

Effects of initial state preparation on the distance dependence of electron transfer through molecular bridges and wires

Spiros Skourtis^{a)}*Department of Physics, University of Cyprus, 1678 Nicosia, Cyprus*Abraham Nitzan^{b)}*School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel*

(Received 21 November 2002; accepted 24 June 2003)

The dependence of electron transfer rates and yields in bridged molecular systems on the bridge length, and the dependence of the zero-bias conduction of molecular wires on wire length are discussed. Both phenomena are controlled by tunneling across the molecular bridge and are consequently expected to show exponential decrease with bridge length that is indeed often observed. Deviations from this exponential dependence for long bridges, in particular a crossover to a very weak dependence on bridge length, were recently observed experimentally and discussed theoretically in terms of thermal relaxation and dephasing on the bridge. Here we discuss two other factors that potentially affect the bridge length dependence of these phenomena. First, in experiments initiated by an initial preparation of a nonstationary “donor” state the initial energy is not well defined. A small contribution from initially populated eigenstates that are of mostly bridge-level character may dominate transmission for long bridges, resulting in weak or no bridge-length dependence. Second, in steady state experiments the distribution of initial states (for example, the Fermi distribution at the electrodes in conduction experiments) will cause deviations from exponential dependence on wire length because even a small population in higher energy states will dominate the transmission through long wires. For the first scenario we show that the crossover behavior observed for electron transfer in DNA between *G* and *GGG* species separated by *AT* chains can be largely reproduced just by initial state effects. © 2003 American Institute of Physics. [DOI: 10.1063/1.1601597]

I. INTRODUCTION

The distance dependence of electron transfer rates and yields is obviously an important attribute of the process.¹ The tunneling nature of this transfer is manifested in a characteristic exponentially decreasing behavior with increasing bridge length. Figure 1 shows a well-known simple model for this phenomenon. In Fig. 1(a) the electron transfer takes place between donor (*D*) and acceptor (*A*) species through a molecular bridge *B* represented by a set of *N* consecutive levels with nearest-neighbor coupling. In Fig. 1(b) the donor and acceptor are replaced by two metal electrodes, represented by dense manifolds of (quasifree) electron states. Both models are characterized by the bridge length *N*, the coupling *V* of the first and last bridge levels to the donor and acceptor (or the leads) states, respectively, the bridge inter-level coupling *V_B* and the electronic energy gap ΔE_B between the bridge energy ϵ_B and the injection energy (i.e., the donor energy in the electron-transfer system and the Fermi energy in the conduction case). For simplicity we take same nearest-neighbor couplings in the bridge and same couplings between the bridge and the donor/acceptor species. Also we

assume resonant donor and acceptor energies, $\epsilon_D = \epsilon_A$, and a single bridge energy. The conclusions we reach in the following do not depend on these simplifications. The Hamiltonian of the *DBA* system is

$$H_{DBA} = \epsilon_0 |0\rangle\langle 0| + \epsilon_{N+1} |N+1\rangle\langle N+1| + \sum_{l=1}^N \epsilon_l |l\rangle\langle l| + (V|0\rangle\langle 1| + hc) + (V|N+1\rangle\langle N| + hc) + \sum_{l=1}^{N-1} (V_B |l\rangle\langle l+1| + hc). \quad (1)$$

We use interchangeably the notations *D* and *A* or 0 and *N* + 1, respectively. For a transition between two metals the superexchange limit is often referred to the case where $|\Delta E_B| \gg |V_B|$. In this case both the rate in the model of Fig. 1(a) and the zero-bias conduction in Fig. 1(b) are approximately proportional to $(V_B/\Delta E_B)^{2N}$, implying length dependence

$$\text{rate, yield, current} \sim \exp(-\beta N), \quad \beta = 2 \ln(\Delta E_B/V_B). \quad (2)$$

^{a)}Electronic mail: skourtis@ucy.ac.cy^{b)}Electronic mail: nitzan@post.tau.ac.il

