbar a_i^*(\tau) \partial_\tau a_i(\tau) + (\mu^e - E_i) a_i^*(\tau) a_i(\tau)] d\tau - V_{12}^{\text{eff}} \int_0^{\beta\hbar} [a_1^*(\tau) a_2(\tau) + a_2^*(\tau) a_1(\tau)] d\tau. \quad (35)$$

In deriving Eq. (35) we used the relation valid for the fermionic operators $(a_i^*(\tau) a_i(\tau))^2 = a_i^*(\tau) a_i(\tau)$, $a_i^*(\tau) a_i^*(\tau) = 0$, and the commutation rules.³⁸ In Eq. (35), the diabatic energies E_i are given by the expression

$$E_i = I_i - \sum_j \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot \mathbf{m}_j - (\alpha/2) \sum_{j,k} \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot (\mathbf{1} - \alpha \tilde{\mathbf{T}})_{jk}^{-1} \cdot \mathbf{T}_{k0} \cdot \mathbf{m}_{0i} - (\alpha/2) \sum_{j,k} \mathbf{m}_0^2 \cdot \mathbf{T}_{0j} \cdot (\mathbf{1} - \alpha \tilde{\mathbf{T}})_{jk}^{-1} \cdot \mathbf{T}_{k0} \cdot \mathbf{m}_0^2 \quad (36)$$

and the effective ET matrix element is

$$V_{12}^{\text{eff}} = V_{12} - \mathbf{m}_0^2 \cdot \mathbf{R}[\bar{\mathbf{m}}_0]. \quad (37)$$

The charge-transfer matrix element (37) is renormalized by the reaction field of the solvent

$$\mathbf{R}[\bar{\mathbf{m}}_0] = \sum_j \mathbf{T}_{0j} \cdot (\mathbf{m}_j + \alpha (\mathbf{1} - \alpha \tilde{\mathbf{T}})_{jk}^{-1} \cdot \mathbf{T}_{k0} \cdot \bar{\mathbf{m}}_0)$$

including the reaction field of the induced dipoles (R_e) on the mean solute dipole $\bar{\mathbf{m}}_0 = (\mathbf{m}_{01} + \mathbf{m}_{02})/2$ and the instantaneous field of the solvent permanent dipoles (R_p). The former can be written in the linear response approximation as

$$R_e[\bar{\mathbf{m}}_0] = 2\mu_e \bar{\mathbf{m}}_0 \quad (38)$$

with μ_e referring to the response function of the induced solvent dipoles (the solvation free energy of the dipole m_{0i} is thus $\mu_e m_{0i}^2$). In the continuum approximation it reads

$$\mu_e = \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1} \frac{1}{R_0^3}, \quad (39)$$

where $R_0 = \sigma_0/2$ is the solute HS radius and ϵ_∞ is the high-frequency solvent dielectric constant. The instantaneous field of the solvent permanent dipoles can be attributed to an equilibrium field created by a fictitious solute dipole $\mathbf{m}_0^{\text{fic}}$,^{14a} such that

$$\mathbf{R}_p[\mathbf{m}_0^{\text{fic}}] = \sum_j \mathbf{T}_{0j} \cdot \mathbf{m}_j = 2\mu_p \mathbf{m}_0^{\text{fic}},$$

where μ_p is the response function of the liquid permanent dipoles. It reads in the continuum description (ϵ_s is the static solvent dielectric constant)

$$\mu_p = \left[\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1} \right] \frac{1}{R_0^3}. \quad (40)$$

We thus can recast V_{12}^{eff} in the form

$$V_{12}^{\text{eff}} = V_{12} - 2\mu_p(\mathbf{m}_0^{12} \cdot \mathbf{m}_0^{\text{fc}}) - 2\mu_e(\mathbf{m}_0^{12} \cdot \bar{\mathbf{m}}_0). \quad (41)$$

Somewhat similar relations for the renormalized equilibrium charge-transfer coupling have been obtained in previous studies employing dielectric continuum models for the solvent.^{16a-c,17d}

The derivation performed above indicates also the origin of the problem with the self-consistent variational principle in the limit of fast solvent electrons.^{8,16} If we had replaced the Hamiltonian H in Eq. (2) by its ground state matrix element, we would get instead of Eq. (32) correlations of the form

$$\int_0^{\beta\hbar} \int_0^{\beta\hbar} n_i(\tau) \mathbf{G}(\tau - \tau') n_k(\tau') d\tau d\tau',$$

where $n_i(\tau) = \langle \phi_0 | a_i^*(\tau) a_i(\tau) | \phi_0 \rangle$. Then the use of the kernel (34) would result in terms $\propto n_i(\tau) n_k(\tau)$ that do not appear in a rigorous treatment.

The instantaneous energy E^e can now be obtained by integrating over the Grassman amplitudes $a_i^*(\tau)$, $a_i(\tau)$ in Eq. (31) with the action (35). The same procedure for the chemical potential μ^e in Eq. (30) yields $\mu^e = (E_1 + E_2)/2$. As a result, the energy E^e is given by

$$E^e = \frac{1}{2}(E_1 + E_2) - \beta^{-1} \ln[2 \cosh(\beta \Delta \bar{E}/2)], \quad (42)$$

where $\Delta \bar{E} = \sqrt{\Delta E^2 + 4|V_{12}^{\text{eff}}|^2}$ and $\Delta E = E_2 - E_1$. Equation (42) coincides with the free energy of the spin-boson Hamiltonian^{2,8,22c} calculated to zeroth order in ω_0/ω_s . An improvement of this result for an arbitrary ω_0/ω_s is possible for a quantum solvent $\beta\hbar\omega_s \gg 2$. In this case, the infinite perturbation series over the hopping Hamiltonian $H_0^{(12)}$ can be summed in the basis of the coherent solvent states.^{7a} The result of this procedure is the energy (42) with the ET matrix element V_{12}^{eff} replaced by

$$\bar{V}_{12} = V_{12}^{\text{eff}} \exp(-\frac{1}{2}S_e), \quad S_e = \mu_e \Delta m_0^2 / \hbar \omega_s. \quad (43)$$

The exponential factor renormalizing the hopping frequency is the classical Holstein result³⁹ rederived in the literature several times later on.^{7a,9,16d,17f} Unfortunately, this procedure cannot be extended to take into account the coupling of the off-diagonal ET matrix element to the solvent electronic excitations responsible for dispersion forces. We therefore retain the dispersion term in Eq. (20) in the form corresponding to the Pekar adiabatic time-separation (3). In the next section we construct a hybrid potential incorporating the result of the Drude oscillator model for the dispersion solvation into the free energy E^e derived in this section.

