Coherence in electron transfer pathways

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Abstract

Central to the view of electron-transfer reactions is the idea that nuclear motion generates a transition state geometry at which the electron/hole amplitude propagates coherently from the electron donor to the electron acceptor. In the weakly coupled or nonadiabatic regime, the electron amplitude tunnels through an electronic barrier between the donor and acceptor. The structure of the barrier is determined by the covalent and noncovalent interactions of the bridge. Because the tunneling barrier depends on the nuclear coordinates of the reactants (and on the surrounding medium), the tunneling barrier is highly anisotropic, and it is useful to identify particular routes, or pathways, along which the transmission amplitude propagates. Moreover, when more than one such pathway exists, and the paths give rise to comparable transmission amplitude magnitudes, one may expect to observe quantum interferences among pathways if the propagation remains coherent. Given that the effective tunneling barrier height and width are affected by the nuclear positions, the modulation of the nuclear coordinates will lead to a modulation of the tunneling barrier and hence of the electron flow. For long distance electron transfer in biological and biomimetic systems, nuclear fluctuations, arising from flexible protein moieties and mobile water bridges, can become quite significant. We discuss experimental and theoretical results that explore the quantum interferences among coupling pathways in electron-transfer kinetics; we emphasize recent data and theories associated with the signatures of chirality and inelastic processes, which are manifested in the tunneling pathway coherence (or absence of coherence).

Keywords
electron transfer; coherence; interference; electron tunneling

1. Introduction

The development of a quantum mechanical description of chemical bonding was a monumental accomplishment of twentieth century chemistry. The quantum nature of electronic structure - and hence of molecular structure - is an essential and central part of chemistry. Yet, once the molecular structure is defined, the interactions between molecules (and their assembly into supramolecular structures) can be understood largely by classical ideas. Even in the case of chemical reactivity, quasi-classical notions are often very powerful. In electron-transfer reactions, however, the dual nature of the electron is essential for the reaction to occur because the reactions require quantum tunneling of electrons through barriers that would be insurmountable for classical electrons. In addition, electron transfer may occur over large distances so that multiple electron tunneling pathways are possible, and the sensitivity of the tunneling barrier to the nuclear motion may depend strongly on the medium structure and its fluctuations.
The canonical view of electron-transfer reactions considers that nuclear motion coupled to
the reductant (reactant) electronic state, often some collective solvent polarization
coordinate, generates a transition state geometry at which the electron amplitude propagates
coherently between quasi-degenerate electron donor and acceptor states. The transition is
often treated as arising from coherent electronic propagation on a time scale during which
the nuclei are nearly “frozen.” Because the tunneling barrier is highly anisotropic, it is useful
to identify particular combinations of bonded and nonbonded coupling routes, tunneling
pathways, along which the transmission amplitude flows. When more than one such
pathway exists, the propagating amplitudes interfere, if the propagation remains coherent.
The coherent electronic amplitude propagation may become manifest in a number of ways,
e.g., electron-transfer reactions show orbital symmetry effects that are characteristic of
coherent interferences. Despite the deep consequences of electronic coherence in electron-
transfer reactions, understanding the experimental signatures and control of coherence
effects in electron transfer is in its infancy.

2. Coupling Pathways

When the donor-acceptor coupling changes little on the time-scale of nuclear motion
through the crossing-point of the reactant and product potential surfaces, the electron-
transfer rate may be written in the weak coupling regime as [1-4]:

\[ k_{ET} = \frac{2\pi}{\hbar} |H_{int}|^2 \rho_{FC} \]  (1)

Within this picture, pathway interferences can be understood to arise from amplitude
propagation along pathways of local hybrid orbitals, or among local bonding and
antibonding orbitals [5-7]. Such a pathway analysis provides a powerful tool for describing
electronic interactions in large systems, including proteins [8]. For weak donor-acceptor
interactions (the nonadiabatic limit), tunneling occurs largely via a through-bond mechanism
[9] in most cases. Theoretical analysis of the coupling patterns observed in \textit{ab initio}
calculations reveals that interferences among virtual electron and virtual hole states can
account for the experimentally observed rates and their dependence on bridging structure
[10-14]. It is important to appreciate, however, that pathways through hydrogen bonded [15]
and nonbonded contacts can contribute significantly to the electronic coupling, especially in
thermally fluctuating systems and in systems where the purely through-bond pathway (if it
exists at all) is very long [8]. Indeed, under the right conditions, these “weak links” may
dominate (see studies of Waldeck and Zimmt [16] for through-solvent couplings in donor-
bridge-acceptor structures and studies of Waldeck [17] and Majda [18] for interchain
couplings in monolayer films).

