Charge Transfer, Symmetry, and Dissipation in Donor-Acceptor Molecules

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We study charge transfer between donor-acceptor molecules subject to a mirror symmetry constraint in the presence of a dissipative environment. The symmetry requirement leads to the breakdown of the standard single reaction coordinate description, and to a new charge transfer model, in the limit of low temperature, based on two independent reaction coordinates of equal relevance. We discuss implications of these results to charge transfer between DNA base pairs, whose geometrical configuration is modified by the addition of the migrating charge in conformity with the discussed symmetry constraint.

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Charge transfer between large organic molecules in aqueous solvent plays a key role in biochemical reactions, particularly those involving animal and plant metabolism [1,2]. Compared to electronic transport in solid state materials, electron transfer in and between proteins is characterized by low values of the tunneling matrix elements and strong coupling between the electronic and nuclear degrees of freedom [3]. As a result, charge transfer mainly occurs when the nuclear coordinates happen to adopt a value for which the donor (D) and the acceptor (A) state energies are nearly degenerate.

In the conventional Born-Oppenheimer, or adiabatic, description, such a degeneracy region transforms to a saddle point in the energy landscape separating the D and A states, while the transfer rate can be computed from the classical Kramers theory for activated chemical reactions in a dissipative medium [4–6]. However, because of the low value of the tunnel frequency Δ_0 for biomolecular charge transfer, the adiabatic assumption is often not valid and, as a result, a full quantum-mechanical description is required to determine the charge transfer rate. The interaction of the nuclear degrees of freedom with the solvent medium plays an important role in this respect. On the one hand, coupling to a finite-temperature heat bath allows the system access to the degeneracy points by thermal activation. On the other hand, friction between the nuclear degrees of freedom and the dissipative solvent — according to the fluctuation-dissipation theorem — increases the time spent by the nuclear degrees of freedom in the degeneracy region [7,8].

The analytical theory of D-A charge transfer between biomolecules is based on the assumption that, among the many nuclear degrees of freedom involved, there is always a *single* dominant one: the reaction coordinate Y. This reaction coordinate leads across the lowest saddle point in the adiabatic energy landscape separating the D and A states. Charge transfer takes place when Y is within the Landau-Zener distance $l_{\mathrm{LZ}} \propto \hbar\Delta_0/\Delta F$ [9,10] of the degeneracy point, with ΔF the typical force level on the nuclear degrees of freedom at the degeneracy point [11]. Crossover to the adiabatic regime occurs when the time spent in the Landau-Zener region τ_{LZ} is large compared to the typical tunneling time Δ_0^{-1}. Single reaction coordinate D-A theory is a basic tool not only for describing donor-acceptor charge transfer processes but also for describing chemical reactions involving macromolecules in general.

Charge transfer to or from large organic molecules can involve the Jahn-Teller effect [12]. By removing one of the electrons from a degenerate highest occupied molecular orbital (HOMO), the electronic energy of the system is lowered by reducing the symmetry of the HOMO through a structural distortion of the molecule. This structural distortion can adopt alternative symmetry related forms. The Jahn-Teller mechanism has been demonstrated, for instance, for the aromatic benzene cation $C_6H_6^+$ [13,14]. It is the aim of this Letter to demonstrate that the single coordinate description fails in the presence of structural degeneracy as provided by the Jahn-Teller mechanism. To demonstrate this claim, consider charge transfer between two identical molecules. The electronic degree of freedom will be represented by Pauli spin matrices with $\sigma_z = 1$ denoting the electron in the D state and $\sigma_z = -1$ in the A state. The electron is coupled to the same two nuclear degrees of freedom of the D and A molecules Y_1 and Y_2, respectively. The Hamiltonian is

$$H = \frac{P_{Y_1}^2}{2M} + \frac{P_{Y_2}^2}{2M} + V(Y_1, Y_2, \sigma_z) + \frac{\hbar\Delta_0}{2}\sigma_x + \sum_{\alpha,i=1,2}\left[\frac{p_{\alpha,i}^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2\left(x_{\alpha,i} + c_\alpha\frac{Y_i}{m_\alpha\omega_\alpha^2}\right)^2\right]. \quad (1)$$

Here M is the effective mass and V the potential energy of the two nuclear degrees of freedom. Two collections of harmonic oscillators $\{x_{\alpha_i}\}$, with mass m_α and frequency ω_α, represent the environmental degrees of freedom. They are coupled separately to the two nuclear degrees of freedom by the linear term proportional to c_α in Eq. (1). The coupling generates a frictional drag on Y_1 and Y_2

with a friction constant [15]:

$$\eta = \lim_{\omega \to 0} \frac{\pi}{2\omega} \sum_{\alpha} \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \delta(\omega - \omega_\alpha). \quad (2)$$