III. EFFECTIVE POTENTIAL

The Drude oscillator model does not specify the polarizabilities used as input parameters determining the amplitudes of harmonic induced dipole fluctuations in the Drude Hamiltonians (8) and (9). The important virtue of the two-state model is that it provides the dispersion potential in terms of the solute transition dipoles. The comparison of the two models hence tells us what kind of polarizabilities should be substituted into the instantaneous diabatic energies E_i following from the Drude model.

Equations (36) and (37) obtained above for a two-state solute model are easily extendable to a more general solute basis ϕ_k , $k = 1, \dots, M$. The diabatic energies are then

$$E_i = I_i - \sum_j \mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot \mathbf{m}_j - (\alpha/2) \sum_{j,k,l} \mathbf{m}_0^{il} \cdot \mathbf{T}_{0j} \cdot (\mathbf{1} - \alpha \tilde{\mathbf{T}})_{jk}^{-1} \cdot \mathbf{T}_{k0} \cdot \mathbf{m}_0^i \quad (44)$$

and the matrix element V_{im} between the solute states i and m is renormalized to

$$\tilde{V}_{im} = \left[V_{im} - \sum_j \mathbf{m}_0^{im} \cdot \mathbf{T}_{0j} \cdot \mathbf{m}_j - (\alpha/2) \sum_{j,k,l} \mathbf{m}_0^{il} \cdot \mathbf{T}_{0j} \cdot (\mathbf{1} - \alpha \tilde{\mathbf{T}})_{jk}^{-1} \cdot \mathbf{T}_{k0} \cdot \mathbf{m}_0^m \right] \exp\left(-\frac{\mu_e(\mathbf{m}_{0i} - \mathbf{m}_{0m})^2}{2\hbar\omega_s}\right).$$

With account for the nonlocal dispersion effects considered in Sec. II A, the last term in Eq. (44) can be recast as follows:

$$u_{0 \rightarrow s,i}^{\text{ind}}(0j) + u_{0s,i}^{\text{disp}}(0j) = -\frac{\alpha^\infty g_K^\infty}{2} \left[(\hat{\mathbf{s}}_0 \cdot \mathbf{T}_{0j} \cdot \mathbf{T}_{j0} \cdot \hat{\mathbf{s}}_0) |m_{0i}|^2 + (\hat{\mathbf{p}} \cdot \mathbf{T}_{0j} \cdot \mathbf{T}_{j0} \cdot \hat{\mathbf{p}}) \sum_{l \neq i} |m_{0l}^{il}|^2 \right], \quad (45)$$

where α^∞ is given by Eq. (13) and the high-frequency Kirkwood factor g_K^∞ is defined in Eqs. (20) and (21) and in Appendix A. In Eq. (45) $\hat{\mathbf{s}}_0 = \mathbf{m}_{0i}/m_{0i}$ and $\hat{\mathbf{p}} = \mathbf{m}_0^{il}/m_0^{il}$ are unit vectors which in a general case do not coincide and $u_{0 \rightarrow s,i}^{\text{ind}}(0j)$ refers to the induction interaction between the solute permanent dipole and the induced dipole positioned at the j th solvent molecule. The dispersion potential in Eq. (45) is determined by the sum over the diabatic solute transition dipoles m_0^{il} .⁴⁰ For the vacuum solute polarizability built on \mathbf{m}_0^{il}

$$\alpha_{0i,\alpha\gamma} = 2 \sum_{l \neq i} \frac{m_{0,\alpha}^{il} m_{0,\gamma}^{li}}{I_l - I_i}, \quad (46)$$

we get for a two-state solute⁴¹

$$\alpha_{01,\alpha\gamma} = 2 \delta_{\alpha,p} \delta_{p,\gamma} |m_0^{12}|^2 / \Delta I, \\ \alpha_{02,\alpha\gamma} = -2 \delta_{\alpha,p} \delta_{p,\gamma} |m_0^{12}|^2 / \Delta I, \quad (47)$$

and

$$u_{0s,i}^{\text{disp}}(0j) = -\frac{|\alpha_{0i} \Delta I| \alpha^\infty g_K^\infty}{4} \frac{3(\hat{\mathbf{r}}_{0j} \cdot \hat{\mathbf{p}})^2 + 1}{r_{0j}^6},$$

where $\hat{\mathbf{r}}_{0j} = \mathbf{r}_{0j}/r_{0j}$. This coincides with the Drude model result (26) in the limit of $\omega_0/\omega_s \rightarrow 0$ and the anisotropic solute polarizability (47) with the only nonzero component along $\hat{\mathbf{p}}$. The fact that the diabatic energies (36) and (44) are of zeroth order in ω_0/ω_s is responsible for the distinction

between the two models when the difference of the solute-solvent dispersion couplings in the two states is considered. From Eq. (45) we see that $\Delta u_{0s}^{\text{disp}}(0j) = u_{0s,2}^{\text{disp}}(0j) - u_{0s,1}^{\text{disp}}(0j)$ is governed by the virtual electronic transitions to the levels other than the two ET states. In the two-state truncation of the solute basis the dispersion potential is hence state-independent. This contradicts however the quantum mechanical perturbation theory.³¹ The origin of the discrepancy becomes clear if we apply the two-state truncation to both the solute and the solvent in the quantum mechanical perturbation framework. For the isotropic solvent and anisotropic solute polarizabilities the difference of the dispersion potentials becomes

$$\Delta u_{0s}^{\text{disp}}(0j) = -\frac{g_K^\infty \alpha^\infty \omega_s}{2} (\hat{\mathbf{p}} \cdot \mathbf{T}_{0j} \cdot \mathbf{T}_{j0} \cdot \hat{\mathbf{p}}) \times |m_0^{12}|^2 \left(\frac{1}{\omega_s - \omega_0} - \frac{1}{\omega_s + \omega_0} \right). \quad (48)$$

This gives $\Delta u_{0s}^{\text{disp}}(0j)$ from Eq. (45) when $\omega_0/\omega_s \rightarrow 0$ is assumed, which is also the condition of employing the δ -function kernel (34). However, the difference (48) is of first order in ω_0/ω_s and for $\omega_s \gg \omega_0$ reads

$$\Delta u_{0s}^{\text{disp}}(0j) = -g_K^\infty \alpha^\infty \frac{\omega_0}{\omega_s} (\hat{\mathbf{p}} \cdot \mathbf{T}_{0j} \cdot \mathbf{T}_{j0} \cdot \hat{\mathbf{p}}) |m_0^{12}|^2. \quad (49)$$

The same result follows from the London dispersion potential with the two-state solute polarizability (47). We thus see that the dispersion interaction and the induction coupling of the solute permanent dipole to the solvent polarizability are essentially the same in the Drude oscillator and the two-state models when the Pekar limit (3) is in order. We can therefore improve the result of the two-state derivation by substituting the Drude oscillator result for the dispersion potential into the diabatic energies E_i entering the free energy E^e .