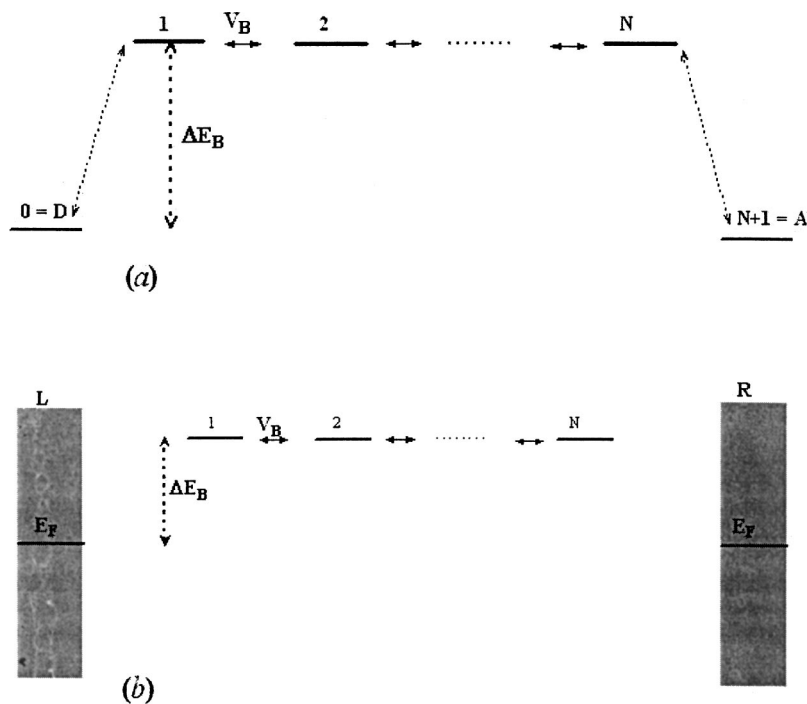


FIG. 1. Energy levels diagrams for the model considered in the present discussion: (a) electron transfer between a donor (D) and acceptor (A) states. (b) Electron transmission between two electrodes (continuous manifolds of states represented by the gray areas). See the text for further details.

The parameter β depends on the particular bridge molecule used. For many molecules it lies in the range 0.5–2.0.^{2,3}

Such exponential length dependence qualifies a molecular wire as an insulator. In contrast, coherent transfer at resonance ($\Delta E_B = 0$) does not depend on N , while classical conducting behavior shows an Ohmic length dependence of the conduction g , $g \sim N^{-1}$. Classical conducting behavior occurs when dephasing interactions dominate the resonant transfer, transforming a ballistic motion into a hopping, essentially diffusive, transfer.¹

In addition to these coherent and incoherent transfer limits, interesting intermediate cases have been discussed theoretically and demonstrated experimentally. These cases show a crossover from the exponential N dependence that characterizes off-resonance coherent transfer, to a behavior described by $(A + BN)^{-1}$ with A and B constants. In phenomenological approaches this behavior is accounted for by a superposition of two processes, coherent tunneling that dominates the transfer for small N and drops exponentially as N increases and activation onto the bridge followed by incoherent hops along it.^{4,5} The constant A is related to the thermal activation time, and for intermediate values of N it may happen that $A \gg BN$ and that the transfer rate or yield beyond the crossover from the exponential behavior may appear practically independent (within experimental error) of the bridge length.⁶ In the limit of large N the transfer (or conduction) assumes the Ohmic, N^{-1} behavior. These different processes do not necessarily contribute to the overall transmission in an additive way.^{7,8}

Recent experimental observations of the above-described crossover behavior lend support for this thermal mechanism. However, as is shown in the following, a crossover from exponential decrease with bridge length to a weak dependence on this length may arise also from other physical

origins. In the present paper we examine and compare two such possibilities.

(a) For processes that are initiated by a sudden preparation of the initial donor state the actual initial energy is not well defined because this state is not an eigenstate of the DBA Hamiltonian. Some (small) population must be placed on eigenstates of the DBA systems that are delocalized on the bridge. The probability that this population is detected on the other side of the bridge does not depend on the bridge length. For long enough bridge this population can dominate the observed transfer.

