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Distance Dependent Coherence Variation in DNA Charge-Transfer Processes

Heeyoung Kim and Eunji Sim*

Department of Chemistry and Institute of Nano-Bio Molecular Assemblies, Yonsei University, 134 Sinchondong Seodaemungu, Seoul 120-749, Korea

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We explore distance dependent variation of the coherence length relevant to DNA charge-transfer processes within $5'$-GA$_n$G$_3$-$3'$ DNA sequences. Recently developed on-the-fly filtered propagator functional path integral approach was employed to sort out transport trajectories with significant contribution and to analyze correlation between electronic states. In particular, the coherence length was quantitatively determined through characteristics of off-diagonal quantum trajectories. Simulated coherence lengths and experimentally observed rate constants [*Nature* **2001**, *412*, 318] were found to be consistent such that, up to $n = 2$, the exponential decrease of the rate constants is associated with the donor−acceptor coherence driven charge transfer. In contrast, the rate constants become insensitive to the distance for $n \geq 3$ in which donor and acceptor are no longer significantly correlated. It was also found that the coherence within a collective state governs the overall charge transfer, which is composed of a part of a sequence within the coherence length from the donor.

1. Introduction

For the past decade, tremendous efforts in molecular electronics have been accompanied by the emergence of interests in the charge transfer (CT) mechanism of electronic systems. Molecular electronic devices are designed to allow electronic properties to be controlled on a molecular level. To manipulate molecules for intended electronic properties, predictable and systematic control of the CT mechanism within a molecular structure is highly desired. It was recently found to be possible to alter the CT mechanism in DNA by varying nucleobase sequences.[1−3] Long-range CT mechanism of DNA depends on the order and the type of component necleobase pairs.[4−7] This implies that the CT mechanism is regulated by the system quantum coherence which is caused by the system configuration such as relative energies and coupling strength between electronic states as well as the friction due to the environment. Thus, the CT mechanism is specified when the degree of coherence can be estimated on the basis of the system configuration and dissipative friction. This, in turn, leads to manipulation of electronic properties as desired in molecular electronics. Systematic and quantitative assessment of the degree of coherence, however, has been relatively rare.

In this letter, degree of coherence is quantified by a coherence length (CL), which is defined as the number of correlated quantum states that form combined wavefunctions as a result of strong interference. For instance, CL of a conducting DNA sequence indicates the number of neighboring nucleobase pairs within which collective coherent states are constructed. Strong correlation facilitates CT within the collective coherent state, and thus, the coherent characteristics of the collective state function as the driving force for overall CT processes.

CT mechanisms can be classified by the degree of coherence as follows. In the incoherent hopping dominant regime, coherence of the system is negligible so that each electronic state interacts with its neighboring states only. The number of electronic states to form collective coherent states is 2, the smallest CL for charge exchange to occur. The A-hopping in DNA CT is classified as this category.[8−10] In the strongly coherent limit, however, since the entire sequence is coherent, the CL is equal to the number of electronic state of the system, and the superexchange mechanism governs the charge exchange between donor and acceptor.[11] Suppose that the entire $5'$-GA$_n$G$_3$-$3'$ DNA sequence is coherent. The CL is then equal to $n + 2$. Incoherent nearest-neighbor hopping and superexchange tunneling mechanisms have been most widely considered, and the difference between the two mechanisms seems to be clear. As far as the CL is concerned, however, intermediate values are also probable. A fraction of the CT system, that is, more than two nearest-neighbor states, may remain strongly correlated compared with the rest. In other words, there exists a CT mechanism which is driven by the partial coherence of the system. The fraction of strongly correlated states forms collective coherent states within which nearest-neighbor hopping as well as tunneling between distant states can occur. This type of intermediate CT mechanism is different from the two conventionally suggested mechanisms. Nevertheless, it is not straightforward to distinguish the three mechanisms.