What seems still to be missing from the diabatic energies (44) is the induction potential coupling the solute induced dipole with the solvent permanent dipoles

$$U_{s \rightarrow 0,i}^{\text{ind}} = \sum_{jk} u_{s \rightarrow 0,i}^{\text{ind}}(0jk),$$

$$u_{s \rightarrow 0,i}^{\text{ind}}(0jk) = -\frac{1}{2} \mathbf{m}_j \cdot \mathbf{T}_{j0} \cdot \boldsymbol{\alpha}_{0i} \cdot \mathbf{T}_{0k} \cdot \mathbf{m}_k. \quad (50)$$

Except for the terms with equal indices $j=k$, this potential is a three-particle one. It causes a coupling of the solvent dipoles which depends on the solute state. We recently assessed the corresponding interaction energy based on experimental data on optical thermochromism.⁴² It should still be recalled that the outcome of integrating out the electronic degrees of freedom of the solute is the instantaneous energy E^e composed of the diabatic energies E_i (36) and the solvent-dependent ET matrix element \tilde{V}_{12} (43). The expansion of E^e over the small (in the far from resonance region) parameter $|\tilde{V}_{12}|/|\Delta E|$ gives

$$E^e = \frac{E_1 + E_2}{2} \mp \frac{\Delta E}{2} \mp \frac{(\tilde{V}_{12})^2}{\Delta E}, \quad (51)$$

where “−” and “+” correspond to the ground and excited energy surfaces. When we substitute \tilde{V}_{12} from Eq. (37) into the above relation and take the diabatic limit $V_{12} \rightarrow 0$, the last summand yields the analog of the induction potential (50). The switch of the sign of the last summand in Eq. (51) corresponds to the change in the sign of the solute polarizability of a two-state solute in Eq. (47). It implies that the two-state polarizability can indeed be substituted into the induction potential (50).

The derivation just performed enables us to draw two important conclusions (i) the Drude oscillator and two-state models are isomorphic in predicting diabatic free energies E_i when the solute polarizability (46) built from diabatic solute transition dipoles is used in the Drude model and (ii) the zero order Pekar approximation (3), mathematically expressed by Eq. (34), should be used with caution and at least the first order in ω_0/ω_s correction to the kernel (34) is needed to reproduce correctly the variation of the dispersion potential $\Delta u_{0s}^{\text{disp}}$. The Drude oscillator model has however its own limitations which we consider next.

The diabatic energies E_i are the partial free energies obtained from calculating the partition functions over only the fast electronic degrees of freedom of the solvent and the solute. In contrast to the Hamiltonians H_i , the thermodynamic character of the energies E_i is reflected by their dependence on temperature shown in Eq. (26). This appears due to the summation over the thermal excitations of the solute harmonic oscillator representing the solute induced dipole in the Drude oscillator model. The Drude oscillator reasonably represents a two-state solute only for high excitation energies $\beta \hbar \omega_0 \gg 1$ when only the ground and first excited states are effectively involved. For $\beta \hbar \omega_0 \approx 1$, the Drude model introduces a manifold of closely spaced vibronic levels absent in a two-state solute. Therefore, the appearance of the solute-solvent dispersion potential (27) proportional to temperature is an artifact of the Drude model when applied to a two-state DAC. This result however points to the fact that the dispersion potential acquires temperature dependence if one of the two interacting particles contains closely spaced (degenerate or nearly degenerate on the $k_B T$ energy scale) electronic levels. This situation may occur in complex molecular moieties composing the DAC.

We can now write down the effective diabatic potential of a two-state ET solute with a polar polarizable solvent

$$E_i = I_i + U^{\text{rep}} + U_s^{\text{disp}} + U_{0s,i}^{\text{dip}} + U_{0s,i}^{\text{disp}} + U_{0 \rightarrow s,i}^{\text{ind}} + U_{s \rightarrow 0,i}^{\text{ind}}. \quad (52)$$

The dipolar potential here is

$$U_{0s,i}^{\text{dip}} = \sum_j u_{0s,i}^{\text{dip}}(0j), \quad u_{0s,i}^{\text{dip}}(0j) = -\mathbf{m}_{0i} \cdot \mathbf{T}_{0j} \cdot \mathbf{m}_j. \quad (53)$$

The induction potentials for the isotropic solvent and anisotropic solute (47) polarizabilities read

$$U_{0 \rightarrow s,i}^{\text{ind}} = \sum_j u_{0 \rightarrow s,i}^{\text{ind}}(j),$$

$$u_{0 \rightarrow s,i}^{\text{ind}}(0j) = -\frac{\alpha^\infty m_{0i}^2}{2} \frac{3(\hat{\mathbf{s}}_0 \cdot \hat{\mathbf{r}}_{0j})^2 + 1}{r_{0j}^6}, \quad (54)$$

$$U_{s \rightarrow 0, i}^{\text{ind}} = \sum_{jk} u_{s \rightarrow 0, i}^{\text{ind}}(0jk),$$

$$u_{s \rightarrow 0, i}^{\text{ind}}(0jk) = -\frac{\alpha_{0i} m^2 D(0j) D(k0)}{2 r_{0j}^3 r_{k0}^3}, \quad (55)$$

where $D(0j) = 3(\hat{\mathbf{p}} \cdot \hat{\mathbf{r}}_{0j})(\hat{\mathbf{r}}_{0j} \cdot \hat{\mathbf{s}}_j) - \hat{\mathbf{p}} \cdot \hat{\mathbf{s}}_j$ and $\hat{\mathbf{s}}_j = \mathbf{m}_j/m$. The solute polarizabilities in (55) are given by the two-state expression (47). The dispersion potential in Eq. (52) reads in the Drude oscillator model

$$U_{0s, i}^{\text{disp}} = \sum_j u_{0s, i}^{\text{disp}}(0j),$$

$$u_{0s, i}^{\text{disp}}(0j) = -\frac{\alpha_{0i} g_K^\infty \alpha^\infty}{4} \frac{\hbar \omega_0 \omega_s}{\omega_0 + \omega_s} \frac{3(\hat{\mathbf{p}} \cdot \hat{\mathbf{r}}_{0j})^2 + 1}{r_{0j}^6}. \quad (56)$$

With the two-state polarizability in Eq. (56), Eq. (49) predicts the dispersion potential to vary very weakly with optical excitation amounting to only $2\Delta I/(\hbar \omega_s) \ll 1$ fraction of its ground state value. This contradicts some spectroscopic experiments yielding noticeable changes in the dispersion solute-solvent coupling.⁴² The discrepancy is due to the use of the two-state model. Especially for the excited state, other solute electronic levels should be included for a correct evaluation of dispersion forces. A system composed of at least three electronic levels may be considered for qualitative treatment of excited state polarizabilities. We will use the three-state model for treating the effect of dispersion forces on the energy gap dependence of ET rates in a future publication.²⁷