(b) For processes in which thermal relaxation on the donor and acceptor sites is fast, while that on the bridge can be disregarded (e.g., for a molecule suspended in vacuum between two metal leads, provided that the intramolecular vibrational relaxation is slow on the time scale of electron transport) the observed transfer rate, flux, or yield should be averaged over the initial thermal energy distribution. For higher energies closer to the bridge energies the dependence on bridge length is weaker and for energies in resonance with the bridge levels it disappears. For increasing bridge length the contribution of higher energies is more important. This implies a deviation from the exponential behavior (2) that was obtained for a given ΔE_B .

In Sec. II we examine the dependence on bridge length arising under these two scenarios that do not involve thermal relaxation on the bridge. We find that the first possibility leads to crossover from exponential to length independence that is similar to that predicted by the thermal relaxation model. In fact we show that the experimental results of Giese and co-workers⁹ on the distance dependence of electron-transfer in DNA can be fitted into this scenario. This result is compared to the second scenario where at room temperature there are marked deviations from exponential behavior, how-

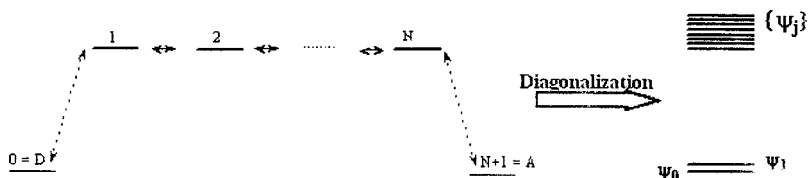


FIG. 2. Local states (left) and diagonal states (right) for the DBA model under consideration.

ever no sharp crossover behavior. It is in principle possible to distinguish experimentally between these different effects on the bridge length dependence of electron transfer and conduction. We return to this point in Sec. III.

II. ELECTRON TRANSFER FOLLOWING A SUDDEN INITIAL PREPARATION OF THE DONOR STATE VERSUS ELECTRON TRANSMISSION IN A SCATTERING PROCESS

In what follows we take $\epsilon_D = \epsilon_A \equiv \epsilon_0$. We focus on the process that follows an initial population of the state D (or 0). The actual process of electron transfer between donor and acceptor sites involves nuclear reorganization at these sites. This reorganization is the principal source of irreversibility in this process where other sources may arise from radiative or nonradiative decay of the donor and acceptor states or from electron capture from the bridge. Here we will consider a simpler model where decay of donor and acceptor states as well as possible decay of bridge states is incorporated by assigning complex values with negative imaginary parts to the corresponding energies $\epsilon_0 - i\gamma_0$, $\epsilon_1 - i\gamma_1, \dots, \epsilon_{N+1} - i\gamma_{N+1}$. The $(N+2)$ complex eigenstates and eigenenergies of H_{DBA} are denoted $|\psi_j\rangle$ and $E_j - i\Gamma_j$ (with real E_j). The time evolution that follows the initial population of the donor state is given by¹⁰

$$|\Psi(t)\rangle = \sum_{j=0}^{N+1} \langle \psi_j | D \rangle |\psi_j\rangle e^{-(i/\hbar)(E_j - i\Gamma_j)t},$$

$$|\Psi(t=0)\rangle = |D\rangle. \quad (3)$$

So that the time-dependent probabilities that the electron is in the donor/acceptor states are

$$P_D(t) = \left| \sum_{j=0}^{N+1} R_{DD}^{(j)} e^{-(i/\hbar)(E_j - i\Gamma_j)t} \right|^2 \quad (4)$$

and

$$P_A(t) = \left| \sum_{j=0}^{N+1} R_{DA}^{(j)} e^{-(i/\hbar)(E_j - i\Gamma_j)t} \right|^2, \quad (5)$$

where

$$R_{DD}^{(j)} = \langle \psi_j | D \rangle \langle D | \psi_j \rangle,$$

$$R_{DA}^{(j)} = \langle \psi_j | D \rangle \langle A | \psi_j \rangle = R_{AD}^{(j)*}. \quad (6)$$

In order to make contact later with the experimental work of Ref. 9 and the theoretical analysis of Ref. 5 we focus on the bridge-length dependence of the yield ratio

$$F = \frac{Y_A}{Y_D} = \frac{\gamma_A \int_0^\infty dt P_A(t)}{\gamma_D \int_0^\infty dt P_D(t)}. \quad (7)$$

