Mediation of Long Range Charge Transfer by Kondo Bound States

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We present a theory of non-equilibrium long range charge transfer between donor and acceptor centers in a model polymer mediated by magnetic exciton (Kondo) bound states. Our model produces electron tunneling lengths easily exceeding $10\mathring{A}$, as observed recently in DNA and organic charge transfer systems. This long ranged tunneling is effective for weak to intermediate donor-bridge coupling, and is enhanced both by weak to intermediate strength Coulomb hole-electron attraction (through the orthogonality catastrophe) and by coupling to local vibrational modes.

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Charge transfer (CT) via quantum mechanical tunneling of electrons or holes through a molecular bridge between well separated donor (D) and acceptor (A) sites, is central to many biological processes [1–4], and may play a key role in molecular electronics applications [5,6]. For proteins, the CT rate typically decays exponentially in the D/A separation with the inverse tunneling length $\beta = 1.1 \pm 0.2 \mathring{A}^{-1}$ [2]. However, evidence for anomalously small β values (of order $0.1\mathring{A}^{-1}$) has accrued for CT between metallic intercalating complexes or organic complexes in DNA [3,4], CT from ferrocene attached to conjugated polymers [5,6], and a few other systems [7]. Values of $\beta \sim 1\mathring{A}^{-1}$ are well accounted for in effective one-electron theories with the D/A levels typically residing in the middle of the large insulating (4-6 eV) gaps of the polypeptide bridges of proteins [8]. Understanding smaller β values has generally required "fine tuning" of the D/A levels close to the lowest unoccupied molecular level (LUMO) [9]. For DNA, this issue is coupled to the magnitude of the electronic energy gap in DNA, an exciting and hotly debated subject [10–13].

In this paper, we show that long range CT, with tunneling lengths $\beta^{-1} \geq 10\mathring{A}$ can be achieved in model systems through mediation by a semiconducting, molecular analogue of the Kondo state in which a localized electron or hole moment is antiferromagnetically coupled to a hole or electron donated to the bridge [14]. While our model for the tunneling bridge is a conjugated polymer, the conclusions are generic for a gapped molecule. The bound state mechanism provides a robust basis for "fine tuning" D levels close to the LUMO. We carry out our calculations both with a semi-analytic variational method [15] as well as the density matrix renormalization group (DMRG) approach, and the results agree very well. Adding the dielectrically screened electron-hole Coulomb interaction to the Kondo coupling leads to an enhancement of tunneling for weak to intermediate Coulomb strength through the orthogonality catastrophe, and a crossover to deep Coulomb binding for larger Coulomb interaction. Coupling to local vibrational modes of the metal complexes also enhances the CT rate, and can lead to normal or inverted regimes de-

pending upon the strength of the binding and the D/A distance.

CT via a single tunneling event is intiated out of equilibrium either by the absorption of light (photolysis) or transfer of charge by radicals (radiolysis) so that an electron or hole at the D complex is energetically excited above an empty level in the A complex; in this paper we focus on photolytically prepared charge transfer. In the simplest "diabatic" theory for which the electron tunneling matrix element H_{DA} is small, the CT rate k_{ct} is well described by a golden rule/linear response approach (Marcus theory [1]), with

$$k_{ct}(T) = \frac{2\pi}{\hbar}|H_{DA}|^2 F(T) \tag{1}$$

where $F(T)$ is the Franck-Condon factor [1]. H_{DA}, which is the main subject of this paper, carries the dominant distance dependence.

The CT scenario involves three steps, and can only arise when, as in Fig. 1, the excited D complex energy lies at or near the bridge LUMO (a similar situation can be realized for hole transfer with suitably reversed energetics). Upon excitation (step 1), the D complex donates an electron to the bridge, leaving behind a remnant hole spin with antiferromagnetic coupling to the bridge electron (this interaction drives the Kondo binding in step 2). In step 3, the electron is transferred to the distant donor level.