In the absence of any symmetry constraints, the lowest order coupling between the nuclear and electronic degrees of freedom is of the form $(Y_1 - Y_2)\sigma_z$. Treating $(Y_1 - Y_2)$ as the reaction coordinate leads to the standard single coordinate formalism. However, when we impose the mirror symmetry, $Y \to -Y$, $\{x_\alpha \to -x_\alpha\}$, this term is forbidden. Expanding the potential energy to the lowest order in the lowest order in the nuclear coordinates under the symmetry constraint gives a Landau-Ginsburg type potential:

$$V(Y_1, Y_2, \sigma_z) = \frac{1}{2}k(Y_1^2 + Y_2^2) + \frac{1}{4}v(Y_1^4 + Y_2^4) - \frac{\lambda k}{4}[(1 + \sigma_z)Y_1^2 + (1 - \sigma_z)Y_2^2]. \quad (3)$$

Here k is a spring constant, v describes the stabilizing effect of the lowest order anharmonic term, and λ is the dimensionless coupling constant between electronic and nuclear degrees of freedom.

We restrict ourselves to the case $1 < \lambda < 2$. In this regime, the donor-state energy surface $\langle\uparrow|V|\uparrow\rangle$ has two minima, at $Y_1 = \pm\sqrt{k(\lambda - 1)/v}$, $Y_2 = 0$, corresponding to a charge deformed molecule in one of two alternative mirror-related structures. We denote the "left" and "right" donor structures, respectively, by $|L\uparrow\rangle$ and $|R\uparrow\rangle$. The acceptor state energy surface $\langle\downarrow|V|\downarrow\rangle$ has two corresponding minima but rotated over $\pi/2$ in the (Y_1, Y_2) plane, as shown in Fig. 1. To locate the degeneracy points, we must solve for $\langle\uparrow|V|\uparrow\rangle = \langle\downarrow|V|\downarrow\rangle$, which yields two degeneracy lines $Y_1 = \pm Y_2$ that cross at the origin of the (Y_1, Y_2) plane. The lowest degeneracy point, the putative transition state, is the origin with an energy barrier $\Delta E = \frac{1}{4}k(\lambda - 1)^2/v$.

To see why a single reaction coordinate description cannot be consistent in the presence of the symmetry constraint, consider the two possible trajectories shown in Fig. 1 in the (Y_1, Y_2) plane for a thermally activated hop in the donor state from the L to the R configuration. The trajectories are classified by the impact parameter q, the distance of closest approach to the origin. A typical trajectory will cross the two degeneracy lines at least once. At each crossing point a charge transfer event can take place, with the system eventually ending in one of the two acceptor minimum states. Within a single reaction coordinate description for the charge transfer events, each degeneracy line is then at the center of a Landau-Zener region of width $l_{\mathrm{LZ}}(q) \propto \hbar\Delta_0/k\lambda q$. For low impact parameters, the two Landau-Zener regions of the degeneracy lines start to overlap when q drops below $l_{\mathrm{LZ}}(q)$, i.e., when q is less than $\xi = \sqrt{\hbar\Delta_0/k\lambda}$. As a result, there is a region of size ξ surrounding the origin where charge transfer is inherently *two dimensional*. If the thermal energy is low compared to the barrier height ΔE, then it is precisely this 2D region that will dominate the charge transfer reaction so the single reaction coordinate assumption cannot be valid.