These quantities are easily calculated from Eqs. (4) and (5),

$$Y_A = \gamma_A \int_0^\infty dt P_A(t)$$

$$= \gamma_A \sum_j \sum_{j'} \frac{R_{DA}^{(j)} R_{AD}^{(j')}}{(i/\hbar)(E_j - E_{j'} - i(\Gamma_j + \Gamma_{j'}))}, \quad (8)$$

$$Y_D = \gamma_D \int_0^\infty dt P_D(t)$$

$$= \gamma_D \sum_j \sum_{j'} \frac{R_{DD}^{(j)} R_{DD}^{(j')}}{(i/\hbar)(E_j - E_{j'} - i(\Gamma_j + \Gamma_{j'}))}. \quad (9)$$

For any bridge-length N , following diagonalization of the Hamiltonian H_{DBA} the yield Y_A and the yields ratio R are easily evaluated. It is also of interest to consider the case where rapid dephasing due to environmental interactions destroys all coherences in the eigenstates representation of the system's density matrix on a time scale fast relative to the electron transfer. In this case, following the preparation of the donor state, the $t=0$ density matrix can be taken diagonal and consequently

$$\rho_{\text{inc}}(t) = \sum_{j=0}^{N+1} R_{DD}^{(j)} |\psi_j\rangle \langle \psi_j| e^{-(1/\hbar)(2\Gamma_j)t}. \quad (10)$$

The subscript inc refers to the incoherent case. This leads to the yields

$$Y_{A,\text{inc}} = \gamma_A \sum_j \frac{|R_{DA}^{(j)}|^2}{(2/\hbar)\Gamma_j}, \quad Y_{D,\text{inc}} = \gamma_D \sum_j \frac{(R_{DD}^{(j)})^2}{(2/\hbar)\Gamma_j}, \quad (11)$$

which should be used in Eq. (7) to yield F_{inc} .

Finally, it is also of interest to examine the implication of a common approximation, the super-exchange model, to our problem. This approximation provides a good description of the transfer dynamics in the limit $|\Delta E_B| \gg |V_B|$, and is attained by replacing the $N+2$ levels description of the bridge assisted electron transfer by a two level description in which the donor and acceptor interact directly with an effective coupling determined by their coupling to the bridge and by the bridge electronic properties. The rationale behind this approximation² is that in the weak coupling limit considered the two lowest eigenenergies (or in fact their real parts) are well separated from the rest of the spectrum and the corresponding eigenfunctions $|\psi_0\rangle$ and $|\psi_1\rangle$ are dominated by the donor and acceptor states, $|0\rangle$ and $|N+1\rangle$, see Fig. 2. Consequently, $|R_{DA}^{(0)}|, |R_{DA}^{(1)}| \gg |R_{DA}^{(j)}|$, $j \neq 0, 1$ and the sums (8), (9), and (11) will be dominated by the $j=0, 1$ eigenstates. Inverting the argument, the donor and acceptor states, and their interstate dynamics can be described in the reduced representations of just these two eigenstates. The effective coupling is often identified with half the splitting between the corre-