In general, the CT mechanism is determined by the dependence of rate constants on the system configurations and environmental parameters such as donor−acceptor distance and temperature. The superexchange CT rate constants have been considered to exhibit dramatic exponential dependence on the distance, while incoherent hopping rate constants to be quite insensitive. For instance, based on distance dependence of rate

* Corresponding author. E-mail: esim@yonsei.ac.kr. Fax: +82-2-364-7050.

constants, Giese et al. empirically predicted that the CT within 5′-GA$_n$G$_3$-3′ be through superexchange mechanism at short distances and shifts to incoherent hopping mechanism as the number of adenine bridges increases.[8] Such an approach drew reasonable conclusion as long as the two extreme limits are concerned. On the contrary, for the case of the intermediate degree of coherence, ambiguities in determining CT mechanism become a limitation for an empirical and phenomenological analysis. Evidence of the intermediate CT mechanism was recently reported and discussed: for a long-range CT in DNA, Schuster et al. described a structural distortion dependent mechanism, that is, phonon-assisted polaron hopping.[12,13] Barton et al. investigated the role of charge delocalization over a range of electronic states in the CT using fluorescence quenching.[14,15] Zewail et al. estimated the coherence of the B transport of adenine and thymine bridging sequences to be maintained on the order of the next-neighbor base-pair distances.[16] They also suggested that the long-range CT in DNA is a slow process rather than an efficient wire-type transfer.[17] Theoretically, Conwell et al. evaluated that the electronic wavefunction over DNA structure is delocalized within five or six states constructing a polaron.[18,19]

The goal of this letter is to calculate the degree of coherence on a systematic and quantitative basis and to determine the CT mechanism of 5′-GA$_n$G$_3$-3′ in terms to the CL. To attain this goal, we employ a recently developed path integral based approach in which off-diagonal quantum trajectories are characterized.[20] The letter is organized as follows: in section 2, we discuss the path integral formalism focusing on the correlation of forward and backward trajectory with respect to the system coherence. Section 3 is devoted to the determination of the CL through the analysis into quantum mechanical pair trajectories and their quantitative contribution to CT processes. Concluding remarks appear in section 4.

2. Reduced Trajectory Space and Coherence Length

To model the CT process in DNA sequences, consider a tight-binding model system that is bilinearly coupled with a set of harmonic oscillator bath modes. The system Hamiltonian to describe DNA CT system is represented as a matrix in which energy gaps and coupling strengths between electronic states are described as follows

$$\mathbf{H_s} = \begin{pmatrix} 0 & V_{DB} & 0 & \cdots & 0 \\ V_{DB} & \Delta E_{DB} & V_{BB} & & \vdots \\ 0 & & \ddots & & 0 \\ \vdots & & V_{BB} & \Delta E_{DB} & V_{BA} \\ 0 & \cdots & 0 & V_{BA} & \Delta E_{DA} \end{pmatrix} \quad (1)$$

Environment is described by the debye form of the spectral density. We took potential parameters from ref 20.

In order to explore the CT dynamics, we evaluate the density matrix of the transport as

$$\tilde{\rho}(t) = Tr_b[e^{-iHt/\hbar}\rho(0)\,e^{iHt/\hbar}] \quad (2)$$

with $\rho(0)$ being the total initial density matrix while Tr_b denotes the trace with respect to all bath degrees of freedom. Assuming that the factorization of the initial density matrix of the system and the environment, Feynman and Vernon's influence functional path integral formalism discretizes eq 2 into a sum of products of the bare system propagator, $\mathbf{S}$, and the influence functional, $\mathbf{F}$, given by[21,22]

$$\tilde{\rho}(t) = \sum_{\substack{i \\ \text{all paths}}} \mathbf{S}(\Gamma_i^{(N)})\mathbf{F}(\Gamma_i^{(N)}) \quad (3)$$

The summation runs through all possible pair trajectories that are discretized by a time step $\Delta t = t/N$ such that the ith pair trajectory $\Gamma_i^{(N)}$ includes both the forward and the backward propagating trajectories.

