A Superexchange-Mediated Sequential Hopping Theory for Charge Transfer in DNA

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A formulation that readily allows quantitative comparisons with experimental chemical yields in long-range charge transfer in DNA is developed. The theory is based on a superexchange-mediated sequential hopping model that takes into account the multistep charge migrations (hopping) among guanine bases and the individual substep of superexchange (tunneling) through adenines and/or thymines. An exact Ohm's law is established for kinetic multistep hopping processes, while the scattering matrix technique is exploited to determine the coherent unistep contributions. Presented are also the quantitative comparisons with the experimental measurements in some DNA molecules involving intrastrand and/or interstrand charge transfer processes in aqueous solution. The dependence of product yield on both the length and the sequence of DNA is clearly demonstrated.

I. Introduction

Understanding of long-range charge transfer in DNA is of central significance for the control and repair of DNA oxidative damage[1,2] and for the development of DNA-based molecular technology.[3,4] Despite a large number of experimental[5−10] and theoretical[9−18] studies, the mechanism of the long-range charge transfer in DNA remains a challenge due to the complexity of various lengths and sequences of the molecules, together with their water environment.

In a DNA molecule, four bases adenosine (A), guanosine (G), thymidine (T), and cytidine (C), participating in Watson−Crick pairing as AT and GC, are arranged in a specified double strand sequence. The long-range charge transfer in a DNA sequence involves an oxidative hole charge hopping successively from one G base to the next G, either adjacent or nonadjacent, until it reaches the hole acceptor or a triple GGG unit. There are no other oxidized bases found except for G^+ (actually $G^{+\bullet}$) during the charge transfer processes.[5−10] This experimental fact is in agreement with the redox potentials of G^+/G, C^+/C, A^+/A, and T^+/T, which are estimated as 7.77, 8.68, 8.26, and 8.87 eV, respectively.[19] Thus, the local AT segment constitutes a potential barrier between two charge hopping G-base sites. The long-range charge transfer in a DNA may therefore be treated as a problem of hole transfer/transport in a specified potential (cf. Figure 1) that consists of a sequence of barriers (AT segments) and wells (GC pairs). The more base pairs the AT segment has, the wider the barrier is.

The charge transfer dynamics and its mechanism are also greatly influenced by the solvent such as water surroundings. The local electronic energy at each base unit is fluctuated due to its interaction with surrounding water molecules and coupling with the vast numbers of vibrational/librational motions in DNA. The energy fluctuation leads to decoherence or dephasing that is crucially important to the long-range charge transfer dynamics. However, for a given strength of energy fluctuation, the dephasing effect at each base site depends strongly on the energy difference between the charge carrier and the base. The effective dephasing rate decreases dramatically as the detuning increases.[20]

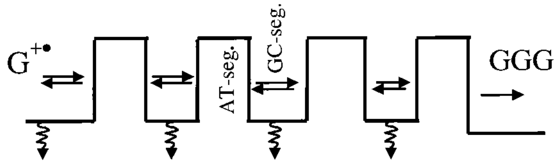

Figure 1. Schematic diagram for the sequential tunneling model of long-range charge transfer in a DNA sequence. Each potential barrier or well represents a local AT or GC segment, with its height or depth being determined by the oxidation energy and its width by the number of local base pairs. The model assumes that the charge tunnels coherently through each AT segment and dephases completely at each G base site, at which side-reaction of $G^{+\cdot}$ may also occur. The forward and backward arrows denote the coherent charge-transfer wave function amplitudes used in transfer matrix representation (cf. eq 15).