IV. DISCUSSION

The goal of the present paper was to derive instantaneous free energies of electronic states localized at the DAC. Equation (52) provides us with the diabatic free energies depending on the nuclear configuration of the solvent. Moments of the diabatic energy gap $E_2 - E_1$ calculated in a molecular framework give us ET activation parameters. Work on this is under way.²⁷ The derivation using the two-state model results also in the BO free energy E^e (42) composed of the diabatic energies E_i and the ET matrix element \tilde{V}_{12} (41), (43), renormalized from its vacuum value V_{12} by the instantaneous field of the nuclear solvent degrees of freedom and by equilibrium solvation of the solvent bound electrons. The effective ET matrix element \tilde{V}_{12} is related to the intensity of absorption transitions⁴³ and to radiative rate constants for emission.⁴⁴ We discuss below the relation of our free energies E^e to other approximations known in the literature and then finish with the spectroscopic consequences of the solvent dependence of the ET matrix element.

A. Instantaneous free energies

The instantaneous free energy E^e in Sec. II B has been obtained by eliminating the solute and solvent electronic degrees of freedom in the system density matrix according to Eq. (2). Therefore, no nuclear averaging has yet been performed and the instantaneous free energy E^e depends on the solute and solvent nuclear configuration. The free energy E^e

can further be employed to obtain a nonequilibrium functional of a collective solvent coordinate that can be used in applications related to reaction dynamics, ET, and optical spectroscopy in condensed phases. For instance, starting from the Marcus theory,¹⁴ the inertial solvent polarization $\mathbf{P}(\mathbf{r})$ is considered as the main collective solvent coordinate determining the solvent effect on ET and optical spectra in liquids. The nonequilibrium free energy functional $F[\mathbf{P}(\mathbf{r})]$ giving the free energy cost of creating a nonequilibrium polarization $\mathbf{P}(\mathbf{r})$ in the solvent can be obtained from E^e as a restricted trace over the solvent nuclear coordinates

$$\exp(-\beta F[\mathbf{P}(\mathbf{r})]) = \text{Tr}_{cl} \left(\delta \left[\mathbf{P}(\mathbf{r}) - \sum_j \mathbf{m}_j \delta(\mathbf{r} - \mathbf{r}_j) \right] \exp[-\beta E^e] \right). \quad (57)$$

The analogous functional used by Kim and Hynes¹⁶ follows from Eq. (57) when E^e is replaced with $E' = \langle \phi_0 | H | \phi_0 \rangle$ [see discussion of Eq. (4) in the Introduction].

The free energy E^e in Eq. (42) has been derived under the only assumption $\beta \hbar \omega_s \gg 1$ and is valid for any ratio ω_0/ω_s (with the dispersion potential taken from the Drude model). It does not therefore rely on the adiabatic Pekar condition (3). Equation (42) reduces to the free energy of the spin-boson Hamiltonian in the Pekar adiabatic limit $\omega_0/\omega_s \rightarrow 0$.² The only effect of removing the adiabatic time separation condition is thus the renormalization of the ET matrix element [Eq. (43)]. A similar conclusion has in fact been drawn by Song and Stuchebrukhov⁹ in connection with the calculation of the ET rate constant. Previous calculations of the solvation free energy of a two-state system^{6b,c,7a,b,8,22b} have been chiefly performed in terms of the spin-boson Hamiltonian. In order to provide a comparison to the results reported in the literature we thus need to transform our description in terms of the creation and annihilation operators to that in the spin variables. We first introduce some simplifications decreasing the number of system parameters. In the spin-boson model the fluctuations of the off-diagonal matrix element are commonly neglected.^{6,8,22b} In our model, it implies that we need to assume the diabatic transition moment \mathbf{m}_0^{12} equal to zero. Further, we replace the dipole-dipole molecular interactions between the solute dipole and solvent induced dipoles by the reaction field (38) directed along the solute dipole moment.¹⁰ In order to have only one solute-solvent coupling constant, we set $m_{01} = 0$ and $m_{02} = \Delta m_0$. Finally, since we are interested in this section only in electronic solvation, we put the solvent permanent dipoles equal to zero. As a result, the solute Hamiltonian can be rewritten in terms of spin and boson operators as follows:

$$h = (H_0^e + H_{0s}) / (\hbar \omega_s)$$

$$= C + \frac{1}{2} - \frac{S_e}{4} + b^+ b + v \sigma_x - \Delta f \frac{\sigma_z}{2} + \sqrt{S_e} \frac{\sigma_z}{2} (b^+ + b), \quad (58)$$

where b^+ and b are the creation and annihilation operators of the medium phonon, σ_x and σ_z are the Pauli matrices (eigenvalues ± 1). Equation (58) is constructed to include

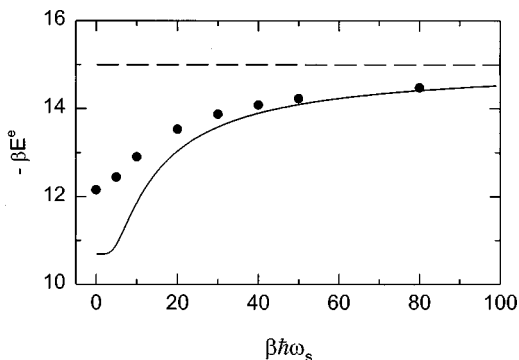


FIG. 1. Dependence of the free energy of an unbiased two-state system ($\Delta f=0$) on the bath frequency. The points are results of calculations by Jongeward and Wolynes (Ref. 6c). The solid line corresponds to Eq. (59) and the dashes represent the adiabatic Pekar approximation. The system parameters are: $\beta\lambda_e=20$ and $\beta|V_{12}|=5$.

only unitless values $v=V_{12}/\hbar\omega_s$, $\Delta f=\Delta I/\hbar\omega_s-S_e$, and $C=(I_1+I_2)/\hbar\omega_s$. Further, we define the zero of energy that corresponds to setting $C=0$. The parameter S_e is the ratio of the solvation energy of the differential solute dipole by the solvent electronic polarization $\lambda_e=\mu_e\Delta m_0^2$ to the energy of bath excitations, $S_e=\lambda_e/\hbar\omega_s$, [Eq. (43)]. Now, after determining the condition of isomorphism between our description and the spin-boson model, we can compare Eq. (42) to exact numerical results obtained in the framework of that model. Jongeward and Wolynes^{6c} reported renormalized group calculations of the free energy of an unbiased spin-boson model with $\Delta f=0$ for different phonon frequencies ω_s . For $\Delta f=0$ and $C=0$ Eq. (42) becomes

$$E^e = -\frac{\lambda_e}{2} - \beta^{-1} \ln[2 \cosh(\beta\tilde{V}_{12})]. \quad (59)$$