Experimental realization of the appropriate D energetics seems possible. For example, for the Ru-complex metallointercalator used in DNA CT experiments [3], a 480 nm photoexcitation transfers electrons from Ru(II) to the ligand (L^*) from which electron transfer to the DNA presumably occurs (there is no direct Ru-DNA overlap), leaving a hole spin in the t_{2g} Ru shell. For DNA gaps of 1-2 eV, it is plausible that the excited Ru(III)-L^* complex lies above the electron addition threshold, though estimates of the gap range from 0 eV [12,13], 1-2 eV [10,16], and on up to 7 eV [17]. The 3.9 eV photoexcitation energy of the adenine isomer 2-aminopurine (Ap) is very comparable or in excess of the HOMO-LUMO gap for isolated bases [4], although the initial CT matrix element to neighboring DNA bases is likely weaker than

in the metallointercalator case, for which the ligand resides between adjacent base pairs with more effective π-overlap. Excitation of Rh(phi)$_2$(bpy)$^{3+}$ will produce conditions favorable for hole transfer to adjacent sequences of DNA-A bases [18,19]. For the 5-(p-tolyl)-tetracene donor of ref. [5], the D photoexcitation energy is nearly equal to the p-phenylenevinylene bridge gap for bridges of 3-5 units, and judging from the trend, should become higher for longer bridges. Thus, our considerations are clearly relevant to these systems.

With these energetics, the Kondo singlet bound state (KS) [20] is the most stable charge zero singlet state, though the charge ± 1 spin $1/2$ state (free moment) can be globally stable in a molecule or semiconductor [21]. Rapid KS formation is required to compete with other processes, as discussed in Fig. 1. A lower bound estimate for KS formation is $\tau_K \approx \hbar/E_B$, where E_B is the binding energy, in analogy to the reasoning used for Kondo resonance formation time in quantum dots [22]. τ_K is of the order of a few femtoseconds for $E_B = 0.1 - 0.2$eV. In the semiconducting/molecular context, it will be divided by a Franck-Condon factor F_K since the excited D level resides above the bound state. Provided $F_K \leq 0.001$ [24], KS formation will likely beat luminescence (nanosecond time scale) and phonon radiative decay to the A state (large polaron formation) which can be estimated, utilizing polyacetylene parameters [23], to be of order 100 ps. We stress that (i) no simple polaron dynamics will cause k_{ct} to decay exponentially in the D/A separation, and (ii) any polaron mediated contribution to k_{ct} is bounded above by the large polaron result [25].

We simply model the insulating bridge as a dimerized tight binding chain of length N (N even) with Hamiltonian $\mathcal{H}_B$ given by [23]

$$\mathcal{H}_B = - \sum_{i=1,\sigma}^{N} (t + (-1)^i t')(c_{i+1\sigma}^\dagger c_{i\sigma} + h.c.) \qquad (2)$$

where $c_{i+1\sigma}^\dagger$ creates an electron of spin σ at site i. This model describes the π_z bands of polyacetylene, and can easily be extended to other conjugated polymers (as in refs. [5,6]), but the bound state formation is not special to this model bridge. For large N, this model produces two bands with a full width of $4t$ and a gap of $2\Delta = 4t'$. The acceptor complex is placed adjacent to site N of the chain, and modeled as an Anderson impurity in the empty orbital regime [14], with energy ϵ_A. To simplify the analysis, we have taken the Coulomb repulsion U between D holes to be infinite, and as in the Ru case we assume there is a single hole in an otherwise filled shell, with energy relative to the filled shell of ϵ_D. The hybridization Hamiltonian coupling the D/A complexes and bridge is

$$\mathcal{H}_{BDA} = \sum_\sigma [V_D X_{0\sigma} c_{1,-\sigma} + V_A a_\sigma^\dagger c_{N\sigma} + h.c.] \ , \qquad (3)$$

where $|D0>$ is the filled shell state of the Donor and $|D\sigma>$ the state of a single hole and $X_{0\sigma} = |D0><D\sigma|$. We choose ϵ_D above the LUMO, and ϵ_A to be within the gap.