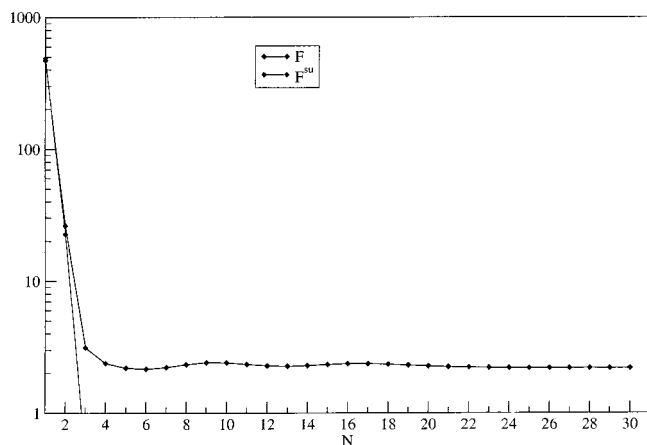


FIG. 3. Comparison of the relative yields F and F^{su} plotted against the number of bridge states N for a Hamiltonian H_{DBA} with $\epsilon_D = -i\gamma_D$, $\epsilon_A = -i\gamma_A$, $\epsilon_1 = \Delta E_B - i\gamma_1$, and $\epsilon_l = \Delta E_B$ for $l = 2 - N$. The parameters chosen are: $\Delta E_B = 0.15$ eV, $V = 0.089$ eV, $V_B = 0.03$ eV, $\gamma_D = 8 \times 10^{-5}$ eV, $\gamma_A = 4 \times 10^{-2}$ eV, and $\gamma_1 = 1 \times 10^{-2}$ eV.

sponding eigenvalues. Applying this approximation to the above-defined yields leads to equations identical to Eqs. (8) and (9) for the coherent initial state and Eq. (11) for the incoherent initial distribution, except that now the sums over j and j' are limited to the two lowest eigenstates $j = 0, 1$. We denote the yields obtained in this approximation Y_D^{su} and Y_A^{su} (or $Y_{D,\text{inc}}^{\text{su}}$ and $Y_{A,\text{inc}}^{\text{su}}$). The corresponding ratios, Eq. (7), will be denoted F^{su} and $F_{\text{inc}}^{\text{su}}$.

Figures 3 and 4 show results obtained from applying these considerations. The Hamiltonian H_{DBA} is used with $\epsilon_D = -i\gamma_D$, $\epsilon_A = -i\gamma_A$, $\epsilon_1 = \Delta E_B - i\gamma_1$ and $\epsilon_l = \Delta E_B$ for $l = 2 - N$. The values of ΔE_B , V , and V_B are those used for a DNA bridge by Bixon and Jortner.⁵ Figure 3 shows the results obtained by using Eqs. (8) and (9) for the full description as well as for the effective two state model. Figure 4 shows similar results obtained for the incoherent initial condition, Eq. (11). The following observations can be made.

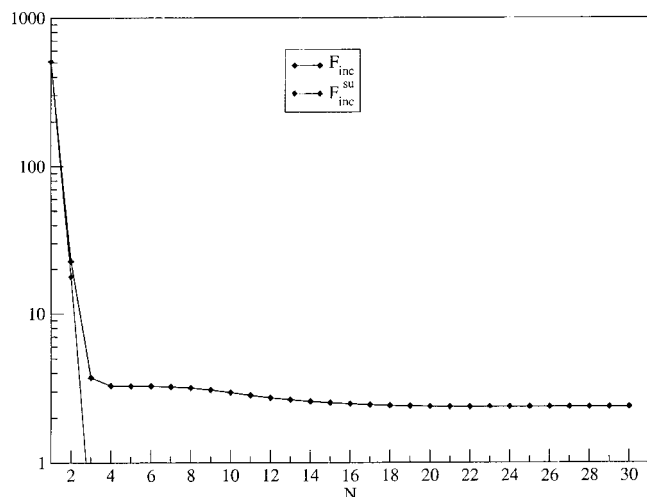


FIG. 4. Comparison of the incoherent relative yields F_{inc} and $F_{\text{inc}}^{\text{su}}$ shown against the number of bridge states for the same Hamiltonian parameters as in Fig. 3.

(a) A crossover from a fast, exponential-like decrease with increasing bridge length to independence on this length is observed both for the coherent and incoherent initial distributions in the complete $(N+2)$ -state calculation.

(b) Such a crossover is not obtained in the super-exchange approximation where the contribution of only the two lowest eigenstates to the transfer calculation is taken into account.

(c) Rapid dephasing of the initial distribution (Fig. 4) seems to have a relatively weak effect on the length dependence. The length dependence of the yield ratio is qualitatively similar in the coherent and incoherent cases; in fact it is almost the same for the parameters shown.

(d) For some choice of parameters the yield ratio may oscillate as a function of bridge length (Fig. 3). This interesting interference behavior will be probably erased in realistic situations because of dephasing interactions and inhomogeneous broadening effects.