Since the contributions of CT pair trajectories, that is, integrands in eq 3, are independent of each other in the summation, it is also possible to analyze and characterize individual pair trajectory selectively. Smart path generation and filtering algorithm of the recently developed on-the-fly filtered propagator functional-path integral approach allows omitting statistical sampling procedure and iteratively integrating to compute the time-evolution of the reduced density matrix with a finite bath memory, τ_m. Clearly, the contributing trajectories inherently contain dynamics information of CT processes and, in turn, the coherence of the system.[23] One issue that has to be resolved is to find the sorted trajectory property that is characteristic of the system coherence. Importance of off-diagonal trajectories in representing coherent quantum effects was discussed in terms of semiclassical treatment of chaotic quantum transport: Richter and Sieber demonstrated that, for systems with uniformly hyperbolic dynamics, inclusion of off-diagonal contributions to double-sums over classical paths gives a weak-localization correction, which arises from the coherence within quantum transport systems.[24] In addition, we previously showed that the deviation between forward and backward trajectory is strongly related to the coherence of the system.[20]

In order to emphasize the importance of the forward−backward pathway relationship, we represent a pair trajectory $\Gamma \equiv \{a_k, k = 0\cdots N\} + \{b_k, k = 0\cdots N\}$ as the sum of a forward (a_k) and a backward (b_k) pathway. We can also define deviation between the forward and backward pathways as Δ_k at kth time point; therefore, $a_k = b_k + \Delta_k$. Using this notation, we find the influence functional takes the form

$$F = \exp\left(-\sum_{k=0}^{N}\sum_{k'=0}^{k}\frac{\epsilon_{kk'}}{\hbar}\Delta_k\Delta_{k'} - i\sum_{k=0}^{N}\sum_{k'=0}^{k}\frac{\varphi_{kk'}}{\hbar}\Delta_k[\Delta_{k'} + 2b_{k'}]\right) \quad (4)$$

where $\epsilon_{kk'}$ and $\varphi_{kk'}$ are real and imaginary parts of the influence coefficients.[20] The contribution of each pair trajectory to the CT dynamics, that is, the integrand of eq 3, is determined through complex interplay between non-Markovian memory interaction and the degree-of-coherence. As shown in eq 4, owing to the negative sign in the exponent, the smaller Δ, the larger the contribution. In addition, since the degree-of-coherence diminishes with Δ, there is a maximum deviation $|\Delta|_{max}$ such that states that are within the distance of $|\Delta|_{max}$ are coherent while states that are separated further than $|\Delta|_{max}$ are incoherent. The contribution of off-diagonal trajectories that consist of incoherent pairs of forward and backward pathways is negligible and can be ignored in the path integration without accuracy loss. Following the definition of the CL, CL = $|\Delta|_{max}$ + 1. This implies that only the pair trajectories satisfying $b_k - |\Delta|_{max} \le a_k \le b_k + |\Delta|_{max}$ contribute significantly.

Determination of the CL can be performed in two directions. One approach is to perform analysis on Δ of the sorted pair trajectories when the reduced density matrix is obtained. On the other hand, there is a more practical alternative which alleviates the computation load drastically. Suppose a trajectory space $\mathbf{C}$ that includes all possible forward−backward trajectory pairs of a given Hilbert space. Define $\mathbf{C}_m$ as a subset of the $\mathbf{C}$ space so that the $\mathbf{C}_m$ includes trajectories whose forward−

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backward path difference does not exceed m sites at any time, that is, $b_k - m \leq a_k \leq b_k + m$ at any k. The CL implicates that one can obtain converged results by integrating over a reduced trajectory space of coherently linked forward−backward pair trajectories; that is,

$$\tilde{\rho}(t) \approx \sum_{\substack{i \\ [\mathbf{C}_{|\Delta|_{\max}}]}} \mathbf{S}(\Gamma_i^{(N)})\mathbf{F}(\Gamma_i^{(N)}) \tag{5}$$

In other words, by determining the smallest $\mathbf{C}_{|\Delta|_{\max}}$ space that gives rise to the converged results, one can ensure that all the important trajectories are already taken into account in path integration and that CL $= |\Delta|_{\max} + 1$.

An advantage of our approach using the forward and backward path relation in determining the CL of the system is that it is unnecessary to compute eq 5 exactly, unlike conventional approaches where numerical accuracy of $\tilde{\rho}(t)$ is crucial in using off-diagonal elements.[25] The quantum trajectory analysis allows the conclusion not to be based on the numerical accuracy of $\tilde{\rho}(t)$ itself, but rather on the trend of convergence with respect to the reduced trajectory space. As a result, the representation of the coherence is independent of the integration condition of eq 5. This leads to the choice of an arbitrary integration time step Δt for computation convenience.