In Fig. 1 we compare the results of Jongeward and Wolynes to Eq. (59). As expected, the prediction (59) deviates from the exact free energy with decreasing $\beta\hbar\omega_s$, but is very close to it for high quantum frequencies. For small $\beta\hbar\omega_s$, the variational procedure in terms of the effective ET matrix element and S_e considered as independent variational variables^{22b} provides more flexibility and outperforms Eq. (59). The adiabatic Pekar limit $\tilde{V}_{12}\rightarrow V_{12}$ is also shown in Fig. 1 and we see that the renormalization of the ET matrix element may give a noticeable contribution to the free energy. In fact, for usual ET conditions, we have $\beta\hbar\omega_s \approx 200-400$ and Eq. (59) is expected to be very accurate. Despite being less exact than other approaches,^{6c,22b} it has an essential advantage of simplicity and its accuracy is sufficient to describe solvation by the bound solvent electrons.

As noted above, the free energy (42) is valid for an arbitrary ratio of the solute and solvent electronic frequencies ω_0/ω_s . In order to compare our result to the theory of Kim and Hynes,^{16d} we consider the ground state energy. It corresponds to the limit $\beta\rightarrow\infty$ in Eq. (42)

$$e_g = \lim_{\beta\rightarrow\infty} (E^e/\hbar\omega_s) = -S_e/2 - \sqrt{\Delta f^2/4 + |v|^2} \exp(-S_e). \quad (60)$$

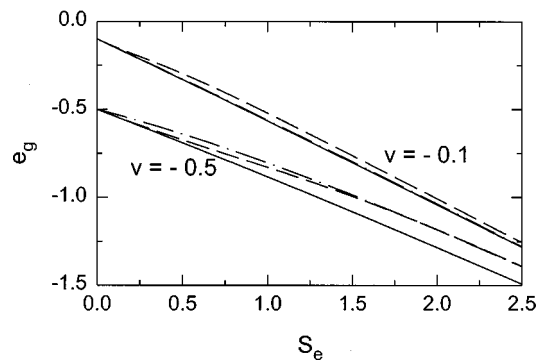


FIG. 2. Ground state energy of an unbiased ($\Delta f=0$) two-state system vs the reduced solvation energy $S_e=\lambda_e/\hbar\omega_s$. The full lines are the exact results calculated from the numerical diagonalization according to Allen and Silbey (Ref. 20). The dashed lines refer to the Kim and Hynes theory (Ref. 16d [Eq. (61)]). The dash-dotted lines correspond to the present formulation given by Eq. (60). The calculations were performed for two values of the reduced vacuum ET matrix element $v=V_{12}/\hbar\omega_s$. For $v=-0.1$ Eq. (60) is undistinguishable from the exact result.

For large energy gaps $|\Delta f/2| \gg |v|$ the adiabatic energy e_g transforms into the diabatic energy that is the same in all theories for the same physical models. A crucial test of the validity of a particular approximation for e_g can thus be achieved in the region $|\Delta f/2| \leq |v|$. We therefore will calculate the ground state energy at different solvation energies λ_e at the point of zero diabatic energy gap $\Delta f=\Delta I/\hbar\omega_s-S_e=0$. In this way we are also capable to test the theory in the broad range of electronic adiabaticity parameters $\Delta I/\hbar\omega_s \approx \omega_0/\omega_s$, since at $\Delta f=0$ we get $\omega_0/\omega_s=S_e=\lambda_e/\hbar\omega_s$. We will compare Eq. (60) to the results of numerical diagonalization of the spin-boson Hamiltonian (58) in the basis of 50 wavefunctions used by Allen and Silbey.²⁰ The reduced ground state energies are plotted in Fig. 2 vs S_e for two values of the reduced ET matrix element v . Kim and Hynes proposed an approximate solution for the ground state energy devised to apply to all values of the electronic adiabaticity parameter and we also included their results in Fig. 2. In our notation the Kim and Hynes ground state energy reads ($\mathbf{P}_{\text{or}}=0$, $\mathcal{E}_{\text{ex}}=0$, $\mathcal{E}_{\text{av}}=-\mathcal{E}_{\Delta}$ in their notation^{16d} for the simplified system considered in this section)

$$e_g = -\frac{S_e}{2} - x \frac{\Delta f}{2} + yv - \frac{S_e}{2} \frac{vy^2}{y-2v}, \quad (61)$$

where x and y are variational parameters determined by the equation

$$-S_e \frac{2xyv(y/2-2v)}{(y-2v)^2} + 2vx + \Delta fy = 0 \quad (62)$$

with the normalization condition $x^2+y^2=1$.

As is seen in Fig. 2, both Eqs. (60) and (61) work well for small $v=-0.1$, with Eq. (60) being more accurate. For larger $|v|$ both predictions deviate upward from the exact

result at $S_e \gg 1$ and this difference remains constant as S_e increases. For usual ET conditions $\hbar \omega_s$ is in the range 5–10 eV and $S_e \ll 1$. Also even for strongly coupled systems $|v|$ is hardly likely to exceed 0.5. Therefore, we can expect that both Eqs. (60) and (61) provide a comparable accuracy for the ground state energy. Equation (60) has, however, the obvious advantage of analytical simplicity compared to Eqs. (61) and (62).⁴⁵ Also the ground state energy is a specific limit of the more general relation for the free energy (42) that is absent from the Kim and Hynes formulation.^{16d}

B. Effective ET matrix element

Since the seminal work of Mulliken,^{43a} intensities of optical transitions and radiative rate constants are treated in terms of the adiabatic transition dipole moment $\mathbf{M}_0^{12} = \langle \Psi_1 | \hat{\mathbf{m}}_0 | \Psi_2 \rangle$ built on the adiabatic two-state basis Ψ_1, Ψ_2 diagonalizing the two-state Hamiltonian H_0^e in Eq. (28). The vacuum transition dipole \mathbf{M}_0^{12} is given by the vector sum^{43,46}

$$\mathbf{M}_0^{12} = \mathbf{m}_0^{12} \frac{\Delta I}{\Delta J} - \Delta \mathbf{m}_0 \frac{V_{12}}{\Delta J}, \quad (63)$$

where $\Delta J = \sqrt{\Delta I^2 + 4V_{12}^2}$ and the diabatic transition moment \mathbf{m}_0^{12} is defined in Sec. II B. The adiabatic transition dipole in condensed phases can be derived in the same way that we used in calculating the renormalized ET matrix element in Eq. (43). The transformation of the solvent basis to that of coherent states result in the condensed phase adiabatic transition dipole

$$\mathbf{M}^{12} = \left[\mathbf{m}_0^{12} \frac{\Delta E}{\Delta \bar{E}} - \Delta \mathbf{m}_0 \frac{V_{12}^{\text{eff}}}{\Delta \bar{E}} \right] \exp(-\frac{1}{2} S_e). \quad (64)$$