It should be noted that the physical origin of the crossing that leads to the nonexponential behavior seen in Figs. 3 and 4 simply results from the assumption that the initial preparation process has placed a (small) fraction f of the population directly on the bridge. Such a situation follows naturally from the assumption that the initially prepared state is the zero order donor state rather than an eigenstate of H_{DBA} . Therefore, a small amount of population in eigenstates dominated by the bridge may be initially excited. In this case the behavior displayed in Fig. 4 is predicted to be temperature independent. An estimate for the length N_c at which the crossover takes place is easily obtained in terms of the parameter β , Eq. (2), and f according to $N_c = -\beta^{-1} \ln f$. Note that the dominance of bridge-like eigenstates in the electron transfer in the long bridge limit is in fact a failure of the super-exchange model.¹¹ Such behavior was also observed for time-dependent Hamiltonians $H_{DBA}(t)$ in molecular-dynamics simulations of fluctuating protein donor-bridge-acceptor systems.¹²

A related but different experimental setup in which electron transmission at a given energy can be monitored as a function of bridge length is a scattering-type experiment in which an electron is incident at a given energy on the DBA system from, say, the donor side. In this case the donor state is replaced by an incoming state of a well-characterized energy. This incoming state may represent an incident electron beam (e.g., as in Ref. 13), or it may be the bulk electronic state of a metal electrode [Fig. 1(b)]. For the setup in Fig. 1(b) the measured quantity is the conduction between the left (L) and right (R) electrodes. At zero temperature the zero bias conduction is given by the Landauer formula

$$g = \frac{e^2}{\pi\hbar} T(E_F). \quad (12)$$

E_F is the Fermi energy in the two leads, e —the electron charge and $T(E)$ is the transmission probability for an electron incident from the left electrode at energy E to emerge on the right. The more general finite temperature result reads

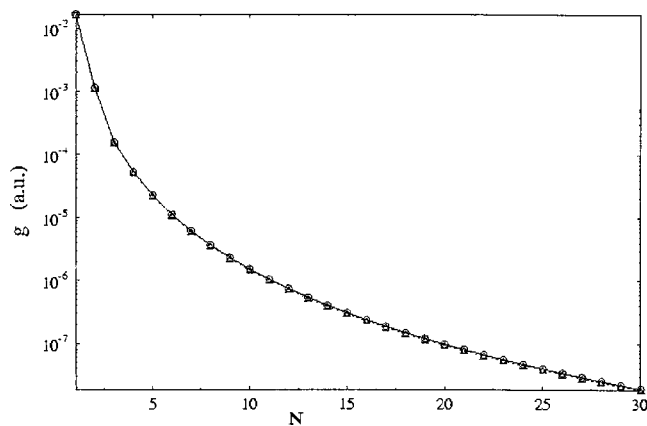


FIG. 5. The zero-bias conductance obtained from Eq. (13) for the model of Fig. 1(b), using the parameters: $\Delta E_B = E_B - E_F = 0.15$ eV, $V_B = 0.03$ eV, $\gamma_1^{(L)} = \gamma_N^{(R)} = 0.05$ eV.

$$g = \lim_{\Phi \rightarrow 0} \left[\frac{e}{\pi \hbar \Phi} \int_0^\infty dE T(E) (f(E) - f(E + e\Phi)) \right] \\ = \frac{e^2}{\pi \hbar} \int_0^\infty dE T(E) \frac{\partial f(E)}{\partial E}, \quad (13)$$

where $f(E)$ is the Fermi distribution and Φ the voltage drop.

Suppose that only state 1 of the bridge is coupled to the left lead, and only state N to the right lead. Then $T(E)$ is given by^{14,15}

$$T(E) = |G_{N1}(E)|^2 \gamma_1^{(L)}(E) \gamma_N^{(R)}(E), \quad (14)$$

where $\gamma_1^{(L)}(E)$ and $\gamma_N^{(R)}(E)$ are the decay widths of bridge levels 1 and N associated with their coupling to the corresponding left and right leads. The dependence on bridge length is obtained from the N dependence of $|G_{N1}(E)|^2$ and it is an exponential decay as in Eq. (2) if $E \neq E_B$. At finite temperatures different injection energies contribute according to Eq. (13) and there is a marked deviation from the exponential behavior obtained at $T=0$, as is seen in Fig. 5. Note that in this case we do not observe a sharp crossover from exponential to no or weak N dependence. The reason for the different bridge dependence obtained for this experimental setup is that the initial electron energy of each incoming donor state is well defined and there is no initial population on the bridge.