Note that the redox potential energy difference between G^+/G and any of others is much large compared with room temperature thermal fluctuation. Thus, the transferring of charge from one G to another G base is operated in on-resonance, while its passing through the AT segment between two G bases is in far-off-resonance. As a result of frequency-dependent dephasing effect, the former (on-resonance process) is largely incoherent and termed as hopping, while the latter (off-resonance process) is largely coherent and termed as tunneling or superexchange. These arguments lead to the superexchange-mediated sequential hopping model of long-range charge transfer in DNA. This picture has been widely used recently[12−16] and will also be adopted in this work. In other words, the following two distinct limiting processes will be treated separately and then combined. One is the incoherent sequential (multistep) G−G hopping and another the coherent unistep (superexchange) tunneling through the AT segment in between. Conventionally, the former is described by a multistep kinetic rate formulation, while the latter is described by the Marcus electron transfer theory.[12−18] This paper will demonstrate the coherent scattering matrix technique as an alternative approach to the superexchange in long-range charge transfer in DNA.

The remainder of this paper is organized as follows. In section II we start with the conventional multistep kinetic rate description of the incoherent sequential G−G hopping processes. The main contributions in this section are the derivation of an

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analytical formulation for the chemical kinetic rate product yields, and further, the establishment of an exact Ohm's law for those experimentally measurable quantities. The latter result also suggests the use of transport theory in mesoscopic physics,[21−25] such as the coherent scattering matrix method in section III, as an alternative approach to treat the effect of coherent AT segment on the chemical yields. Thus, section III finalizes a simple and explicit expression to evaluate the product yields of long-range charge transfer in DNA with arbitrary lengths and sequences. In section IV, the theoretical formulation is compared to the experiments of Giese and co-workers.[9,10] Together with some comments on the relation between the present approach and the conventional long-range charge transfer theory, this paper is finally concluded in section V.

II. Incoherent Sequential G−G Hopping Processes: Kinetics versus Ohm's Law

A. The Background − Kinetic Rates Scheme. As mentioned earlier, the superexchange-mediated sequential hopping model allows to treat the incoherent and coherent, two theoretical limiting processes, separately. In this section, we focus on the first one, the incoherent sequential charge hopping from one guanine G to another G, by using the following commonly adopted kinetic scheme[13,16]

$$\begin{array}{llll} \mathrm{G} \overset{k_1}{\rightleftarrows} & \mathrm{G} \cdots \overset{k_{N-1}}{\rightleftarrows} & \mathrm{G} \overset{k_N}{\rightleftarrows} \mathrm{GGG} & \\ \downarrow \gamma_1 & \downarrow \gamma_2 \cdots & \downarrow \gamma_N & \\ \mathrm{P}_1 & \mathrm{P}_2 \cdots & \mathrm{P}_N & \end{array} \tag{1}$$

The charge donor is the G^+ at the first guanine site, while the acceptor is a triple guanine GGG segment. Implied in eq 1 are also $k'_j = k_j$; except for $k'_j = 0$, for the backward reaction rates. The kinetic scheme eq 1 is consistent with Figure 1 in which the tunneling (superexchange) through an individual AT segment is characterized by a kinetic rate k_j. These unistep coherent tunneling rates will be investigated in the next section. In eq 1, P_j denotes the byproduct with the generation rate of γ_j due to the reaction of the G^+ cation at the jth potential well site (cf. Figure 1) with the surrounding water molecules.

Let us denote $\mathbf{G}(t)$ as the population vector for the charge at various G sites, and $\mathbf{P}(t)$ as that for the byproducts. The population for the long-range charge transfer to the acceptor GGG site is denoted as $P_{\mathrm{GGG}}(t)$. The charge is initially at the donor G site, i.e., $G_j(0) = \delta_{j1}$, and $P_j(0) = P_{\mathrm{GGG}}(0) = 0$. The kinetic scheme in eq 1 amounts to the following relations:

$$P_j(t) = \gamma_j \int_0^t \mathrm{d}\tau\, G_j(\tau) \tag{2a}$$

$$P_{\mathrm{GGG}}(t) = k_N \int_0^t \mathrm{d}\tau\, G_N(\tau) \tag{2b}$$

and

$$\dot{\mathbf{G}}(t) = -\Lambda \mathbf{G}(t) \quad \text{or} \quad \mathbf{G}(t) = \exp(-\Lambda t)\mathbf{G}(0) \tag{3}$$

