Charge transfer, Symmetry and Dissipation

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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 theory, in the limit of low temperature, based on two independent reaction coordinates of equal relevance. We discuss implications of these results to charge transfer in DNA.

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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 proteins and DNA is characterized by low values of the tunneling matrix elements and strong coupling between the electronic and nuclear degrees of freedom [3]. 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, and the transfer rate reduces to the classical Kramers theory for activated chemical reactions in a dissipative medium [4, 5, 6]. However, because of the low value of the tunnel frequency \( \Delta_0 \) for biomolecular charge transfer, the adiabatic assumption is often not valid and, as a result, a quantum-mechanical description is required to determine the charge transfer rate. The interaction of the nuclear degrees of freedom with the solvent medium allows coupling to a finite-temperature heat bath and \( \Delta_0 \) is large compared to the typical force level on the nuclear degrees of freedom [7].

In the presence of symmetry constraints. To be specific, 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 molecule \( Y_1 \), respectively, \( Y_2 \). The Hamiltonian is:

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

(1)

Here, \( M \) is the effective mass and \( V \) the potential energy of the two nuclear degrees of freedom. Two collections \( \{ x_{\alpha} \} \) of harmonic oscillators represent the environmental degrees of freedom. They are coupled separately to the nuclear degrees of freedom, and generate a frictional drag on \( Y_1 \) and \( Y_2 \) with a friction constant [12]:

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

(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, we can apply the standard single coordinate formalism. However, if we impose a mirror symmetry \( Y \to -Y \), \( \{ x_{\alpha} \to -x_{\alpha} \} \) then 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:
which yields two degeneracy lines. The Landau-Zener theory 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 \(\alpha\) from the origin. The top trajectory, with a large impact parameter \(q\), crosses the two degeneracy lines separately. Charge-transfer at the crossing points allows transfer to the acceptor state \(|\downarrow\rangle\) (dashed arrows). The bottom trajectory, with a low impact parameter, enters both the 2D region and the coherent tunneling region.

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

Here, \(k\) is a spring constant, \(v\) describes the stabilizing effect of the lowest order anharmonic term, and \(\lambda\) 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 \(|\ell\rangle\) and \(|\text{R} \, \uparrow\rangle\). 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 is not consistent in the presence of the symmetry constraint, we show in Fig. 1 two possible trajectories in the \((Y_1, Y_2)\) plane for a thermally activated hop in the donor state from \(|\ell\rangle\) to \(|\text{R} \, \uparrow\rangle\). The trajectories are classified by the impact parameter \(q\), the distance of closest approach to the origin. A typical trajectory will cross each of 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 at the center of a Landau-Zener region of width \(l_{1,2}(q) \propto \hbar \Delta_0/k \lambda q\). For low impact parameters, the two Landau-Zener regions of the degeneracy lines start to overlap when \(l_{1,2}(q)\) drops below \(q\), i.e., when \(q\) is less than \(\xi = \sqrt{\hbar \Delta_0/k \lambda}\). As a result, there is a region of size \(\xi\) surrounding the origin where charge transfer is inherently two dimensional. If the thermal energy is low compared to the barrier height \(\Delta E\), then this 2D region will dominate the charge transfer reaction and the single reaction coordinate assumption is not valid.

In order to analyze a 2D charge transfer event we generalize the Smoluchowski-Zusman (SZ) method 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 \(\omega_c\), the relaxation rate of the reaction coordinates. For the 1D case though, the SZ method reproduces the weak coupling non-adiabatic result in the limit of low tunneling rates.

In a 2D SZ description, the \(2 \times 2\) 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:

\[
\frac{\partial n_{i,j}}{\partial t} = \frac{1}{\eta} \nabla \left\{ F_{i,j} + k_B T \, \nabla n_{i,j} \right\} - \frac{i}{\hbar} [H_{\sigma}, n_{i,j}], \tag{4}
\]

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

with \(F_{i,j} = -\nabla \langle i | V | j \rangle\) the \(2 \times 2\) force matrix derived from Eq. (3). The first term on the right hand side of Eq. (3) 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 \(H_{\sigma}\) given by Eq. (4). Note that the energy difference between spin up and spin down has a saddle point at the origin. The characteristic length scale appearing in \(H_{\sigma}\) is the 2D Landau-Zener length \(\xi\) encountered above. A comparison of \(H_{\sigma}\) with the Smoluchowski operator produces the second length scale \(\alpha_{2D} = (\hbar k_B T/\eta k)^{\frac{1}{2}}\), which is the characteristic variation length of \(n_{i,2}\). In the regime of strong damping, \(\alpha_{2D}\) is small compared to \(\xi\).

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

\[
\text{Im} \ n_{1,2} (\vec{Y}, t) \approx 4 \sqrt{2} \pi \xi^2 \left[ n_{1,1}(0, t) - n_{2,2}(0, t) \right] \delta (\vec{Y}).
\] (6)

The 2D delta function in Eq. (6) for the nuclear degrees of freedom is actually a gaussian with a width of order \( \alpha_{2D} \). 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 \( \alpha_{2D} \) of the origin of the \((Y_1, Y_2)\) plane. Substituting Eq. (6) in Eq. (11), we find that the diagonal terms of the density matrix obey a classical Smoluchowski equation with a “sink” at the origin:

\[
\frac{\partial n_{1,1}}{\partial t} = \frac{1}{\eta} \left\{ \vec{F}_{11} + k_B T \vec{V} \right\} n_{1,1} - 4\pi \sqrt{2} \Delta_0 \xi^2 (n_{1,1} - n_{2,2}) \delta (\vec{Y}),
\] (7)

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

The decay rate of the donor state can be computed from Eq. (3) and Eq. (4) using standard methods:

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

Here, \( \omega_c^{-1} = \eta / k (\lambda - 1) \) is the classical life-time of the transition state, and \( \Gamma_0 \) 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 \( \Delta E_b \) 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 \( \tau_{2D} \) 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 \( \xi = \sqrt{\hbar \Delta_0 / k T} \) and identifying \( \Delta_0 \tau_{2D} \) as the adiabaticity parameter we recover the above expression for \( g_{2D} \). Interestingly, even though the quasi-classical 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 \( \alpha_{1D} = \left( k_B T / \eta \Delta F \right)^{1/3} \) of the degeneracy point. Compared to \( \alpha_{2D} = \left( k_B T / \xi \right)^{1/4} \) for the present case, we see that for \( T \to 0 \) the regime of coherent tunneling in 2D is always larger than in 1D.

We conclude by noting that, a DA charge transfer system can be viewed as a two-state quantum system coupled to quasi classical macroscopic degrees of freedom (the nuclear coordinates). Systems of this type form the basic elements for quantum computation, the “qubits”. For our result to be of any interest in this context, the adiabaticity parameter \( \Delta_0 \tau_{2D} \) must be very large compared to one, of the order of \( 10^4 \) or larger \cite{13}. Since the symmetry constraint leads to the divergence of the adiabaticity parameter in the low temperature limit, DA systems obeying such a constraint would be better suitable for that purpose. A possible realization of the symmetry constraint is encountered for charge transfer between two DNA bases. Molecular dynamics simulations by Chen et al. \cite{14} report that the in-plane mirror symmetry of individual DNA bases is broken when a hole occupies the purine base. The mirror symmetry for stacked bases along a B DNA chain is not exact due to the propeller twist but the two alternative L and R structures of a charged base still may be sufficiently close for the present model to be relevant. It would be very interesting to test whether charge transfer events along DNA correlate with thermally activated hops between the L and R states.

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