

# Theory of Electric Conductance of DNA Molecule

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Received: December 8, 2002

Electric conductance of DNA molecules was studied theoretically. We have adopted the tight binding small polaron model and used the Landauer and the Kubo formalisms to calculate the molecular conductance both in the quasicohherent and the incoherent regime. In the experiment of the poly(dA)–poly(dT) and the poly(dG)–poly(dC) DNA molecules, a unique current–voltage ( $I$ – $V$ ) curve,  $I \propto \sinh(bV)$ , was observed. The distinct temperature dependences of the coefficient  $b$  observed in the two DNA molecules may indicate that, although the poly(dG)–poly(dC) molecule is in the incoherent regime, the poly(dA)–poly(dT) is in the quasicohherent regime. The latter is explained by the quasideagonal zero energy process of the nondiagonal small polaron hopping process. Besides the temperature dependences of  $b$ , the length dependences of the electric current in the two regimes were derived, which may have important implications for the future experiment.

## Introduction

In this decade, active debates have been made among experimentalists on the transport property of DNA molecules, which range from highly conductive metallic-like behavior to insulating behavior.<sup>1–6</sup> Possible sources of experimental troubles are contribution from ionic conduction in ligand water which might be adhesive to DNA molecule, complications originating from dirty contacts, and uncontrolled sequence of bases in random and/or  $\lambda$ -DNA. Theoretical studies have been focused on the analogy between the theory of electric conductance and the electron transfer theory. The competing role between the unistep “superexchange mechanism” in which the chemical reaction rate is proportional to  $\exp(-\beta_s R)$  ( $R$  is the distance along which electron is transferred and  $\beta_s$  is a constant) and the multistep hopping conduction mechanism have been widely discussed both theoretically and experimentally.<sup>7–18</sup> At room temperature, the hopping conduction mechanism may be predominant over the superexchange mechanism. Based on chemical reaction kinetics, it was claimed that the electric conductance of a DNA molecule whose length is larger than a critical value should be understood on the basis of the multistep hopping mechanism. Low temperature experiments are highly desired when we try to understand whether proposed theoretical models are really working or not in this fascinating molecular system.

Very recently, Yoo et al. have succeeded in measuring electric conductance of well-defined poly(dA)–poly(dT) and poly(dG)–poly(dC) DNA duplexes.<sup>19</sup> They measured the low-temperature conductance down to 4 K. Another point in their experiment is that their DNA molecule is free from randomness in the base sequence. It is clear that theoretical analysis of their experimental results should provide direct information on the mechanism of electric conduction in the DNA molecule. We have analyzed their experimental results with the small polaron model. We used the Landauer formula and the Kubo formula to calculate the conductance<sup>20–23</sup> of the DNA molecule. We incorporate the

small polaron effect<sup>24,25</sup> into our tight binding model, and the finite temperature effect is included there.<sup>26</sup>

Our calculation shows that the mechanism of the electric conduction in the poly(dG)–poly(dC) and the poly(dA)–poly(dT) DNA molecules is quite different. Although the temperature dependence of the coefficient  $b$ ,  $I \propto \sinh(bV)$ , in the poly(dG)–poly(dC) molecule is derived similarly as one does the Marcus’ reorganization energy, the temperature independence of  $b$  in the poly(dA)–poly(dT) molecule is derived exclusively from the phase coherence in the transmission coefficient. The latter is originated from the quasideagonal zero energy process of the small polaron hopping model.

## Theory

**A. Quasicohherent Regime.** The conductance of the DNA molecule  $G(V)$  can be expressed in terms of the bias voltage ( $V$ ) derivative of the electric current  $I$  that flows through the DNA molecule<sup>20–23</sup>

$$G(V) \equiv \frac{\partial I}{\partial V} \quad (1)$$

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) \{f(E - \mu_1) - f(E - \mu_2)\} dE \quad (2)$$

$$\cong \frac{2e}{h} \int_{\mu_1}^{\mu_2} T(E) dE$$

where  $\mu_1 = E_f - \eta$  eV and  $\mu_2 = E_f + (1 - \eta)$  eV.  $E_f$  is the Fermi energy and  $\eta$  is the voltage division factor.<sup>20–23</sup>  $T(E)$  is the energy ( $E$ ) dependent transmission coefficient

$$T(E) = \text{tr}[\Gamma_L g_c \Gamma_R g_c^\dagger] \quad (3)$$

where  $g_c$ ,  $\Gamma_L$ , and  $\Gamma_R$  are the Green function of the complex made of the DNA molecule and the leads and the couplings with left and right leads, respectively