Wavefunction interference provides a mechanism for manipulating electronic coupling and
hence electron-transfer rates. For example the ‘C-clamp’ molecule 1, shown in Figure 1, is
designed so that the electronic coupling pathways through the covalent bridge between the
donor and the acceor destructively interfere for a rigid/symmetric structure with mirror
plane symmetry. Because fluctuations in the nuclear configuration cause the electronic
coupling to fluctuate, the rms coupling is not strictly zero, although it is significantly weaker
(an order of magnitude) for 1 than for 2 because of the symmetry of the acceptor [19, 20].

When a solvent molecule resides in the cleft of the ‘C-clamp’, it can provide a pathway for
electronic coupling that is not symmetry forbidden and involves fewer virtual steps than the
purely covalent pathways. For these reasons, the through solvent coupling pathways
dominate over the through-bond coupling pathways to control the electron transfer. While
this example, and others [21], provides important experimental support for coherent
electronic amplitude propagation across the bridge, these measures of coherence are indirect.
When the bridge is a solvent molecule, its position and influence on electronic coupling will be thermally fluctuating. Our work on the effects of bridge fluctuations in biological and small molecule electron transfer reactions has shown that, in cases where the tunneling matrix element is determined by multiple interfering tunneling pathways, the coupling matrix element is indeed rapidly fluctuating. In this regime, nonequilibrium structural fluctuations that enhance the tunneling matrix element can determine the electron-transfer rate [22-26]. For low tunneling barriers (e.g., some duplex DNA bridges), structural fluctuations can even create bridge resonances that enhance the electron-transfer rate [27].

We have proposed a molecular ‘double-slit’ experiment that could be used to examine the coherent nature of electron tunneling directly in an electron-transfer reaction [28-30]. This ‘thought experiment’ was constructed as a molecular analogue (see Figure 2) of phenomena often probed in mesoscale device experiments. In the limit that the electron amplitude propagates coherently from the donor to the acceptor via its coupling pathways, interference and orbital-symmetry constraints as described above should hold. In contrast, when the tunneling electron excites local bridge vibrations (inelastic tunneling), the excitation “labels” the physical pathway traversed and the coherence among pathways is destroyed. Figure 2 illustrates one molecule whose donor electronic orbital symmetry is $a^\prime$ and its acceptor orbital symmetry is $a$. Thus, this electron transfer is symmetry forbidden. Yet an alternative acceptor group symmetry (e.g., containing C≡N groups) would make the transfer allowed.

In the first case, the electron transfer would be symmetry forbidden but vibronically allowed. By using a tight-binding model for orbitally forbidden donor-acceptor interactions, we showed that the electronic coupling was zero (dashed line in figure) unless inelastic transitions (excitation of a CN vibration) on one pathway occurred (solid line in figure). The vibronic transition ‘reports’ which pathway is followed by the electron and destroys the two-pathway interference. Currently, the experimental group of Rubtsov and coworkers [31] is attempting to realize an experiment of this kind. They have succeeded in perturbing electron-transfer kinetics by exciting bridge-localized mid-IR vibrational modes. Inelastic tunneling mechanisms have also been studied in the context of inelastic tunneling spectroscopy [32, 33]. Further, for double-slit molecular devices, pure dephasing (rather than dephasing caused by inelastic transitions) was shown to wash out effects of symmetry forbidden electron transfer when dephasing was sufficiently strong [34].

3. Current transfer

In the limit of weak donor-bridge and bridge-acceptor interactions, the bridge-mediated tunneling is described perturbatively, as

$$H_{\text{int}} = \sum V_{dn} \left[ \frac{1}{E_{\text{tunn}} - E_n^{(B)}} \right] V_{at}$$  \hspace{1cm} (2)

[1-4]. The term in brackets is pure real, as it depends on (measurable) state energies. Because the Hamiltonian describing the system is a pure real operator, the donor and acceptor states may be chosen to be pure real functions, unless the preparation of states dictates otherwise. Indeed, the experimental state preparation can be used to impart phase information on the donor and acceptor states.