3. Results and Discussion

A. Distance Dependent Reorganization Energy. The friction caused by the system−environment interaction affects the system coherence. It has been widely known that the donor−acceptor reorganization energy, λ_{DA}, due to the atomic rearrangement of the system from donor to acceptor state, changes with respect to donor−acceptor distance, d_{DA}, or the number of bridges. Therefore, the consequent CL of DNA sequences is influenced by the model distance dependence of λ_{DA}. Experimental values of the DNA reorganization energy are not yet available and even theoretical values are in dispute. Nevertheless, literature mostly suggest that λ_{DA} increases rapidly as a function of d_{DA} at short distances and levels off at longer distances.[26−28] Therefore, in this letter, we modeled λ_{DA} distance dependence in reference to the results of Siriwong et al.[28] with the following three assumptions: (1) the CT is activationless among neighboring donor and acceptor, that is, for 5′-GG$_3$-3′ sequence. (2) As A/T bridging pairs are added, λ_{DA} is increased as a function of n such that $\lambda_{DA} \propto \sqrt{n+1}$ for 5′-GA$_n$G$_3$-3′ sequence. (3) Finally, bridging diabatic potential surfaces are distributed evenly in between the donor and the acceptor.

As mentioned before, the absolute values of CL depend on the choice of λ_{DA}. Despite an ad hoc assumption made in (1), we believe that our model provides a qualitatively accurate trend of CL distance dependence. Previously, we have reported an insignificant decrease in the CL of the short-range DNA CT as λ_{DA} changes from 50 cm^{-1} to 15 000 cm^{-1}.[29,30] In other words, as long as the model of the distance dependent λ_{DA} is qualitatively accurate and found in the reasonable range quantitatively, the calculated CL can be a reliable indicator of coherence variation trends. The values of λ_{DA} used in this letter are summarized in Table 1.

B. Distance Dependent Coherence Length. DNA dimers consisting of a single type of nucleobase pairs have strong coherence. For heterogeneous dimers, however, the oxidation potential of a G/C pair is 3790 cm^{-1} lower than that of the A/T pair, which provides bias that weakens the coherence between neighboring pairs. Strong coherence between GG dimers can

TABLE 1: Distance Dependence of 5′-GA$_n$G$_3$-3′ Sequences

bridge	λ_{DA} (cm^{-1})	$\mathbf{C}_{|\Delta|_{\max}}$	collective state[a]
A	1642	$\mathbf{C}_2$[b]	**GAG$_3$**
AA	2011	$\mathbf{C}_3$[b]	**GAAG$_3$**
AAA	2322	$\mathbf{C}_2$	**GAA**AG$_3$
AAAA	2596	$\mathbf{C}_2$	**GAA**AAG$_3$
AAAAA	2844	$\mathbf{C}_2$	**GAA**AAAG$_3$

[a] Underlines represent strongly coherent subset sequences when charge is injected to the donor nucleobase pair. [b] Full trajectory space is required.
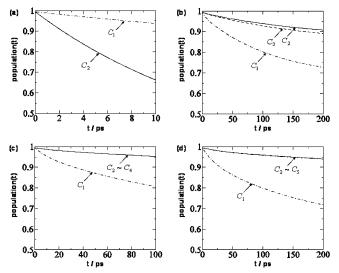

Figure 1. Time evolution of donor population of (a) 5′-GAG$_3$-3′, (b) 5′-GA$_2$G$_3$-3′, (c) 5′-GA$_3$G$_3$-3′, and (d) 5′-GA$_4$G$_3$-3′ sequences with respect to the path integration of reduced trajectory spaces. $\mathbf{C}_i$ denotes reduced trajectory spaces used in the path integration of eq 4. In order to determine the correlation within trajectory pairs, an arbitrary integration condition of $\Delta t = 1.0$ fs and $\tau_m = 6$ fs were chosen for all cases.