$$g_c(E) = (E - H_{\text{mol}} - \Sigma_L - \Sigma_R)^{-1} \quad (4)$$

$$\Gamma_\alpha(E) = i(\Sigma_\alpha - \Sigma_\alpha^\dagger) \quad (5)$$

$H_{\text{mol}}$  is the molecular Hamiltonian. All of the couplings between the DNA molecule and the left and the right leads ( $\alpha = L$  and  $R$ ) are introduced through the self-energy  $\Sigma_\alpha$  which is given in terms of the physical coupling constant  $\tau_\alpha$

$$\Sigma_\alpha = \tau_\alpha^\dagger g_c \tau_\alpha \quad (6)$$

The theoretical scheme is one of the most frequently used schemes in mesoscopic physics as well as molecular electronics. It is equivalent with the scattering matrix formalism. The molecular Green function and the self-energy can be calculated from microscopic theories such as the molecular orbital theory or the density functional theory. Various approximations and simplifications have been used for the semi-infinite problem to calculate the self-energy. Rather than to come into details of such real chemistry calculations, here we use a simplified model to study the length dependence, the voltage dependence, and the temperature dependence of the conductance of the DNA molecule.

If we use the recursive Green function method, the molecular Green function  $g_{\text{mol};1,N}$  may be expressed very simply as follows:<sup>20–23</sup>

$$g_{\text{mol};1,N}(E) = \frac{\nu^{N-1}}{(E - \epsilon - \Sigma_{N-1})(E - \epsilon - \Sigma_{N-2}) \cdots (E - \epsilon - \Sigma_1)(E - \epsilon)} \quad (7)$$

where we used uniform interatomic transfer/hopping term  $\nu$  and uniform site energy  $\epsilon$ . The intramolecular self-energy term  $\Sigma_p$  appeared in the recursive Green function method is given by the following continued fraction:

$$\Sigma_p(E) = \nu^2 \frac{1}{E - \epsilon - \nu^2 \frac{1}{E - \epsilon - \nu^2 \frac{1}{E - \epsilon - \nu^2 \frac{1}{\ddots}}}} \quad (8)$$

where the continued fraction is terminated at the  $p$ -th order. In the large gap limit  $E - \epsilon > \nu$ , the molecular Green function may be approximated by

$$g_{\text{mol};1,N}(E) = \frac{1}{\nu} \left( \frac{\nu}{E - \epsilon} \right)^N \approx \frac{1}{\nu} \exp(-\bar{\beta}_E r) \quad (9)$$

$$\bar{\beta}_E = \log \left( \frac{E - \epsilon}{\nu} \right) \quad (10)$$

where  $r = N$  is the length of the DNA molecule. This equation is equivalent with that given by Mujica et al.,<sup>27</sup> but our method is simpler than their partitioning technique. The Green function of the complex composed of the DNA molecule and the leads  $g_c$  is given by the Dyson equation

$$g_c^{-1} = g_{\text{mol}}^{-1} - \Sigma_L - \Sigma_R$$

In the large gap limit, the self-energy  $\Sigma_L$  and  $\Sigma_R$  may be neglected. Hence,  $g_c \approx g_{\text{mol}}$ . If the interatomic term is originated from the zero-energy process<sup>26</sup> of the small polaron model for

the Einstein mode,  $\langle \nu^2 \rangle_{\text{av}}$  may be given by the following equation:

$$\langle \nu^2 \rangle_{\text{av}} \approx t^2 \exp \left( -\frac{\Delta}{k_B T} \right) \quad (11)$$

where  $t$  is the transfer integral for electron,  $\Delta$  is the generalized activation energy for the hopping,  $T$  is the temperature, and  $k_B$  is the Boltzman constant. Here we have assumed that the total number of phonons is preserved during the hopping to keep  $\langle \nu^2 \rangle_{\text{av}}$  uniform. The above formula is derived in the Appendix. Now the Green function may be approximated as follows:

$$g_c(E - \eta eV)^2 \approx \frac{1}{t^2} \exp(-\beta_E r) \exp(-\alpha_E r) \exp \left( -\frac{E_a}{k_B T} \right) \quad (12)$$

$$\beta_E = 2 \log \left( \frac{E - \epsilon}{t} \right) \quad (13.a)$$

$$\alpha_E = -2 \frac{\eta eV}{E - \epsilon} \quad (13.b)$$

where  $E_a = (N - 1)\Delta$ . The value of  $E_a$  depends crucially on the electron–phonon coupling constant  $M_{\vec{q}}$ . For example, if the real space electron–phonon coupling is limited to the adjacent sites, then  $M_{\vec{q}} = O(1/\sqrt{N})$  and hence  $|\tilde{u}_{\vec{q}}|^2 = (N - 1)|u_{\vec{q}}|^2$  is independent of  $N$ . The formula  $E_a = (N - 1)\Delta$  does not necessarily indicate that it is proportional to  $N$ , but it can be independent of  $N$ ;  $E_a = k_B T \Sigma_{\vec{q}} |\tilde{u}_{\vec{q}}|^2 \tanh(\beta \omega_{\vec{q}}/4)$ .