By preparing initial states with linearly or circularly polarized light, it is possible to imprint linear or angular momentum on the prepared states. Eigenfunctions of linear or angular momentum operators have a definite phase relationship among their amplitudes; i.e., amplitudes at sites differ by the factor $\exp[-ik\theta]$, where $k$ and $\theta$ are pure real numbers. This phase factor can have significant consequences for electron tunneling pathway interference, and for the reaction dynamics [35-37]. What is this influence? Given that Fermi’s golden
rule (Eqn 1) relates the electron-transfer rate to $|H_{DA}|^2$, how does $H_{DA}$ change when the donor state momentum switches sign? Switching the sign of the momentum changes the phase factor of the $V$ terms in Eq. 2, changing $H_{DA}$ to $H_{DA}^*$ and leaving the value of $|H_{DA}|$ unchanged. This observation is supported by the fact that the energy eigenstate spectrum of a structure and its mirror image (i.e., the molecule with opposite prepared angular momentum state) are identical. Yet, recent experiments find that the electron-transfer dynamics of positive versus negative angular momentum donor states may differ [38, 39]. Electron-transfer yields in photoemission experiments are found to be significantly different for systems where the electrons are ejected with right versus left circular polarized light. How is this yield asymmetry possible if the electron-transfer kinetics (eq. 2) is identical?

While the squared coupling matrix elements are “unaware” of the polarization of the prepared initial state, the quantum dynamics of electronic propagation is in fact sensitive to left versus right circular polarization if the donor excited state contacts the bridge at more than one point (imparting phase information about the initially prepared state to the propagation in the bridge; see Fig. 3). With more than one contact point, the complex phase interferences that occur in the bridge cause a phase lag for arrival at the acceptor of the differently prepared momentum states. That is, the charge oscillation frequency ($H_{DA}/\hbar$) is identical, but the difference in donor angular momentum causes a phase shift in the arrival of the wave packet at the acceptor for the two different initial state polarizations. If the donor excited state has a finite lifetime, the phase difference for electron arrival at the acceptor produces different quantum yields for charge transfer from the two prepared states [35-37]. Interestingly, if the bridges are chiral, reversing the angular momentum of the prepared state has the same effect as reversing the handedness of the bridge.

Preparing the donor in a specific linear or angular momentum state with a short lifetime (compared to the donor-acceptor oscillation frequency), and contacting the bridge in more than one point, produces different electron-transfer yields for left versus right angular momentum states as a consequence of the coherent interference of electron transmission pathways. The effect described above is predicted to be much larger for resonant transport than for tunneling transport (see right panel of Fig. 3) [35-37]. This difference is in fact observed in tunneling [38] versus resonant regime [39] experiments.

### 4. The effects of initial state preparation on the electron-transfer mechanism

Current transfer, as discussed above, is an example of electron transfer control by initial state preparation. Interestingly, the dependence of the through-bridge electron transmission probability on the internal phase of the electron donor state is robust to dephasing, even if the dephasing includes donor and acceptor population relaxation as well as pure dephasing of the bridge amplitude [35]. This leads to the question: to what extent do the details of the initial state preparation affect the electron-transfer dynamics in the presence of dephasing? This question is of importance both in the fields of biological electron transfer and optimal control. With respect to biological electron transfer, the initial state preparation can determine the nature of the electron-transfer pathways and thus the electron-transfer mechanism. For example, in the case of DNA photolyase, where the electron donor is a flavin, nature uses the delocalization properties of the electron donor cofactor’s charge transfer excited states to shift electron density toward the acceptor, which is the DNA thymine dimer [40, 41]. This mechanism could be described as electron transfer by way of photo-selected rather than bridge-mediated pathways. That is, the “displaced” electron population of the excited donor (flavin) state couples strongly to nearby empty acceptor states, thus enhancing the donor-acceptor coupling and the electron-transfer rate. As long as...
the electron-transfer rate is faster than the excited-state population relaxation rate (the case of photolyase), this direct tunneling pathway and rate enhancement should dominate. The rate enhancement should also be robust to pure dephasing effects, because pure dephasing does not affect populations.