Here, Λ is a symmetric and tridiagonal rate matrix. Its nonzero elements are

$$\Lambda_{jj} = \gamma_j + k_j + k_{j-1}; \quad \Lambda_{j+1,j} = \Lambda_{j,j+1} = -\,k_j \tag{4}$$

The initial condition to eq 3 is $G_j(0) = \delta_{1j}$. The Laplace transform of eq 3 reads then

$$(s\mathbf{1} + \Lambda)\tilde{\mathbf{G}}(s) = (1, 0, \cdots 0)^T \tag{5}$$

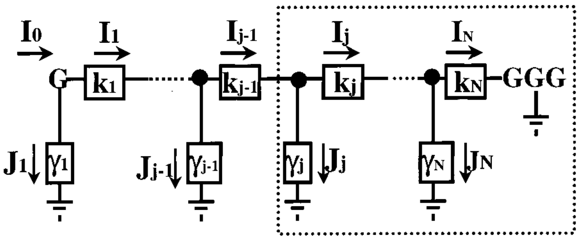

Figure 2. The electric conductances $\{k_j, \gamma_j\}$ connecting configuration that is equivalent to the kinetic rate scheme (eq 1) and maps the normalized DC currents, J_j/I_0 and I_n/I_0, to the stationary chemical yields, Y_j and Y_A, respectively (eq 11).

Here, the superscript T denotes matrix transpose, and

$$\tilde{\mathbf{G}}(s) \equiv \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st}\mathbf{G}(t) \tag{6}$$

Many experiments have involved the measurements of stationary chemical yields $Y_j = P_j(\infty)$ of the competing byproducts and $Y(GGG) = P_{\mathrm{GGG}}(\infty)$ of the charged (i.e., oxidized) acceptor molecules.[9,10] With eqs 2 and 6, these chemical yields can be expressed as

$$Y_j = \gamma_j \tilde{G}_j(0); \quad Y(\mathrm{GGG}) = k_N \tilde{G}_N(0) \tag{7}$$

The normalization reads as $Y(\mathrm{GGG}) + \sum_j Y_j = 1$. The remainder of this paper will focus on these experimental observations.

B. Chemical Yields versus Ohm's Law. This subsection aims at the analytical expressions for the chemical yields, which are further related to the normalized electric currents via a direct mapping between the kinetic rates and the conductances. To obtain the expressions for chemical yields (eq 7), we shall solve (cf. eq 5)

$$\Lambda\tilde{\mathbf{G}}(0) = (1, 0, \cdots, 0)^T \tag{8}$$

The analytical solution to eq 8 can be obtained via setting the tridiagonal symmetric rate matrix to be $\Lambda \equiv \mathbf{L}^T\mathbf{L}$, where $\mathbf{L}$ is the lower trigonal. As Λ is tridiagonal, the nonzero elements in $\mathbf{L}$ are only those of L_{jj} and $L_{j+1,j}$, and can be determined easily via its definition. The solution to eq 8 can thus be obtained via solving first $\mathbf{L}^T x = (1, 0, \cdots, 0)^T$ and then $\mathbf{L}\tilde{\mathbf{G}}(0) = x$.