The conductance  $G(V)$  is approximated as follows:

$$G(V) \approx \frac{2e^2}{h} \{ \eta T(\mu_1) + (1 - \eta) T(\mu_2) \} \quad (14)$$

where we have neglected the voltage dependence of the transmission coefficient  $T(E)$  inside of the DNA molecule<sup>20–23</sup>

$$\frac{\partial T(E)}{\partial V} \approx 0 \quad (15)$$

Hence the conductance of the DNA molecule  $G(V)$  is given by the following equation:

$$G(V) \approx \frac{2e^2}{h} \left( \frac{\Gamma}{t} \right)^2 \exp(-\beta_{E_t} r) \cosh(\lambda eV r) \exp \left( -\frac{E_a}{k_B T} \right) \quad (16)$$

where

$$\lambda = \frac{1}{E_f - \epsilon} \quad (17)$$

In the derivation described above, we put the voltage drop fraction  $\eta = 0.5$ . We have also assumed that the couplings  $\Gamma_\alpha(E)$  take a constant value  $\Gamma$ . We finally obtain the formula for the electric current that flows through the DNA molecule as follows;

$$I \approx \frac{2e^2}{h} \frac{(\Gamma/t)^2}{\lambda e r} \exp(-\beta_{E_t} r) \sinh(\lambda eV r) \exp \left( -\frac{E_a}{k_B T} \right) \quad (18)$$

The theoretical bias voltage dependence and the temperature dependence of the electric current reproduces essential trends of the experimental  $I$ – $V$  curve of the poly(dA)–poly(dT) DNA molecule. The formula may be simplified such that

$I \propto \sinh(bV)$  and  $b = \lambda e r$ . Using the experimental estimate<sup>3</sup> of the hopping distance at 300 K ( $r \approx 1.7$  nm;  $N = 5$  base units) and the standard estimate<sup>28</sup> of the band gap (10 eV) that leads to  $\lambda = 0.1(\text{eV})^{-1}$ , the value of  $b$  is evaluated to be  $b = 0.5 \text{ V}^{-1}$ , which is in fair agreement with that obtained by doing a fit to the experimental  $I$ - $V$  curve. It should be stressed that the coefficient  $b$  in the quasicohherent regime is temperature independent, which is quite different from that in the incoherent regime. The Ahrenius type temperature dependence of the activated transport factor given in eq 18 was observed in the experiment of the poly(dA)-poly(dT) DNA molecule. This form may be derived in the incoherent regime, too, and hence, it may not be a key feature to decide the mechanism. Actually, the same temperature dependence of the factor was observed both in the poly(dA)-poly(dT) and the poly(dG)-poly(dC) molecules, whereas the temperature dependence of  $b$  is quite different in these two molecules. In deriving the formula (18), we have assumed that the Fermi level of the lead lies between the large HOMO-LUMO gap of the DNA molecule. We supposed that the electric conduction of the DNA molecule is taking place in the nonresonant condition. We have also assumed that the total number of phonons is preserved during the nondiagonal small polaron hopping process<sup>26</sup> but not in each momentum state. This makes the nondiagonal small polaron hopping quasicohherent like the diagonal transition. On the other hand, it exhibits the Ahrenius type temperature dependence, which is different from the diagonal one. The temperature independence of  $b$  observed in the poly(dA)-poly(dT) molecule suggests that it is in the quasi-coherent regime.

**B. Incoherent Regime.** The real part of the dynamical conductivity of the small polaron model may be calculated by using the Kubo formula

$$\text{Re}[\sigma(\omega)] = \frac{1 - e^{-\beta\omega}}{2\omega} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle J^\dagger(t) J(0) \rangle \quad (19.a)$$

$$J = i \frac{e t}{\hbar} \sum_{j\delta} \delta c_{j+\delta}^\dagger c_j X_{j+\delta}^\dagger X_j \quad (19.b)$$