We compute H_{DA} by first identifying the appropriate two state system from diagonalizing with either: (1) the DMRG approach, which is exact to within targeted numerical precision [26], and (2) a version of the variational wave function approach for magnetic impurities in metals pioneered by Varma and Yafet as well as Gunnarsson and Schönhammer [15]. We build our variational states by first diagonalizing the bridge with the non-interacting A "impurity" included, and then employ the *Ansatz*:

$$|\psi> = A[|D0> + \sum_{j\sigma} \alpha_j b_{j\sigma}^\dagger |D - \sigma>]|BA> \qquad (4)$$

where $b_{j\sigma}$ creates an electron in orbital j of the bridge-A system, α_j are variational coefficients, and the particle-hole excitations are controlled both by the spin degeneracy N_s (here $N_s = 2$) and the bridge gap. As is well known [14], each added particle-hole excitation contributes a term of relative order $1/N_s$ to the energy. This variational *ansatz* does an excellent job of describing the Kondo state in metals (the second term captures the screening of the local moment, and as such is nonperturbative as opposed to, *e.g.*, direct expansion in U or Möller-Plesset methods). Because of the Hilbert-Space truncation associated with large U, the above wave function cannot be reduced to a single determinant by a unitary transformation. Hence, for our model, DMRG gives an "exact configuration interaction" solution while the variational approach provides a physically motivated basis set reduction solution. For the purposes of calculating H_{DA}, the methods agree exceedingly well.

Given the two lowest "adiabatic" eigenstates, we next identify the out-of-equilibrium "diabatic" states corresponding to the excited electron predominantly localized to the left (D) side, or right (A) side. The Generalized Mulliken-Hush method [27] accomplishes this by finding, within the two-state space, the eigenstates for the electric dipole operator, which maximally localize the charge to left or right. H_{DA} is then approximated by the off-diagonal matrix element of the two-state Hamiltonian in the dipole-diagonal basis.

Our results for H_{DA} vs. bridge length N are shown in Fig. 2(a), where we have set $V_D = V_A$ for convenience, and chosen ϵ_D well above the LUMO, and V_D is of order t [28]. We note the following features of our curves: (i) for short distances, H_{DA} scales with $V_D V_A$, perturbatively, so that stronger initial coupling yields stronger tunneling. On the other hand, for large distances, the weaker V_D gives better tunneling, because the more loosely bound KS cloud has better overlap on the distant A complex. (ii) By taking the bridge spacing to be of the order of $3\mathring{A}$ as in DNA, the slope for our curve with $V_D = 0.75t$ at

long distances corresponds to $\beta \approx 0.1 \mathring{A}^{-1}$, and this corresponds to a binding energy of the order of 0.05-0.2 eV (see Fig. 3). Obviously our model is too simple to realistically describe CT in DNA; rather, we stess the ready achievment of small β values. (iii) The agreement between the DMRG calculations (x's) and variational (lines) is quantitatively excellent in the long distance regime where H_{DA} is quite small, and good in the short distance regime. Hence, our variational approach is a very useful, accurate, physically motivated basis set reduction scheme for this model. (iv) By varying t', V_D, $\tilde{\epsilon}_D$ we can easily obtain the typical protein results ($\beta \simeq 1 \mathring{A}^{-1}$) in our model.

Analytic solutions are possible in two limits. First, in a continuum limit in which the D/A complexes are placed at separation Na in a one-dimensional wire, and $E_B << t'$, we find that $H_{DA} \sim E_B^{1/4} \exp(-\sqrt{2m^*E_B}Na/\hbar)$, with effective mass $m^* = \hbar^2 t'/[2(t^2 - t'^2)a^2]$ and the Kondo binding energy $E_B = V_D^4/(\epsilon_0|\epsilon_D - 2t'|^2)$, with $\epsilon_0 = \hbar^2/(8m^*a^2)$. The prefactor reflects a "slave boson" renormalization of the matrix element V_D [29], and the exponent arises from A/KS overlap. Thus there is a maximum H_{DA} for a given bridge length, though this is practically relevant for only long bridges given the weak prefactor dependence upon E_B. Second, for a discrete bridge H_{DA} is expressed approximately as