After some simple algebra, the analytical expressions for the desired chemical yields (eq 7) can be arranged as follows:

$$Y_1 = \frac{\gamma_1}{\Gamma_1}, \quad Y_j = \frac{\gamma_j}{\Gamma_j}\prod_{l=1}^{j-1}\frac{\Gamma_l - \gamma_l}{\Gamma_l}; \quad j > 1 \tag{9a}$$

$$Y(\mathrm{GGG}) = \prod_{l=1}^{N}\frac{\Gamma_l - \gamma_l}{\Gamma_l} \tag{9b}$$

with

$$\Gamma_N \equiv \gamma_N + k_N, \quad \Gamma_j = \gamma_j + \frac{\Gamma_{j+1}k_j}{\Gamma_{j+1} + k_j}; \quad j < N \tag{9c}$$

The physical meaning of Γ_j that is defined in the inward-recursion relation eq 9c will be given soon. Obviously, the chemical yields (eq 9) depend only on the rate ratios k_j/γ_1 and γ_j/γ_1, with $j = 1, \cdots, N$.

The significance of the analytical solutions to Y_j (eq 9a) and Y(GGG) (eq 9b) can further be recognized as they amount respectively to the normalized DC electric currents J_j/I_0 and I_N/I_0 in Figure 2. Here, the kinetic rates k_j and γ_j are viewed as electric conductances (i.e., inverse resistances), which are connected in the same configuration as the kinetic rate scheme in eq 1. As a result, Γ_j (eq 9c) amounts to the subtotal electric conductance inside the dotted frame in Figure 2. Note that the above rate-to-conductance mapping is up to a common constant (cf. eq 13 and its comments followed), which is, however, irrelevant to either the chemical yields $\{Y_j, Y(\mathrm{GGG})\}$ or to the normalized electric currents $\{J_j/I_0, I_N/I_0\}$ in Figure 2. The electric currents involved in Figure 1 satisfy

$$J_j/I_{j-1} = \gamma_j/\Gamma_j, \quad I_j/I_{j-1} = (\Gamma_j - \gamma_j)/\Gamma_j \tag{10}$$

The above relations lead to the expressions of J_j/I_0 and I_N/I_0 that are exactly the same as those of Y_j (eq 9a) and $Y(\mathrm{GGG})$ (eq 9b), respectively:

$$Y_j = J_j/I_0, \quad Y(\mathrm{GGG}) = I_\mathrm{N}/I_0 \tag{11}$$

We have thus established the Ohm's Law of kinetic rate theory—the exact mapping between the chemical yields (eqs 9) and the normalized DC currents (eq 11).

III. Unistep Tunneling through AT Segments: Coherent Scattering Matrix Approach

A. Comments on Coherent Transfer Parameters. We are now in the position to formulate the unistep rate k_j that characterizes the charge superexchange tunneling through a specified AT segment. The key quantity involved in the following theoretical development will be

$$T_j \equiv k_j/(\gamma_d + k_j) \tag{12}$$

The relative kinetic rate required for eq 1 or 9 is then $k_j/\gamma_d \equiv T_j/(1 - T_j)$. Note that the side reaction rate used in eq 12 is $\gamma_d \equiv \gamma_1$ for the donor G, instead of γ_j for the jth bridge G base. A desired expression of T_j (cf. eq 18), in terms of the local length and sequence of any specified AT segment in a DNA molecule, will be formulated via the coherent scattering matrix approach in the next subsection. To justify the approach to be used, we shall in this subsection make some comments on the significance of T_j (eq 12).

In view of the established mapping between the kinetic rate and electric conductance (inverse resistance), the branching parameter T_j (eq 12) may amount to the coherent charge transmission coefficient in mesoscopic transport theory.[21−25] The justification follows. For a coherent conductor with T_j as its transmission coefficient, the Landauer's electric resistance reads as[21,22]