$\beta$  without suffix denotes  $\beta = 1/k_B T$ . The calculation in the high temperature and incoherent regime has been made at various approximation levels. Here we make a review of the simplest one to help the reader's understanding. We used the same notation as those in the appendix. Standard treatise<sup>26</sup> of the calculations reads as follows:

$$\begin{aligned} \text{Re}[\sigma(\omega)] &= \frac{1 - e^{-\beta\omega}}{2\omega} t^2 \left( \frac{e}{\hbar} \right)^2 \sum_{j,j'} \delta \delta' \int_{-\infty}^{\infty} dt e^{i\omega t} \langle c_j^\dagger(t) c_{j+\delta}(t) c_{j'+\delta}^\dagger c_{j'} \rangle \langle X_j^\dagger(t) X_{j+\delta}(t) X_{j'+\delta}^\dagger X_{j'} \rangle \\ &\approx \frac{1}{2} z t^2 \left( \frac{M_0}{\Omega} \right) \left( \frac{e}{\hbar} \right)^2 c(1-c) \frac{1 - e^{-\beta\omega}}{\omega} U(\omega) \end{aligned} \quad (20.a)$$

$$U(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle X_j^\dagger(t) X_{j+\delta}(t) X_{j+\delta}^\dagger X_j \rangle \quad (20.b)$$

We have used simplifications;  $\langle c_j^\dagger(t) c_{j+\delta}(t) c_{j'+\delta}^\dagger c_{j'} \rangle \approx (1/\Omega) \delta_{jj'} \delta_{\delta\delta'} c(1-c)$ , where  $c$  is the electronic density and also  $\sum_{j\delta} \delta^2 \approx M_0 z$ , where  $z$  is the coordination number.  $W$  is the volume of the lattice, and  $M_0$  is the number of atomic sites. After some algebra using the coherent state, the dynamical

polaron correlation function is calculated as follows:

$$U(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \exp(-2S_T + \varphi(t)) \quad (21.a)$$

$$\varphi(t) = \sum_{\vec{q}} 2|u_{\vec{q}}|^2 [N_{\vec{q}}(N_{\vec{q}} + 1)]^{1/2} \cos[\omega_{\vec{q}}(t + i\beta/2)] \quad (21.b)$$

By changing the variable,  $Z = t + i\beta/2$ , and expanding  $\varphi(Z)$  up to the second order,  $\varphi(Z) \approx \varphi(0) - \gamma Z^2$ , we may be able to use the transition state approximation to the integral in eq 21.a

$$\begin{aligned} U(\omega) &= \exp(-2S_T + 1/2\beta\omega) \int dZ \exp(i\omega Z) \exp[\varphi(Z)] \\ &\approx \exp(-2S_T + 1/2\beta\omega + \varphi(0)) \int dZ \exp(i\omega Z) \exp(-\gamma Z^2) \\ &= \left( \frac{\pi}{\gamma} \right)^{1/2} \exp(-2S_T + \varphi(0)) e^{\beta\omega/2} \exp\left(-\frac{\omega^2}{4\gamma}\right) \\ &\approx \left( \frac{\pi}{\gamma} \right)^{1/2} e^{\beta\omega/2} \exp(-\beta\bar{\Delta}) \exp\left(-\frac{\omega^2}{4\gamma}\right) \end{aligned} \quad (22)$$

At high-temperature  $2N_{\vec{q}} + 1 \approx 2/(\beta\omega_{\vec{q}})$ , hence we used the following approximation in the last expression of eq 22:

$$2S_T - \varphi(0) = \sum_{\vec{q}} |u_{\vec{q}}|^2 [N_{\vec{q}} + 1]^{1/2} - [N_{\vec{q}}]^{1/2} \approx \sum_{\vec{q}} |u_{\vec{q}}|^2 \frac{\beta\omega_{\vec{q}}}{4} = \frac{\bar{\Delta}}{k_B T} \quad (23.a)$$

$$\bar{\Delta} \equiv \frac{1}{4} \sum_{\vec{q}} |u_{\vec{q}}|^2 \omega_{\vec{q}} \quad (23.b)$$

In the same high-temperature limit

$$\gamma = \sum_{\vec{q}} |u_{\vec{q}}|^2 \omega_{\vec{q}} [N_{\vec{q}}(N_{\vec{q}} + 1)]^{1/2} \approx 4\bar{\Delta} k_B T \quad (23.c)$$