III. DISCUSSION AND CONCLUSIONS

The dependence of bridge assisted electron transfer on the molecular bridge length and the dependence of molecular wire conduction on the wire length are obviously interesting and important attributes of these processes. In particular the crossover from exponential to very weak length dependence for increasing bridge lengths has attracted much attention recently, and was rationalized by thermal relaxation and dephasing processes in the bridge. In the present paper we have identified two other factors that affect the bridge length dependence. Both are related to the fact that the injection energy is an important parameter in this consideration.

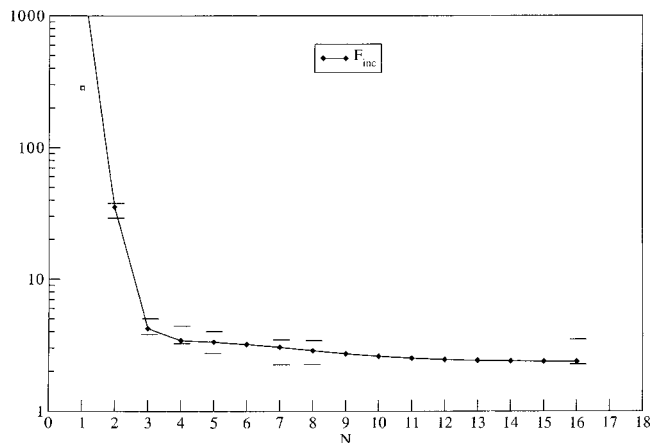


FIG. 6. The relative yield F_{inc} as a function of the number of bridge states for a Hamiltonian H_{DBA} with $\epsilon_D = -i\gamma_D$, $\epsilon_A = -i\gamma_A$, $\epsilon_l = \Delta E_B - i\gamma_l$, and $\epsilon_j = \Delta E_B$ for $l=2-N$. The parameters chosen are: $\Delta E_B = 0.15$ eV, $V = 0.089$ eV, $V_B = 0.03$ eV, the same as those used by Bixon and Jortner (Ref. 5) to fit the experimental results of Ref. 9, and $\gamma_D = 2.935 \times 10^{-5}$ eV, $\gamma_A = 5.87 \times 10^{-2}$ eV, and $\gamma_l = 2.2 \times 10^{-3}$ eV. The error bars are the experimental results of Ref. 9. The $N=1$ point represented by an open square is an experimental lower bound to the actual yield ratio.

The first factor (see Figs. 3 and 4) arises not from the physical nature of the system but from the choice of experimental setup and experimental observable. In an experiment characterized by a sudden (on the experimental time scale) preparation of the initial zero order (“donor”) state the energy is not well defined, some eigenstates dominated by the bridge are also excited (viewed as a tunneling process, these are “above barrier” states), and their contribution to the transmission may dominate the electron transfer for long bridges. The relative importance of this contribution to the observed electron transfer depends of course on the system parameters. In fact, with a reasonable choice of parameters this model can successfully reproduce the experimental results of Giese *et al.*⁹ for hole transfer in DNA duplexes consisting of Guanine donor and acceptor states separated by Adenine–Thymine bridges of varying lengths. In Ref. 9 the yield ratio of the reaction $G^+(AT)_N(GGG) \rightarrow G(AT)_N(GGG)^+$ was measured as a function of bridge length N and the relative yield was found to decrease exponentially for $N < 3$ and to converge to a value of 2.5 ± 0.5 for $N > 3-4$. In the corresponding model given by the Hamiltonian H_{DBA} [Eq. (1)] the hole–donor state of G^+ corresponds to state $|0\rangle$, the hole–acceptor state of $(GGG)^+$ is the state $|N+1\rangle$, and the intermediate Adenine–hole A^+ states are represented by the bridge states $\{|l\rangle\}$. We apply the incoherent model discussed in Sec. II so that the yield ratio is modeled by F_{inc} , since the nature of the preparation process in Ref. 9 suggests rapid loss of electronic coherence. Using (as in Figs. 3 and 4) the parameters of Bixon and Jortner⁵ for ΔE_B , V , and V_B it is possible to fit the experimental data of Giese *et al.* by setting $\gamma_j = 0$ for $j=2, \dots, N$ and varying γ_0 , γ_1 and γ_{N+1} (see Fig. 6). Note that we did not make an exhaustive search for the best fitting parameters as our main purpose here is to demonstrate the potential applicability of the suggested model. Also, it should be emphasized that this observation by no means implies that the present model is

the correct interpretation of this experiment, only that it may offer a possible alternative.