$$R_j = (h/e^2)(1 - T_j)/T_j \tag{13}$$

Here, h is Planck's constant and e the electron charge. The rate-to-conductance mapping is given explicitly as $k_j/\gamma_d \equiv (h/e^2)R_j^{-1}$, with the common scaling parameter of $\gamma_d \equiv \gamma_1$. The total electric resistance measured for N coherent conductors that are *incoherently connected in series*, assuming $\gamma_2 = \cdots = \gamma_N = 0$, is given as $R = \sum R_j + R_c$, where $R_c \equiv h/e^2$ is the so-called contact resistance resulting from the measurement.[21−24] By denoting $R = (h/e^2)/T_\mathrm{eff}$, the effective total transmission coefficient is then obtained as $T_\mathrm{eff} = [\sum(1 - T_j)/T_j + 1]^{-1}$. This is exactly the expression for charge transfer yield $Y(\mathrm{GGG})$ (eq 9b) in the special case, $\gamma_2 = \cdots = \gamma_N = 0$, of study. Obtained in this case is also the conventional Ohm's law of sequential hopping rate: $k_\mathrm{eff}^{-1} = \sum k_j^{-1}$. Here, $k_\mathrm{eff} \equiv \gamma_d T_\mathrm{eff}/(1 - T_\mathrm{eff})$ (cf. eq 12).

Traditionally the superexchange rate k_j is treated via the Marcus electron transfer theoretical framework and, in terms of nonadiabatic coupling strength, solvent reorganization and nuclear Franck−Condon factors.[12−18] In the next subsection, we shall adopt the scattering matrix approach widely used in the quantum transport society.[21−25] The key quantity here is T_j (eq 12), which, as discussed earlier, can be considered as the coherent transmission coefficient in the quantum transport theory. Note that $k_j \propto T_j$ only if $T_j \ll 1$. Physically, T_j is, however, more fundamental than k_j, especially in relation to the DNA-based nanodevice applications.

Care must be taken as the same terminology "transmission coefficient" has also been used in the classical thermal activation rate theory for the probability of successful events of the transition complex converting into reaction product. In this work, the transmission coefficient T_j is referred to the probability of coherent charge being tunneled through a specified AT segment (or a potential barrier in Figure 1).

B. Scattering Matrix Approach to Coherent Transmission Coefficients. We shall make use of the simplest coherent transport scattering matrix technique[26] to formulate the coherent transmission coefficient T_j. The final expression will be written in terms of T_A and T_T for the smallest AT- and TA-bridge units:

$$T_\mathrm{A}: \quad \text{donor} - \genfrac{}{}{0pt}{}{\mathrm{A}}{\mathrm{T}} - \text{acceptor} \tag{14a}$$

$$T_\mathrm{T}: \quad \text{donor} - \genfrac{}{}{0pt}{}{\mathrm{T}}{\mathrm{A}} - \text{acceptor} \tag{14b}$$

and their numbers n_A and n_T in the considered jth AT segment. Physically, the parameters T_A and T_T amount to the charge transfer yields for the systems (eq 14) being assumed the special cases of eq 1. The difference between the intrastrand and interstrand tunnelings may also be distinguished locally and will be discussed later. The resulting expression of T_j or k_j (cf. eq 18 or 19) will then be used together with eq 9 to fit for the parameters T_A and T_T in a series of DNA sequences under the same experimental condition. By doing that, the complications of nonadiabatic coupling strength, solvent reorganization and nuclear Franck−Condon factors involved in the standard Marcus electron transfer theory[12−18] may be properly taken into account for via T_A and T_T. Nevertheless, the ultimate justification of the following scattering matrix approach to T_j will be up to the experimental scrutiny (cf. section IV).

In scattering matrix formulation, the coherent transfer is most conveniently described in terms of the forward (backward) amplitudes a_j (a'_j) and a_{j+1} (a'_{j+1}) of the charge wave function (or the arrows in Figure 1) before and after the jth AT segment (potential barrier) in consideration. We have[23,26]

$$\begin{bmatrix} a_{j+1} \\ a'_{j+1} \end{bmatrix} = \frac{1}{t_j}\begin{bmatrix} 1 & r_j \\ -r_j & 1 \end{bmatrix}\begin{bmatrix} a_j \\ a'_j \end{bmatrix} \equiv \mathbf{T}_j\begin{bmatrix} a_j \\ a'_j \end{bmatrix} \tag{15}$$