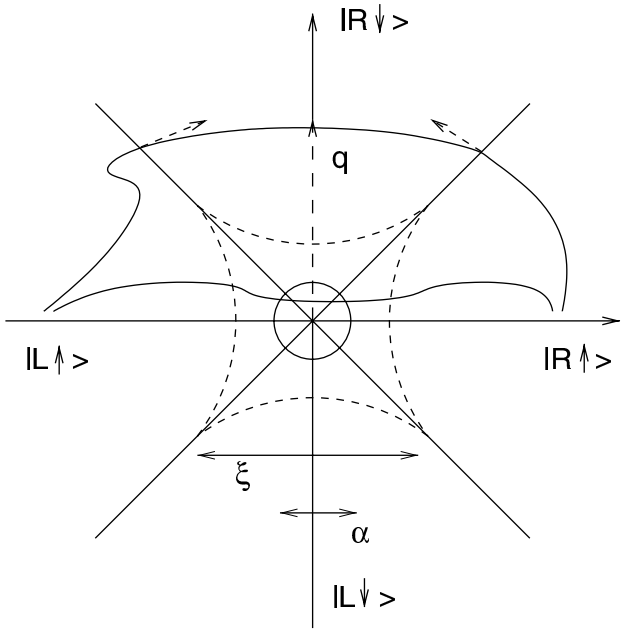

FIG. 1. Two different reaction paths in the Y_1, Y_2 plane of the nuclear coordinates. The locus of degeneracy points between the donor and the acceptor state energies are indicated by the lines $Y_1 = \pm Y_2$. Charge transfer reactions take place within the Landau-Zener region centered at the intersection of the reaction path with each degeneracy line. The top trajectory, with a large impact parameter q, crosses the two degeneracy lines separately, and the corresponding 1D Landau-Zener regions, not shown in the picture, are of order $l_{\mathrm{LZ}}(q)$. At the crossing points, charge transfer to the acceptor state $|R\downarrow\rangle$ (dashed arrows) is allowed, according to the single reaction coordinate description. The 2D Landau-Zener length ξ defines a region surrounding the origin where single-reaction coordinate theory fails. At the center of the 2D region one encounters strong resonant tunneling within a distance α from the origin. The bottom trajectory, with a low impact parameter q, enters both the 2D region of width ξ and the coherent tunneling region of width α. Here the charge transfer process must be described within a 2D framework.

In order to analyze a 2D charge transfer event we generalize the Smoluchowski-Zusman (SZ) method [7,16] to two dimensions. In principle, this method is restricted to the case of strong damping, when the thermal energy $k_B T$ is large compared to $\hbar\omega_c$, with ω_c the relaxation rate of the reaction coordinates. For the 1D case though, the SZ method reproduces the weak coupling nonadiabatic result in the limit of low tunneling rates.

In a 2D SZ description, the 2×2 density matrix $n_{i,j}$ of the "spin" degrees of freedom (i, j now indicate spin up

and down, respectively) obeys the following transport equation:

$$\frac{\partial n_{i,j}}{\partial t} = \frac{1}{\eta}\vec{\nabla}\{\vec{F}_{i,j} + k_B T\vec{\nabla} n_{i,j}\} - \frac{i}{\hbar}[H_\sigma, n_{i,j}], \quad (4)$$

$$H_\sigma = \frac{\hbar\Delta_0}{2}\sigma_x - \frac{\lambda k}{4}[Y_1^2 - Y_2^2]\sigma_z, \quad (5)$$

where η is the frictional drag of Eq. (2) and $\vec{F}_{i,j} = -\vec{\nabla}\langle i|V|j\rangle$ is the 2×2 force matrix derived from Eq. (3). The first term on the right hand side of Eq. (4) is the Smoluchowski operator for the 2D diffusive motion of a classical particle in a force field. The second term describes the precession of a spin 1/2 degree of freedom with the spin Hamiltonian H_σ given by Eq. (5). Note that the energy difference between spin up and spin down has a saddle point at the origin. The characteristic length scale appearing in H_σ is the 2D Landau-Zener length ξ encountered above. A comparison of H_σ with the Smoluchowski operator produces the second length scale $\alpha_{2D} = (\hbar k_B T/\eta k)^{1/4}$, which is the characteristic variation length of $n_{1,2}$. In the regime of strong damping, α_{2D} is small compared to ξ.

The equation for the off-diagonal part of the density matrix can be solved under the condition that $n_{1,2}$ varies over length scales that are short compared to those of the diagonal terms $n_{1,1}$ and $n_{2,2}$:

$$\mathrm{Im} n_{1,2}(\vec{Y}, t) \simeq 4\sqrt{2}\pi\xi^2[n_{1,1}(0,t) - n_{2,2}(0,t)]\delta(\vec{Y}). \quad (6)$$

The 2D delta function in Eq. (6) for the nuclear degrees of freedom is actually a Gaussian with a width of order α_{2D}. Inside this Gaussian region, the off-diagonal part of the density matrix is large: the spin degree of freedom is precessing coherently. Physically, this means that resonant tunneling is taking place between the D and A states within a distance α_{2D} of the origin of the (Y_1, Y_2) plane. Substituting Eq. (6) in Eq. (4), we find that the diagonal terms of the density matrix obey a classical Smoluchowski equation with a "sink" at the origin:

$$\frac{\partial n_{1,1}}{\partial t} = \frac{1}{\eta}\vec{\nabla}\{\vec{F}_{11} + k_B T\vec{\nabla}\}n_{1,1} - 4\pi\sqrt{2}\Delta_0\xi^2(n_{1,1} - n_{2,2})\delta(\vec{Y}), \quad (7)$$

$$\frac{\partial n_{2,2}}{\partial t} = \frac{1}{\eta}\vec{\nabla}\{\vec{F}_{22} + k_B T\vec{\nabla}\}n_{2,2} + 4\pi\sqrt{2}\Delta_0\xi^2(n_{1,1} - n_{2,2})\delta(\vec{Y}). \quad (8)$$

The decay rate of the donor state can be computed from Eqs. (8) and (9) using standard methods:

$$\frac{\Gamma}{\Gamma_0} = 4\frac{\sqrt{2(\lambda-1)}}{\lambda}\frac{\frac{\hbar\Delta_0^2}{\omega_c k_B T}}{1 + C\frac{\sqrt{\lambda-1}}{\lambda}\frac{\hbar\Delta_0^2}{\omega_c k_B T}}. \quad (9)$$

Here $\omega_c^{-1} = \eta/k(\lambda - 1)$ is the classical lifetime of the transition state, and Γ_0 is the classical Kramers rate for an activated hop to the transition state. The constant C equals $4\sqrt{2}\ln 2$.