also be weakened by inserting A/T base pairs in between. In Figure 1a, the path integration results of 5′-GAG$_3$-3′ over $\mathbf{C}_1$ and $\mathbf{C}_2$ space differ. The disagreement implicates that owing to the strong donor−acceptor coherence, all possible pair trajectories participate in the CT process. Therefore, in the case of a single adenine bridge, the donor and the acceptor states are still quite strongly correlated such that the entire sequence 5′-GAG$_3$-3′ remains coherent and allows superexchange as well as nearest-neighbor hopping transfer.[31]

When another A/T bridge pair is added, obviously, the larger d_{DA} suppresses the coherence between donor and acceptor even further. As shown in Figure 1b, $\mathbf{C}_2$ integration supplies donor population quite close to the exact $\mathbf{C}_3$ full space integration in contrast to the large discrepancy of $\mathbf{C}_1$ integration. Nevertheless, the difference between $\mathbf{C}_2$ and $\mathbf{C}_3$ results is noticeable, which is associated with weak coherence between donor and acceptor. In other words, donor and acceptor states mediated by two adenine bridges are still moderately coherent enough to facilitate superexchange transfers.

With more than three A/T bridge pairs, the donor−acceptor coherence is no longer strong to promote superexchange transfer. In Figure 1c, only $\mathbf{C}_1$ integration result differs from the rest, that is, the integration over the $\mathbf{C}_2$ reduced trajectory space is equivalent to the full path space integration. The implication is that, for sequences 5′-GA$_n$G$_3$-3′ with $n \geq 3$, only a part of the sequence, 5′-GA$_2$-3′, is coherently linked and this partial coherence is the driving force for the CT process. In Table 1, the reduced trajectory space required to produce numerically
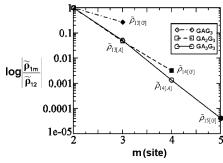
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Figure 2. Relative ratio of magnitude of stationary off-diagonal elements $|\tilde{\rho}_{1m}/\tilde{\rho}_{12}|$, $m = 2, \cdots, n + 1$ for sequences 5′-GAG$_3$-3′ (diamonds), 5′-GA$_2$G$_3$-3′ (squares), 5′-GA$_3$G$_3$-3′ (circles). In particular, solid markers correspond to the coherence between donor and acceptor. $\tilde{\rho}_{1m[\alpha]}$ denotes the off-diagonal density matrix element between the donor and α nucleobase pair at mth site. For all cases, full trajectory space was integrated. Corresponding converged integration condition of Δt and τ_m were used for each sequence. Lines are only to guide the eyes.

converged results, $\mathbf{C}_{|\Delta|_{max}}$, is listed along with the coherently linked partial sequence.

We have so far exploited the characteristics of off-diagonal trajectories to determine the CL whereas a conventional tool for investigating the CL is based on the off-diagonal density matrix elements. It is well-understood that the off-diagonal element $\tilde{\rho}_{im}$ ($i \neq m$) denotes the strength of the coherence between ith and mth states. The ratio $|\tilde{\rho}_{1m}/\tilde{\rho}_{12}|$, $m = 2, \cdots, n + 1$ describes the relative magnitude of the coherence between the donor and the mth state compared with that of the donor and its nearest-neighbor bridge. In order to compare the practicality of different approaches, we also estimated the CL of DNA CT systems by means of the off-diagonal matrix elements. Markers in Figure 2 represent the stationary $|\tilde{\rho}_{1m}/\tilde{\rho}_{12}|$ ratios. We should point out that, in order to use off-diagonal density matrix elements, converging integration conditions had to be carefully chosen to provide accurate results of eq 5, which otherwise requires a huge amount of computational efforts that scales exponentially with the system size and the propagation time.