Here, t_j and r_j are the transmission and reflection amplitudes, respectively.

$$t_j \equiv T_j^{1/2}, \quad r_j \equiv i(1 - T_j)^{1/2} \tag{16}$$

The second identity in eq 15 defines the transfer matrix $\mathbf{T}_j$. The evaluation of T_j is therefore equivalent to determine $\mathbf{T}_j$ and vice versa. We shall also denote $\mathbf{T}_\mathrm{A}$ and $\mathbf{T}_\mathrm{T}$ as the coherent transfer matrices for eqs 14a and 14b, respectively. Note that the transfer matrix is different from the scattering S-matrix. The latter connects the outgoing wave $\{a_{j+1}, a'_{j+1}\}$ with the incoming wave $\{a_j, a'_{j+1}\}$ and is more readily generalized to multidimensional and/or partially incoherent systems.[21−25,27,28]

It is well-known that a coherent transfer matrix can be expressed as the products of its coherent composite coherent transfer matrices.[23,26] It is also easy to show that for a set of transfer matrices of the form in eq 15, its multiplication is commutable (Abelian group). In other words, we have

$$\mathbf{T}_j = \mathbf{T}_{\mathrm{A}}^{n_A}\,\mathbf{T}_{\mathrm{T}}^{n_T} \qquad (17)$$

Here, n_{A} and n_{T} are respectively the numbers of AT and TA base pairs in the specified AT segment. The coherent transmission coefficient can thus be obtained as

$$T_j \equiv T_j(n_{\mathrm{A}}, n_{\mathrm{T}}) = 4/(\,\lambda_{\mathrm{A}}^{n_{\mathrm{A}}}\,\lambda_{\mathrm{T}}^{n_{\mathrm{T}}} + \lambda_{\mathrm{A}}^{-n_{\mathrm{A}}}\,\lambda_{\mathrm{T}}^{-n_{\mathrm{T}}})^2 \qquad (18a)$$

where

$$\lambda_\alpha \equiv (1 + \sqrt{1 - T_\alpha})/\sqrt{T_\alpha}; \quad \alpha = \mathrm{A}, \mathrm{T}, \text{ or } x \qquad (18b)$$

Note that $\lambda_\alpha > 1$. In writing eq 17 or 18, we neglected the orientation variations of base pairs, with respect to the charge-transfer direction, stacking at different positions in DNA double-helix structure. As a result, T_{A} and T_{T} in eq 18 should be considered as a sort of mean-field parameters.

Furthermore, intrastrand and interstrand transfer processes may need to be treated differently in each of the local superexchange substeps. In the former case, two neighboring guanines at the ends of the specified AT segment are in the same strand, while in the latter case they are in different strands. For an interstrand charge transfer process, T_{A} and T_{T} may be considered to have the same value as T_{x} in the mean-field sense as described earlier.

By substituting eq 18 into eq 12, we finally obtain

$$k_j/\gamma_d = 4/(\lambda_{\mathrm{A}}^{n_{\mathrm{A}}}\,\lambda_{\mathrm{T}}^{n_{\mathrm{T}}} - \lambda_{\mathrm{A}}^{-n_{\mathrm{A}}}\,\lambda_{\mathrm{T}}^{-n_{\mathrm{T}}})^2 \qquad (19)$$

or $k_j/\gamma_d = 4/(\lambda_x^n - \lambda_x^{-n})^2$; with $n = n_{\mathrm{A}} + n_{\mathrm{T}}$, for a local intrastrand or interstrand superexchange rate, respectively. The above equation together with eq 9 constitute the final formulation for evaluating the chemical yields in the long-range charge transfer in an arbitrary DNA molecule.