The importance of initial-state preparation in electron-transfer reactions was demonstrated by Skourtis and Nitzan in another context related to molecular charge transfer and conductance in molecular wires [42]. They showed that the initial state preparation can affect the bridge length dependence of the electron-transfer yield for electron transmission and may also determine the switching from an exponential distance decay to a ‘softer’ distance dependence as a function of wire length. Such transitions have been observed in DNA [43] and more recently for PNA [44] hole transfer. This transition in DNA is attributed to a changeover from a superexchange to a thermally activated hopping mechanism [43, 45]. Skourtis and Nitzan point out, however, that a similar effect can be observed in the absence of such a hopping transition as long as: i) the prepared donor state has a small population on the bridge, and ii) the donor state’s initial preparation produces a small subensemble of systems with the electron (or hole) at energies inside the bridge eigenstate spectrum [42]. This subensemble’s contribution to electron transfer is negligible compared to the majority superexchange contribution at short bridge lengths. When the superexchange contribution - which decays exponentially with distance - dies for long bridge lengths, the small subensemble's contribution survives because it involves resonant through-bridge transport - which decays slowly with distance. The above mechanism should not be washed out by pure dephasing because it depends on initial populations.

4. Summary

Signatures of coherence and decoherence surface in many ways in electron-transfer reactions. Pathway decompositions of donor-acceptor couplings assume that amplitudes propagating along alternative paths add coherently before being squared to generate an electron-transfer rate. This assumption appears to be violated in some DNA electron-transfer systems that involve relaxation and trapping of charge between initial and final localizing sites. Orbital selection rules for electron transfer are well known and are, themselves, a manifestation of the coherent propagation of amplitude from donor to acceptor. Symmetry also determines the nature of coupling pathway interferences. Coherence is also manifested in the preparation of the initial state and its subsequent propagation. We have shown that initial states with a well-defined linear or angular momentum, by virtue of their complex valued wave functions, have interferences with bridges that cause a phase lag in electron arrival for momentum states of oppositely signed momentum. In the presence of a finite state lifetime, this produces yield asymmetries for charge transfer coupled through mirror image (enantiomeric) bridge structures. Recent theoretical developments and ongoing experiments are probing how local vibrational modes of a bridge may leave signatures of the tunneling route and thus eliminate pathway interferences. If sufficiently localized vibrational modes can be constructed in high-symmetry bridged molecules, “double-slit” style experiments at the molecular level may become accessible.

Acknowledgments

This material is based in part upon work supported as part of the UNC EFRC: Solar Fuels and Next Generation Photovoltaics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001011 (support of SSS for studies of coherent processes). SSS also thanks the University of Cyprus for partial support of this research (on photolyase). DHW thanks the US National Science Foundation (NSF CHE 0628169 and CHE-0718755). DNB thanks the National Science Foundation (NSF CHE-1012357) for support. Additional support (to DNB and SSS) from DOE ASCR under SciDAC-e award DE-FC02-06ER25764 is gratefully acknowledged.

Procedia Chem. Author manuscript; available in PMC 2013 July 03.
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Fig. 1.
The two donor-bridge-acceptor molecules shown here have the same anthracenyl donor unit and different acceptor units. For 1 the donor to acceptor coupling is symmetry forbidden and for 2 it is symmetry allowed; adapted from [16] with permission.
Fig. 2.
(Left) A symmetry forbidden DBA structure that has CN groups which may act to identify the coupling pathway if vibrationally excited. (Right) Tunneling pathways calculated from the inelastic and elastic mechanisms are plotted versus the vibronic coupling parameter. Electron transfer is enhanced by inelastic processes [29]. Adapted from reference 28, with permission.
Fig. 3.
(Left) Model tight-binding DBA system with two contact points between D and B, and a complex phase relationship between sites 1 and 2. (Right) Predicted electron-transfer yield asymmetries for transport in the resonant regime (blue) and tunnelling regime (black); adapted from [36] with permission.