The 2D decay rate of Eq. (9) is in the same form of the 1D description for donor-acceptor charge transfer provided we interpret $g_{2D} = \hbar\Delta_0^2/\omega_c k_B T$ as the new adiabaticity parameter. For a 1D charge transfer event, the adiabaticity parameter is of the form $g_{1D} \propto \hbar\Delta_0^2/\omega_c\Delta E_b$ with ΔE_b the characteristic energy scale of the nuclear degrees of freedom, such as the activation barrier. In the low temperature limit $k_B T \ll \Delta E_b$, the effective 2D adiabaticity parameter diverges while g_{1D} remains finite. Physically, this means that in the low temperature limit, the adiabatic description is *always* valid in the presence of the symmetry constraint.

We can justify treating g_{2D} as an adiabaticity parameter by estimating the time τ_{2D} spent in the 2D Landau-Zener region during a hop event. By Einstein's relation, the classical diffusion constant D of the nuclear degrees of freedom is $k_B T/\eta$, so that $\tau_{2D} \sim \xi^2/D$ is of order $\xi^2\eta/k_B T$. Using $\xi = \sqrt{\hbar\Delta_0/k\lambda}$ and identifying $\Delta_0\tau_{2D}$ as the adiabaticity parameter we recover the above expression for g_{2D}. Interestingly, even though the quasiclassical method should become generally valid in the low temperature limit, due to the symmetry constraint, the latter enhances the resonant tunneling regime as well. In the 1D description, resonant tunneling takes place within a distance $\alpha_{1D} = (k_B T\hbar/\eta\Delta F)^{1/3}$ of the degeneracy point. Compared to $\alpha_{2D} = (k_B T\hbar/\eta k)^{1/4}$ for the present case, we see that for $T \to 0$ the regime of coherent tunneling in 2D is always larger than in 1D.

DNA may provide a testing ground for the study of D-A charge transfer with symmetry constraints. A number of experiments have reported that radicals are able to move over considerable distances along double-stranded DNA by π orbital overlap [17]. The transport of a radical between two adjacent base pairs can be viewed as an example of a D-A charge transfer process. The charge degree of freedom is strongly coupled to the nuclear degrees of freedom and the latter are coupled to the solvent medium. Molecular dynamics simulations by Chen *et al.* [18] show that charging produces a large deformation of the DNA base pairs. A neutral pair has a mirror-planar symmetry, so there are two possible mirror-related forms for this deformation, as shown in Fig. 2. The reaction coordinate Y_1 (Y_2) of the D (A) molecule of this Letter would then correspond to the normal mode coordinate that has the maximum overlap with the deformation obtained in [18]. The coefficients k and v of Eq. (3) can be obtained by means of a molecular dynamics simulation [19].

For multiple stacked bases along a B-DNA chain, the mirror symmetry is not exact due to the propeller twist. The two alternative L and R structures of a charged base pair, however, may still be sufficiently similar for the present model to be relevant.

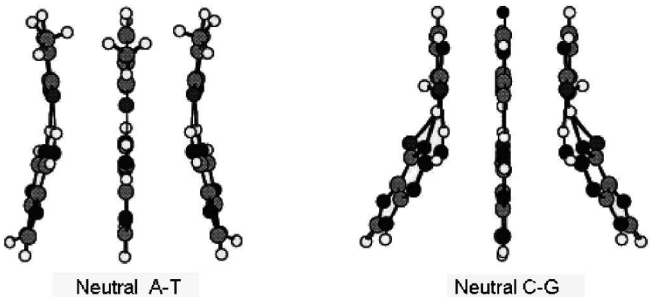

FIG. 2. Side view of charge induced structural deformation in DNA base pairs. Neutral base pairs, shown in the center, have a mirror symmetry that is broken by the addition of an external charge.

Finally, DNA base pairs undergo large-scale, thermally induced structural fluctuations [20], as required by the present model. Testing our description requires a measurement of the temperature dependence of the adiabaticity parameter g_{2D}, which is predicted to diverge as T^{-1}. The donor-state decay rate Γ provides a natural venue to this end, since it depends on g_{2D} as $g_{2D}/(1 + g_{2D})$ and has already been measured for DNA by laser spectroscopy [21].

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