IV. Comparisons with Experiments

We shall hereafter specify T_{A} and T_{T} as the intrastrand and T_x the cross-strand coherent tunneling parameters. Further simplification can be made by assuming that the deprotonation rates for the bridge guanines reacting with water are all equal: $\gamma_j = \gamma_b$; for $j \neq 1$. As a result, there are total of four parameters, $\{T_{\mathrm{A}}, T_{\mathrm{T}}, T_x, \gamma_b/\gamma_d\}$, to be determined in the following.

Table 1 presents the quantitative comparison between the present theory and experimental measurements of Giese and co-workers.[9,10] The fitting parameters are (noting that $\gamma_1 \equiv \gamma_d$ and $\gamma_j = \gamma_b$ if $j \neq 1$)

$$\{T_{\mathrm{A}}, T_{\mathrm{T}}, T_x, \gamma_b/\gamma_d\} = \{0.89, 0.97, 0.97, 0.85\} \qquad (20)$$

Shown in Table 1 are both the values of Y_1 (in parentheses) and Y(GGG). The original experimental data were reported[9,10] in terms of the effective rate $\phi = Y(GGG)/[1 - Y(GGG)]$ and the relative rate $\phi' = Y(GGG)/Y_1$. The donor G^+ and the acceptor GGG that are not shown explicitly in Table 1 are in the same strand as the top line of bridge base(s) in each of DNA sequences. Indicated in the third column are the values of N, the number of local AT-bridge segments used in eq 9.

TABLE 1: Comparison between Experimental and Theoretical Yields Y(GGG) and (Y_1)

no.	bridge	N	exptl[a,b]	theor
i	T A	1	0.97[a]	0.97
ii	AT TA	1	0.76[a]	0.77
iii	TT AA	1	0.90[b]	0.90
iv	ATGT TACA	2	0.75[a] (0.22)	0.74 (0.24)
v	TTGTT AACAA	2	0.73[b]	0.75
vi	TTGTTGTTGTT AACAACAACAA	4	0.47[b]	0.46
vii	ACAT TGTA	2	0.79[a] (0.19)	0.79 (0.13)
viii	ACGTCTGACTCGACT TGCAGACTGAGCTGA	7	0.77[a] (0.13)	0.54 (0.14)

[a] Reference 9. [b] Reference 10. The experimental relative error is about 10%.

In the sequences i-vi in Table 1, all substeps coherent tunneling (superexchange) are intrastrand processes. The experimental values of Y(GGG) in this series are used with the least-squares fit to obtain the three parameters T_{A}, T_{T}, and γ_b/γ_d in eq 20.

In the sequence vii in Table 1, the involved two coherent tunneling substeps are all interstrand processes. The relevant tunneling parameter is only T_x. With the determined value of γ_b/γ_d, the experimental Y(GGG) of this sequence gives the value of T_x shown in eq 20. In the sequence viii, all coherent substeps are also considered as interstrand processes. The theoretical yields are evaluated via the above obtained parameters T_x and γ_b/γ_d.

The reasons for the significant underestimation of the theoretical Y(GGG) for the sequence viii in Table 1 may be understood by noticing the existence of double guanines $\binom{\mathrm{CG}}{\mathrm{GC}}$ as well in the bridge. The redox potential of double guanines is lower than that of G^+/G, leading to a relatively large experimental value of Y(GGG). However, the present model did not take this favorable effect into consideration as eq 1, in which $k'_j = k_j$ had assumed that the redox potentials of bridge GC segments were all equal. We shall treat the case of $k'_j \neq k_j$ elsewhere.[29]

V. Discussion and Summary

In summary, we have derived a relatively simple formulation (eqs 9 and 19) for evaluating chemical yields in long-range charge transfer processes in DNA. As demonstrated in Table 1, the present approach can properly account for the rate dependence on both the length and sequence of a DNA strand. To elucidate the sequence dependence further, let us compare the Y(GGG) value of donor−AAGA−acceptor with that of the reversed bridge sequence, donor−AGAA−acceptor. The theoretical estimated product yields are 0.45 and 0.54, respectively, for the intrastrand charge transfer in these two sequences.