Equation (64) gives the instantaneous value of the transition dipole depending on the nuclear configuration. Its average over the solvent nuclear configurations can be written as⁴⁷

$$\langle \mathbf{M}^{12} \rangle_i = \left[\mathbf{m}_0^{12} - \Delta \mathbf{m}_0 \frac{\langle V_{12}^{\text{eff}} \rangle_i}{\hbar c \bar{v}_i} \right] \exp(-\frac{1}{2} S_e), \quad (65)$$

where we assumed $\Delta \bar{E} \approx \Delta E$ and $\hbar c \bar{v}_i$ refers to the vertical optical transition (\bar{v} is the wavenumber in cm^{-1}) corresponding to absorption ($i=1$) and fluorescence ($i=2$). The equilibrium value of the ET matrix element $\langle V_{12}^{\text{eff}} \rangle_i$ is found by replacing the fictitious dipole $\mathbf{m}_0^{\text{fic}}$ in Eq. (41) by \mathbf{m}_0

$$\langle V_{12}^{\text{eff}} \rangle_i = V_{12} + \frac{(\mathbf{m}_0^{12} \cdot \hat{\mathbf{s}}_0)}{\Delta m_0} \hbar c \Delta \bar{v}_i^p, \quad (66)$$

where

$$\hbar c \Delta \bar{v}_i^p = -2\mu_p (\Delta \mathbf{m}_0 \cdot \mathbf{m}_{0i}) \mp \mu_e (m_{02}^2 - m_{01}^2) \quad (67)$$

is the spectral shift due to differential solvation by dipolar forces and equilibrium solvation by induction forces, with “−” and “+” corresponding to $i=1$ and $i=2$, respectively. $\hbar c \Delta \bar{v}_i^p$ is a component of the total transition energy^{12c,42}

$$\bar{v}_i = \bar{v}_0 + \Delta \bar{v}_i^p + \Delta \bar{v}_i^{\text{disp}}, \quad (68)$$

where $\bar{v}_0 = \Delta I / (\hbar c)$ and $\hbar c \Delta \bar{v}_i^{\text{disp}}$ is the shift due to differential solvation by dispersion forces.

The exponential renormalization factor in Eq. (65) does not deviate noticeably from unity for the usual energy scale $\hbar \omega_s \approx 5 - 10$ eV and can be neglected. The solvent dependence of the equilibrium ET matrix element is hence determined by the magnitude and orientation of \mathbf{m}_0^{12} and the dipolar (permanent+induced dipoles) shift of the spectral line. In polar liquids, the latter is dominated by the component μ_p of solvation by the solvent permanent dipoles. This implies, for instance, that for absorption transitions with $m_{01} \ll m_{02}$ the ET matrix element will be nearly independent of solvent polarity. The dependence of $\langle V_{12}^{\text{eff}} \rangle_i$ on the solvent should be more pronounced for fluorescence transitions.

The orientation of the diabatic transition dipole \mathbf{m}_0^{12} is not specified in the two-state model and should be taken from quantum mechanics or experiment.⁴⁸ The magnitude of the transition dipole $\langle M^{12} \rangle_i$ depends hence on the projections of \mathbf{m}_0^{12} on the solute dipole direction $\hat{\mathbf{s}}_0$ and that perpendicular to it ($\hat{\mathbf{x}}$) in the plane formed by \mathbf{s}_0 and \mathbf{m}_0^{12} . From Eqs. (64), (66), and (68) we get

$$[\langle M^{12} \rangle_i \bar{v}_i]^2 = (\mathbf{m}_0^{12} \cdot \hat{\mathbf{x}})^2 \bar{v}_i^2 + C_i, \quad (69)$$

where

$$C_i = [(\mathbf{m}_0^{12} \cdot \hat{\mathbf{s}}_0)(\nu_0 + \Delta \nu_i^{\text{disp}}) - \Delta m_0 (V_{12} / \hbar c)]^2. \quad (70)$$

Experimental verification of Eq. (69) is difficult because of the unknown coefficients C_i and the x -projection of the diabatic transition dipole \mathbf{m}_0^{12} . The problem can, however, be circumvented by the observation that the component of the solvent reorganization energy due to dispersions is much smaller than that due to dipolar forces for the majority of optical dyes.⁴² This means that

$$\Delta \bar{v}_1^{\text{disp}} \approx \Delta \bar{v}_2^{\text{disp}} = \Delta \bar{v}^{\text{disp}}$$

and the summand C_i disappears in the difference of $[\langle M^{12} \rangle_i \bar{v}_i]^2$ for absorption and fluorescence transitions. When the solvent-induced shift is small compared to the vacuum transition energy, we get a connection of the transition dipoles to the Stokes shift $\Delta \bar{v}_{\text{st}}$

$$[\langle M^{12} \rangle_1 \bar{v}_2]^2 - [\langle M^{12} \rangle_2 \bar{v}_1]^2 = 2(\mathbf{m}_0^{12} \cdot \hat{\mathbf{x}})^2 \bar{v}_0 \bar{v}_{\text{st}}. \quad (71)$$

When experimental data for both absorption and emission transition dipoles are available, Eq. (71) enables one to extract the component $(\mathbf{m}_0^{12} \cdot \hat{\mathbf{x}})$.

The dependence of $\langle \bar{V}_{12} \rangle_i$ on the dipolar spectral shift $\hbar c \Delta \bar{v}_i^p$ in Eq. (66) offers a possibility of the interesting phenomenon of self-localization of the transferred electron. Indeed, $\langle \bar{V}_{12} \rangle_i$ becomes equal to zero when

$$\frac{(\mathbf{m}_0^{12} \cdot \hat{\mathbf{s}}_0)}{\Delta m_0 V_{12}} \hbar c \Delta \bar{v}_i^p = -1. \quad (72)$$

Physically it means that the electron is essentially localized at the donor or acceptor site. The condition (72) may be realized by either changing the dipolar shift $\Delta \bar{v}_i^p$ or by vary-

ing the orientation^{48b} of the diabatic transition dipole \mathbf{m}_0^{12} relative to $\Delta\mathbf{m}_0$. Note that the vacuum off-diagonal matrix elements \mathbf{m}_0^{12} and V_{12} come into the relation (72) as a ratio. This form reflects the requirement of invariance with respect to a phase shift of the wavefunction $\phi_i \rightarrow \exp(i\chi)\phi_i$ which cancels out in the ratio. Depending on the electronic structure of the DAC, the factor $(\mathbf{m}_0^{12} \cdot \hat{\mathbf{s}}_0)/V_{12}$ may become positive or negative (e.g., the ET matrix element can switch its sign with the changing the bridge moiety⁴⁹). This sign will essentially determine the possibility of realizing the self-localization condition (72).