$$|H_{DA}| \approx |V_D V_A \sum_k \frac{\psi(k,1)\psi^*(k,N)}{\epsilon_k - 2t' + E_B}| \qquad (5)$$

where $\psi(k,i)$ is the wave function amplitude at site i of a bridge-only conduction orbital of energy ϵ_k (no A complex). This describes the propagation from the D complex to bridge site 1, then to bridge site N and onto the A complex (hole transfer processes are also possible but less dominant).

Given the semiconducting character of the bridge, the dielectrically screened Coulomb interaction between the D hole and the bridge electron is of manifest importance. This is modeled by the interaction

$$\mathcal{H}_C = -\sum_{j=1}^{N+1} \frac{e^2}{\epsilon j a}[\sum_\sigma X_{\sigma\sigma}]n_j \qquad (6)$$

where $X_{\sigma\sigma} = |D\sigma><D\sigma|$, and n_i is the electron occupancy at site i, and ϵ is the high frequency dielectric constant. There are two important effects: (i) For sufficiently small interaction ($V_c = e^2/(\epsilon a) \leq 1$ eV in practice), the modification of the bridge wave functions leads to a multiplication of V_D by $< BA|\bar{B}A >$ where $|\bar{B}A >$ is the filled valence sea in the presence of the D hole. This is directly analogous to the orthogonality catastrophe of the core level x-ray absorption problem. The effects of this on H_{DA} are shown in Fig. 2(b). Effectively, small V_c reduces V_D and thus enhances H_{DA}. (ii) For larger V_c, Coulomb binding overtakes Kondo coupling, and the stronger binding reduces H_{DA}.

Finally, we introduce coupling to local vibrational modes of the D/A complexes. We make the harmonic approximation for the phonons, and treat the displacements classically, adding to our model

$$\hat{H}_{el,ph} = \lambda \sum_\sigma (x_D X_{\sigma\sigma} + x_A a_\sigma^\dagger a_\sigma) \qquad (7)$$

where λ is the electron-phonon coupling constant, x_D and x_A are the nuclear coordinates, and we add a harmonic potential $\frac{K}{2}\left(x_D^2 + x_A^2\right)$. After the substitution $x_{D/A} \rightarrow \lambda/K \tilde{x}_{D/A}$, with dimensionless coordinates $\tilde{x}_{D/A}$, the Hamiltonian depends only on a single parameter λ^2/K. By neglecting electron-phonon coupling within the bridge [30], we have calculated the total electronic energy of the groundstate and first excited state (two state model) as a function of the nuclear coordinates. These constitute the Born-Oppenheimer potential energy surfaces (PES) for the nuclear motion of the two Anderson impurities. The resonance splitting at the transition state is $2H_{DA}$ [1].

In Fig. 3, we compare with the electron-only Mulliken-Hush approach. Like the Coulomb interaction discussed previously, coupling to phonons leads to an enhanced CT rate. The Mulliken-Hush result corresponds to the limit of vanishing phonon coupling. In the perturbative regime $\lambda^2/K \ll 1$, we find a linear dependence of $\ln(H_{DA}/t)$ on λ^2/K. We can roughly explain this by replacing ϵ_D in the asymptotic, electron-only problem with renormalized energy level $\tilde{\epsilon}_D = \epsilon_D + \lambda^2/K\tilde{x}_D$ and expanding $\ln H_{DA}$ to linear order in λ^2/K. This result varies little with $\tilde{x}_D$, since the reaction path approximately follows $\tilde{x}_A$.