The present formulation of long-range charge transfer is developed by combining two theoretical limits. One is the complete incoherent multistep, or sequential hopping, and another the complete coherent unistep tunneling process. The generalization of the present theory to account for partial coherence is under way and will be published elsewhere.

For sequential hopping rate processes, we adopt the commonly used kinetic scheme (eq 1) and arrive at analytical expressions (eq 9), which constitute the Ohm's law for evaluating chemical yields (cf. Figure 2). This Ohm's law of kinetic rate theory, to our knowledge, has not been recognized in the literature. In the chemical kinetics community, the Ohm's law is by far only narrowly referred to the limiting case of $\gamma_b = \gamma_2 = \cdots = \gamma_N = 0$, in which the present analytical formulation reduces to $k_{\text{eff}}^{-1} = \sum_j k_j^{-1}$. Here, $k_{\text{eff}} \equiv Y(\text{GGG})/[1 - Y(\text{GGG})]$ is in the unit of γ_d. Detailed analyses on Y(GGG) for the case of $k_j = k$ in the presence of $\gamma_b \neq 0$ were reported by Ratner and co-workers[13] and by Bixon and Jortner.[16] One of the important results,[16] which has also been reproduced (not shown) via the present analytical expression, is that $Y(\text{GGG}) \propto e^{-N/N_c}$, when $N > N_c \equiv (k/\gamma_b)^{1/2}$. Therefore, in the case of $Y_1 + Y(\text{GGG}) \neq 1$ that implies $\gamma_b \neq 0$, the Ohm's law established in this work can have either *exponential* or *algebraic* size-dependence of rates.

This work further makes use of the coherent scattering matrix technique (eq 17) to superexchange rate processes. This conceptually simple idea, despite that it has been used extensively in the physical society, is, however, largely unexplored in treating charge transfers in chemical/biological systems. The connection between the present approach and the conventional long-range electron transfer (ET) theory may be established via recasting the superexchange result of eq 18 in a tight-binding description in the absence of nuclear Franck–Condon contribution. Following the Feynman treatment for tunneling through a single impurity,[30] we obtain the tunneling parameter T_α in eq 18b as $T_\alpha = 4V^2/(\Delta^2 + 4V^2)$. Here, V is the tight-binding coupling parameter between two nearest-neighbor base pairs, and Δ the energy gap between the GC (donor) and the AT (or TA) pair (bridge). Substituting this result into eq 18a, we can easily calculate the coherent transmission coefficient through arbitrary sequence of AT/TA pairs. In the weak coupling limit $V \ll \Delta$, and assumming an identical T_α for tunneling through AT and TA pairs, the conventional superexchange behavior is readily obtained as $T_j = 4(V/\Delta)^{2n}$, with a decay parameter of 2 $\ln(\Delta/V)$, as predicted by the standard long-range ET theory. Alternatively, the coherent transmission coefficient of eq 18a can also be associated with a Green's function treatment based on the tight-binding model,[27,31] resulting in $T_j = 4V^2|\,G_{1n}(\Delta)|^2$. Here, $G_{1n}(\Delta)$ is the Green's function of the reduced bridge subsystem in which the self-energy correction from the donor and acceptor is included. The conventional long-range ET theory in which $T_j = (4/V^2)|H_{\text{DA}}^{\text{eff}}|^2$ can be obtained by noting that $H_{\text{DA}}^{\text{eff}} = VG_{1n}(\Delta)V$ for the effective donor–acceptor superexchange coupling element. We have thus arrived at the desired relation between the present coherent scattering matrix approach (eq 18) and the conventional superexchange ET theory in the absence of nuclear Franck–Condon contribution. Moreover, as mentioned earlier and demonstrated via comparison with experimental results, the present parameterization approach to evaluate T_j (eq 12) may also largely take into account the complicated solvent and nuclear contributions.

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