Equation (72) gives the condition of passing through zero of the equilibrium ET matrix element. Due to specifics of the averaging of both the preexponential and Boltzmann components in the Franck-Condon factor, the rate constant of nonadiabatic ET becomes zero at another point given by

$$\frac{(\mathbf{m}_0^{12} \cdot \hat{\mathbf{s}}_0)}{\Delta m_0 V_{12}} hc(\bar{\nu}_0 + \Delta \bar{\nu}_i^{\text{disp}}) = 1$$

and $(\mathbf{m}_0^{12} \cdot \hat{\mathbf{x}}) = 0$, as we show in a separate paper.⁵⁰ The passing of the equilibrium ET matrix element through zero value physically differs from self-localization found in spin-boson systems with ohmic dissipation.^{6a,22a} In that case the disappearance of tunneling happens due to the exponential renormalization factor in Eq. (43). The assumption of the ohmic dissipation leads to an infrared divergence and the equilibrium matrix element disappears with lowering temperature.

ACKNOWLEDGMENT

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APPENDIX A: NONPAIRWISE EFFECTS IN THE DISPERSION POTENTIAL

We consider here the integral

$$u_n = \text{Tr} \left[\alpha_{0i}^{(n)} \cdot \mathbf{T}_{0j} \cdot \int \hat{\mathbf{A}}_n(j_2) \cdot \mathbf{T}_{20} d^2 \right] \quad (\text{A1})$$

appearing as the first expansion term of the logarithm in Eq. (20). From Eq. (18) the dispersion term involving the nonlocal correlation effects is given by the sum of the rotational invariant components

$$u_n = u_n^I + u_n^{\Delta} + u_n^D, \quad (\text{A2})$$

where

$$u_n^I = \alpha_j^{(n)\infty} : (\mathbf{T}_{j0} \cdot \alpha_{0i}^{(n)} \cdot \mathbf{T}_{0j}), \quad (\text{A3})$$

$$u_n^D = \rho \int d^2 h_n^D(r_{j2}) (\mathbf{T}_{j0} \cdot \alpha_{0i}^{(n)} \cdot \mathbf{T}_{02}) : (\alpha_j^{(n)\infty} \cdot \mathbf{D}_{j2} \cdot \alpha_2^{(n)\infty}), \quad (\text{A4})$$

$$u_n^{\Delta} = \rho \int d^2 h_n^{\Delta}(r_{j2}) (\mathbf{T}_{j0} \cdot \alpha_{0i}^{(n)} \cdot \mathbf{T}_{02}) : (\alpha_j^{(n)\infty} \cdot \alpha_2^{(n)\infty}), \quad (\text{A5})$$

where the tensor \mathbf{D}_{ij} is given by Eq. (19). Below for simplicity we use the isotropic form of the solute and solvent polarizabilities

$$\alpha_{0i,\alpha\beta}^{(n)} = \alpha_{0i}^{(n)} \delta_{\alpha\beta}, \quad \alpha_{\alpha\beta}^{(n)\infty} = \alpha^{(n)\infty} \delta_{\alpha\beta}. \quad (\text{A6})$$

Then the integral including h^D can be rewritten using the representation

$$\mathbf{T}_{0j} \cdot \mathbf{T}_{j0} = 3 \int \mathbf{T}_{0j} \cdot \hat{\mathbf{s}} \cdot \mathbf{T}_{j0} (d\omega_s/4\pi), \quad (\text{A7})$$

where here and in Appendix B carets signify unit vectors. We find

$$u_n^D = \frac{27 \alpha_{0i}^{(n)} (\alpha^{(n)\infty})^2}{(4\pi)^3} \int_0^\infty h_n^D(r_{j2}) r_{j2}^5 dr_{j2} \int d\omega_{j2} \times \int d\omega_1 d\omega_2 d\omega_3 \hat{\mathbf{s}}_1 \cdot \mathbf{T}(j_2) \cdot \hat{\mathbf{s}}_2 \hat{\mathbf{s}}_2 \cdot \mathbf{T}(20) \cdot \hat{\mathbf{s}}_3 \hat{\mathbf{s}}_3 \cdot \mathbf{T}(0j) \cdot \hat{\mathbf{s}}_1. \quad (\text{A8})$$

The angular integral over the orientations of the unit vectors $\hat{\mathbf{s}}_1$, $\hat{\mathbf{s}}_2$, and $\hat{\mathbf{s}}_3$ generates⁵¹ the Axilrod-Teller potential

$$\frac{1}{9r_{j2}^3 r_{20}^3 r_{0j}^3} (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3),$$

where θ_1 , θ_2 , and θ_3 are the angles of the triangle formed by the particles labeled 0, 2, and j . It is easy to show that

$$\int \frac{d\omega_{j2}}{r_{02}^3} (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3) = 0$$

and the D-projection has no contribution to the integral (A1).

A similar procedure applied to the Δ -projection gives a nonzero term

$$u_n^{\Delta} = \frac{3\rho \alpha_{0i}^{(n)} (\alpha^{(n)\infty})^2}{r_{0j}^3} \int_0^\infty h_n^{\Delta}(r_{j2}) r_{j2}^2 dr_{j2} \times \int \frac{d\omega_{j2}}{r_{02}^3} [3(\hat{\mathbf{r}}_{0j} \cdot \hat{\mathbf{r}}_{02})^2 - 1]. \quad (\text{A9})$$

The integral over ω_{j2} in Eq. (A9) diverges when $r_{j2} \rightarrow r_{0j}$. This is due to the fact that we have not included the repulsion between the solute and the probe particle, which is correct only for large separations $r_{0j} \gg r_{j2}$. Taking into account that $h_n^{\Delta}(r)$ is a short range function,⁵² we can expand (A9) in r_{j2}/r_{0j} truncating the expansion at zeroth order. This gives

$$u_n^{\Delta} = \frac{6\rho (\alpha^{(n)\infty})^2 \alpha_{0i}^{(n)}}{r_{0j}^6} \tilde{h}_n^{\Delta}(0),$$

where $\tilde{h}_n^{\Delta}(0)$ is the $k=0$ value of the Fourier transform of $h_n^{\Delta}(r)$. Ultimately, the n -amplitude u_n of the solute-solvent dispersion potential takes the form

$$u_n = \frac{6\alpha^{(n)\infty} \alpha_{0i}^{(n)}}{r_{0j}^6} (1 + \alpha^{(n)\infty} \rho \tilde{h}_n^{\Delta}(0)). \quad (\text{A10})$$