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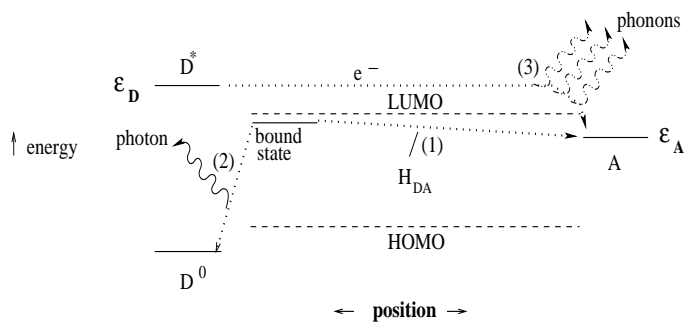
FIG. 1. Dynamics of Kondo bound state (KS) mediated CT. Photolysis leads to the excited state D^0 from which an electron is transferred to the bridge leaving a remnant D hole spin. For sufficiently rapid KS formation, KS mediated CT (1) is more rapid and likely than luminescence (2) or phonon-radiative decay to the acceptor (3).
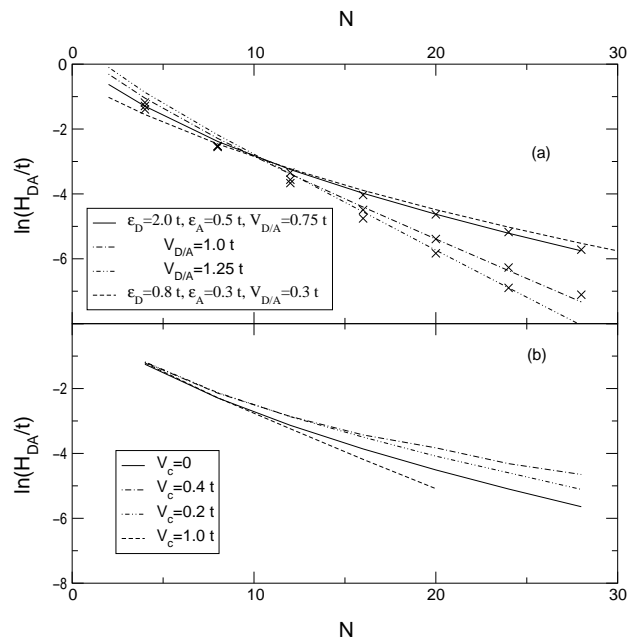

FIG. 2. Bridge length (N) dependence of electron tunnelling matrix element H_{DA} (a) Dependence of H_{DA} on bridge-donor coupling. Lines: variational method. Symbols: DMRG approach. Dotted line: ϵ_D and V_D have been reduced so as to yield the same continuum limit Kondo binding energy as the solid line. (B) Effect of Coulomb interaction V_c between the bridge electron and remnant D hole.
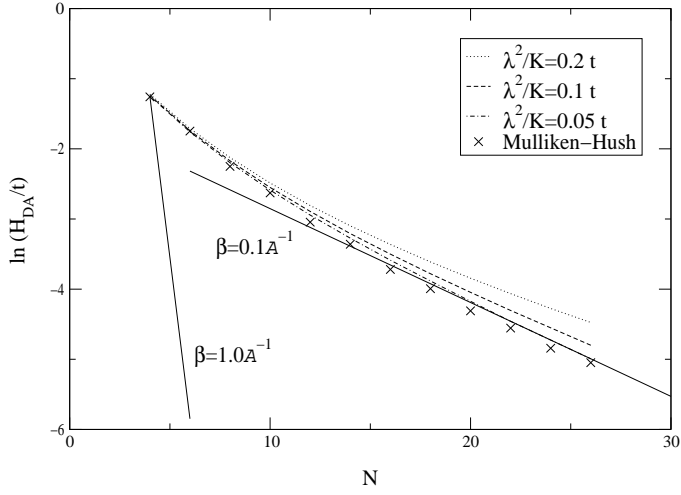
FIG. 3. Distance dependence of H_{DA}: results from the splitting of the Born-Oppenheimer surfaces are compared with the Mulliken-Hush algorithm as a function of base pairs N for parameters $\epsilon_D = 2t$, $\epsilon_A = 0.5t$, $V = 0.75t$. Thick solid lines: exponential decay assuming $a = 3.4\mathring{A}$