In Figure 2, for the 5′-GAG$_3$-3′, $\tilde{\rho}_{13}$ is as large as one-fifth of $\tilde{\rho}_{12}$ indicating that the donor and acceptor are relatively strongly coherent. This agrees well with Figure 1a. For longer sequences, coherence drops exponentially with the distance such that, for 5′-GA$_2$G$_3$-3′, the donor−acceptor coherence $\tilde{\rho}_{14}$ becomes as weak as one hundredth of $\tilde{\rho}_{12}$ while substantial correlation between donor and distant bridge is still evident in terms of $\tilde{\rho}_{13}$. In fact, the coherence decreases even more rapidly than an exponential decay of the 5′-GA$_3$G$_3$-3′. The third bridge's off-diagonal element $\tilde{\rho}_{14}$ is 1000 times as small as that of the first bridge. The correlation between states decreases as a function of the distance and eventually becomes negligible; that is, the states become incoherent. Although it is necessary to discriminate coherence from incoherence, a clear guideline to draw the boundary does not exist. In this study, we set up the boundary such that the donor and the mth state are assumed to be coherent as long as $|\tilde{\rho}_{1m}/\tilde{\rho}_{12}| \geq 10^{-3}$. This is in excellent agreement with Figure 1 in that the coherence within 5′-GA$_n$G$_3$-3′ sequence is up to 5′-GA$_2$-3′ when $n \geq 3$ while the entire sequence is strongly correlated for $n < 3$.

It is obvious that, at the same distance, guanines have stronger coherence compared with the coherence between guanine and adenine. Suppose $\tilde{\rho}_{1m[\alpha]}$ denotes the off-diagonal density matrix element between guanine (the donor) and α nucleobase pair at mth site. In Figure 2, $\tilde{\rho}_{13[G]}$ is about an order of magnitude larger than $\tilde{\rho}_{13[A]}$. On the other hand, $\tilde{\rho}_{14[G]}$ is about twice as large as

$\tilde{\rho}_{14[A]}$. This implies that both the distance and the type of base pair influence the coherence greatly at short distances. Nonetheless, the coherence is weakened with the distance such that it becomes insensitive to the type of nucleobase pair at long distances.

Distance dependence of the estimated CL is consistent with the behavior of experimentally obtained rate constants. Since Giese et al.,[8] dependence of CT rate constants of 5′-GA$_n$G$_3$-3′ on d_{DA} has been understood as follows: at short distances, the CT efficiency (that is the population ratio, P$_{GGG}$/P$_G$) is highly sensitive to d_{DA} which attests to the strong coherence between donor and acceptor. At long distances ($n \geq 3$), however, the rate constant alters slightly in the range of $n = 3$ to 16. They assigned such a behavior to the incoherent hopping CT mechanism (A-hopping).[8] In other words, 5′-GA$_n$G$_3$-3′ DNA sequence exhibits coherence only up to 3 or 4 base pairs. Notice that the result coincides with the collective state driven long-range CT, that is deduced from off-diagonal trajectory analysis. Evidence of the coherent collective state or domain among DNA sequences was also discussed by others.[15,18]

For the 5′-GA$_n$G$_3$-3′ DNA CT, the entire system is coherent up to $n = 2$. Conventional picture of an entirely coherent CT system calls for superexchange tunneling between donor and acceptor. However, we have already shown that through-bridge transfers are also possible for CT systems with strong coherence.[20] Therefore, for short-range CT, we speculate that the superexchange as well as through-bridge CT constitutes the overall process. Because of the long distance spanned by three and more adenine bridge pairs, the donor−acceptor coherence is diminished and only part of the sequence remains coherent. We anticipate that the partial coherence of 5′-GA$_2$-3′ is unaltered even for $n > 5$. The coherent partial sequence plays a very important role in the overall CT mechanism because the adenine bridges that are coherent with the donor participate in the CT even though they are not directly connected to the donor. Therefore, the long-range CT mechanism is through-bridge owing to the collective coherent states rather than the A-hopping mechanism.

4. Concluding Remarks

In this letter, the distance-dependent CT mechanism over adenine bridges is described in terms of the CL on a quantitative basis. By examining the characteristics of off-diagonal trajectories, we determined the correlation strength between electronic states and, in turn, the CL of 5′-GA$_n$G$_3$-3′ DNA CT. The determined CLs were compared with those deduced from the off-diagonal matrix elements. The behavior of experimentally measured rate constants in regard to d_{DA} was discussed in conjunction with the CL variation.

Understanding long-range CT processes over diverse bridging sequences is expected to be highly useful and to contribute significantly to unraveling the relationship between system configuration and CT mechanism. Investigation of the CL for a series of bridging sequences that include not only adenine base pairs but also guanine base pairs in various positions is currently under progress. Quantitative analysis on the relevant CT mechanism and exhaustive trajectory analysis is also studied and to be presented in future publications.

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