For the classical $n=0$ value of u_n the connection of the diagram expansion with classical electrostatics shows³³ that the term in brackets in Eq. (A10) is the Kirkwood factor of the nonpolar solvent polarization

$$g_K^\infty = 1 + \alpha^\infty \rho \tilde{h}^\Delta(0),$$

where g_K^∞ is connected with the high-frequency dielectric constant ϵ_∞ by the relation

$$(4\pi/3)\rho\alpha^\infty g_K^\infty = \frac{(\epsilon_\infty - 1)(2\epsilon_\infty + 1)}{9\epsilon_\infty}.$$

The generalization to $n \neq 0$ is straightforward in terms of the inverse compressibility factors q_n^+ and q_n^- of the longitudinal and transverse dipolar responses usually encountered in the theory of dipolar fluids.⁵² We can define the the Kirkwood factor $g_{K,n}^\infty$ ⁵³ corresponding to the polarizability $\alpha^{(n)\infty}$

$$g_{K,n}^\infty = 1 + \alpha^{(n)\infty} \rho \tilde{h}_n^\Delta(0) = \frac{1}{3q_n^+} + \frac{2}{3q_n^-}, \quad (A11)$$

with q_n^+ and q_n^- related to the solvent polarizability by

$$4\pi\rho\alpha^{(n)\infty} = q_n^+ - q_n^-. \quad (A12)$$

The problem can easily be closed in the mean spherical approximation suggesting that the molecular coordinate averaging of the graphs \mathcal{A}_n can be performed over a step function (low density limit) replacing the real coordinate distribution function of the liquid.³³ This neglects the effect of solvent spatial correlations on the angular distribution function, but results in the simple relation⁵⁴ for q_n^+ and q_n^-

$$q_n^+ = (1 + 4\xi_n)^2 / (1 - 2\xi_n)^4, \quad q_n^- = (1 - 2\xi_n)^2 / (1 + \xi_n)^4. \quad (A13)$$

Equations (A11)–(A13) complete the definition of the Kirkwood factor $g_{K,n}^\infty$ in Eq. (A11).

APPENDIX B: HIGHER ORDER TERMS IN THE SOLUTE-SOLVENT DISPERSION POTENTIAL

We want to compute the whole series of many-body solute-solvent dispersion interactions in Eq. (21). Expanding the logarithm in Eq. (21) we get

$$U_{0s,i}^{\text{disp}} = -\frac{1}{2\beta} \sum_{k=1}^{\infty} \sum_{nj} \frac{1}{k} \text{Tr}[g_{K,n}^\infty \alpha_j^{(n)\infty} \cdot \mathbf{T}_{j0} \cdot \alpha_{0i}^{(n)} \cdot \mathbf{T}_{0j}]^k.$$

For simplicity we assume here the isotropic form (A6) of the polarizability tensors. This decouples the calculation of the sum over the quantum frequencies ω_n and the trace over the Cartesian components of the dipole tensors

$$U_{0s,i}^{\text{disp}} = -\frac{1}{2\beta} \sum_{k=1,n}^{\infty} \frac{[\alpha_{0i}^{(n)} g_{K,n}^\infty \alpha^{(n)\infty}]^k}{k} \sum_j \text{Tr}[\mathbf{T}_{j0} \cdot \mathbf{T}_{0j}]^k. \quad (B1)$$

In order to calculate $\text{Tr}[\mathbf{T}_{j0} \cdot \mathbf{T}_{0j}]^k$ we apply the identity (A7). Accordingly, the trace term in Eq. (B1) can be given by the convolution

$$\text{Tr}[\mathbf{T}_{j0} \cdot \mathbf{T}_{0j}]^k = \frac{3^k}{(r_{0j})^{6k}} D(1,2) * D(2,3) * \dots * D(2k,1), \quad (B2)$$

where $D(1,2) = 3(\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{r}}_{0j})(\hat{\mathbf{r}}_{0j} \cdot \hat{\mathbf{s}}_2) - \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2$, $\hat{\mathbf{r}}_{0j} = \mathbf{r}_{0j}/r_{0j}$, and $D(12) * D(23)$ denotes the angular integral $\int (d\omega_2/4\pi) D(12) D(23)$. The loop convolution in Eq. (B2) is easy to calculate⁵⁴

$$3^k [D(1,2) * D(2,3) * \dots * D(2k,1)] = 2^{2k} + 2.$$

We thus get

$$U_{0s,i}^{\text{disp}} = -\frac{1}{\beta} \sum_{k=1,n}^{\infty} \frac{[\alpha_{0i}^{(n)} g_{K,n}^\infty \alpha^{(n)\infty}]^k}{k} \frac{2^{2k-1} + 1}{r_{0j}^{6k}}. \quad (B3)$$

The sum over n in (B3) can be computed by assuming $g_{K,n}^\infty = g_K^\infty$ and noting that

$$\begin{aligned} & \sum_n [\alpha_{0i}^{(n)} \alpha^{(n)\infty}]^k \\ &= (\omega_0 \omega_s)^{2k} \frac{\partial^{k-1}}{\partial (\omega_0^2)^{k-1}} \frac{\partial^{k-1}}{\partial (\omega_s^2)^{k-1}} \\ & \times \sum_n \frac{\alpha_{0i} \alpha^\infty}{(\omega_0^2 + \omega_n^2)(\omega_s^2 + \omega_n^2)}. \end{aligned} \quad (B4)$$

From Eqs. (B3) and (B4), we get ultimately

$$\begin{aligned} U_{0s,i}^{\text{disp}} &= -\frac{\hbar}{2} \sum_{j,k=1}^{\infty} \frac{2^{2k-1} + 1}{k} \left[\frac{\omega_0^2 \omega_s^2 \alpha_{0i} g_K^\infty \alpha^\infty}{r_{0j}^6} \right]^k \\ & \times \frac{\partial^{k-1}}{\partial (\omega_0^2)^{k-1}} \frac{\partial^{k-1}}{\partial (\omega_s^2)^{k-1}} \left[\frac{\omega_s \coth(\beta \hbar \omega_0/2) - \omega_0}{\omega_0 \omega_s (\omega_s^2 - \omega_0^2)} \right]. \end{aligned} \quad (B5)$$

In the quantum limit (24) the ratio of the second and the first summands in the series (B5) is equal to $3\alpha_{0i} g_K^\infty \alpha^\infty / (4r_{0j}^6)$. Since it is much less than unity for usual polarizabilities and contact molecular separations (see the discussion in the main text), the expansion (B5) is rapidly converging.

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