The first factor discussed above plays a potential role in transient experiments following an initial state preparation. The second factor (see Fig. 5) associated with initial thermal distributions and is potentially important also in steady state experiments. It follows from the simple observation that in most experimental situations the initial distribution of “donor states” is not limited to a single energy even in a long time experiment where the energy can in principle be well defined. In molecular conduction the initial distribution is determined by the temperature and consequently so is the resulting dependence on wire length.

It should be kept in mind that in realistic systems, effects of initial thermal distribution or of sudden preparation of the initial distribution may coexist with thermal relaxation effects. The resulting bridge length dependence will reflect the combination of these factors. Furthermore, in most experimental systems changing the bridge length dependence may affect the bridge electronic structure (within the simple model considered here—the parameters V_B and ΔE_B). Further experimental studies of bridge length dependence of electron transfer and transmission will provide a desirable tool in elucidating the mechanism of these processes.

ACKNOWLEDGMENTS

This research was supported by the US–Israel Binational Science Foundation, by the Israel Ministry of Science, and

by the Israel Science Foundation, by the University of Cyprus, and by the Institute of Chemical Physics, TAU. The authors thank Dr. M. Galperin for his help in producing Fig. 5 and Professor M. Bixon and Professor J. Jortner for helpful discussions.

¹ See for a review, e.g., A. Nitzan, *Annu. Rev. Phys. Chem.* **52**, 681 (2001).

² See for a review, e.g., S. S. Skourtis and D. N. Beratan, *Adv. Chem. Phys.* **106**, 377 (1999).

³ More generally, an additional length dependence may arise from the distance dependence of the reorganization energy, see W. B. Davis, S. Hess, I. Naydenova, R. Haselsberger, A. Ogrodnik, M. D. Newton, and M. E. Michel-Beyerle, *J. Am. Chem. Soc.* **124**, 2422 (2002).

⁴ B. Giese, *Acc. Chem. Res.* **33**, 631 (2000), and references therein.

⁵ M. Bixon and J. Jortner, *Chem. Phys.* **281**, 393 (2002), and references therein.

⁶ A residual exponential drop may be imposed on this kinetic regime if the electron is exposed to additional loss processes on the bridge (for example, electron capture by a surrounding solvent, e.g., water).

⁷ A. K. Felts, W. T. Pollard, and R. A. Friesner, *J. Phys. Chem.* **99**, 2929 (1995).

⁸ D. Segal, A. Nitzan, W. B. Davis, M. R. Wasilewski, and M. A. Ratner, *J. Phys. Chem. B* **104**, 3817 (2000).

⁹ B. Giese, J. Amaudrut, A.-K. Kohler, M. Spormann, and S. Wessely, *Nature (London)* **412**, 318 (2001).

¹⁰ Note that $|\psi_0\rangle$, the lowest energy eigenstate (see Fig. 2), should not be confused with $|0\rangle$, the donor state.

¹¹ Q. Xie, G. Archontis, and S. S. Skourtis, *Chem. Phys. Lett.* **312**, 237 (1999).

¹² S. S. Skourtis, Q. Xie, and G. Archontis, *J. Chem. Phys.* **115**, 9444 (2001).

¹³ L. G. Caron, G. Peruzzo, G. Bader, and L. Sanche, *Phys. Rev. B* **33**, 3027 (1986).

¹⁴ V. Mujica, M. Kemp, and M. A. Ratner, *J. Chem. Phys.* **101**, 6849 (1994).

¹⁵ V. Mujica, M. Kemp, and M. A. Ratner, *J. Chem. Phys.* **101**, 6856 (1994).