It should be noted that eq 23.a coincides with Eq.(A9) in the high-temperature limit, as it should be. Substituting eq 22 into eq 20.a leads to

$$\begin{aligned} \text{Re}[\sigma(\omega)] &\approx \frac{1}{2} z t^2 \left( \frac{M_0}{\Omega} \right) \left( \frac{e}{\hbar} \right)^2 \left( \frac{\pi}{\gamma} \right)^{1/2} c(1-c) \beta \frac{\sinh(\beta\omega/2)}{1/2\beta\omega} \exp\left(-\frac{\omega^2}{4\gamma}\right) \exp\left(-\frac{\bar{\Delta}}{k_B T}\right) \\ &\approx \frac{1}{2} z t^2 \left( \frac{M_0}{\Omega} \right) \left( \frac{e}{\hbar} \right)^2 \left( \frac{\pi}{\gamma} \right)^{1/2} c(1-c) \beta \frac{\sinh(\beta\omega/2)}{1/2\beta\omega} \exp\left(-\frac{\bar{\Delta}}{k_B T}\right) \quad (24.a) \\ &\approx \frac{1}{2} z t^2 \left( \frac{M_0}{\Omega} \right) \left( \frac{e}{\hbar} \right)^2 \left( \frac{\pi}{\gamma} \right)^{1/2} c(1-c) \beta \frac{1 - e^{-\beta\omega}}{1/2\beta\omega} \exp\left(-\frac{(\omega - \beta\gamma)^2}{4\gamma}\right) \quad (24.b) \end{aligned}$$

In the last equation, the approximation of eq 23.c was used. It should be noted that eq 24.b is similar to the Marcus' formula for the electron-transfer rate constant.<sup>29</sup> The sinh form of the frequency response is closely related to the Marcus' theory. Because the transition state approximation used in the derivation

is valid in the high-temperature regime, we have to be careful when we use the resultant equations elsewhere.

The frequency dependent current density  $i(\omega) = \sigma(\omega)E(\omega)$  may provide a good estimate for the static current density under the bias voltage  $V$

$$i(eV) \cong \text{Re}[\sigma(eV)]E(0) \cong \text{Re}[\sigma(eV)]V/d$$

$$\cong zt^2 \left( \frac{M_0}{\Omega} \right) \left( \frac{e}{\hbar} \right)^2 \left( \frac{\pi}{\gamma} \right)^{1/2} c(1-c)(ed)^{-1} \sinh\left( \frac{\beta eV}{2} \right) \exp\left( -\frac{\bar{\Delta}}{k_B T} \right) \quad (25)$$

where  $V$  is the voltage difference between the two electrodes and  $d$  is the distance between them. Although the electric current in the incoherent regime obeys  $I \propto \sinh(bV)$ , the coefficient  $b$  is proportional to the inverse of the temperature. The temperature dependence of the coefficient in the incoherent regime is quite different from that in the quasicohherent regime. It should be noted that the derivations in this subsection were made for infinite periodic systems rather than short molecules. We expect that they have some implications for long molecules in the incoherent regime where relaxation and dephasing lengths are shorter than the molecule. The current  $I = i\Delta S$  is proportional to the inverse of the distance  $d$ ; the electric conduction is Ohmic. This is because  $M_0 \cong \Omega$ . The voltage dependence  $I \propto \sinh(bV)$  and  $b \propto 1/T$  was observed in the poly(dG)–poly(dC) DNA molecule. The Arrhenius type temperature dependence of the activated transport factor given in eq 25 was also observed in the high-temperature region. As eq 23.a is the asymptotic form of eq A9, we may be able to change  $\bar{\Delta}$  by  $E_a$  in eq 25. It is remarkable that such temperature dependence of the current was observed over the wide temperature range in the molecule. This suggests that the transition state approximation used in deriving eq 22 is not very bad even in the low-temperature region of this molecule. The inverse temperature dependence of  $b$  observed in the poly(dG)–poly(dC) DNA molecule suggests that the molecule is in the incoherent regime.

## Discussion

We have proposed two different mechanisms for the electric conduction of the poly(dA)–poly(dT) and poly(dG)–poly(dC) DNA molecules. In the incoherent regime such as the poly(dG)–poly(dC) case, inelastic scatterings that give rise to the inverse temperature dependence of  $b$  as well as the Ohmic like inverse length dependence of the electric current play a major role. In the quasicohherent regime such as the poly(dA)–poly(dT) case, quasielastic scatterings that bring about the temperature independence of  $b$  as well as the “superexchange” like length dependence,  $\exp(-\beta_s R)$ , of the electric current are important. Although the total number of phonons is preserved during the hopping in the latter case, it is not conserved in the former case. The electron–phonon coupling has both of these processes. The former becomes dominant at high temperature and in long molecules. On the other hand, the latter may become important at lower temperature and in short molecules. Experimental and theoretical studies of electron-transfer reaction rates in DNA molecules revealed that there are two competing mechanisms whose predominance depends on the length of molecules.<sup>8,9,15–18,30–32</sup> In the sequential hopping regime where the length of the molecule  $R$  is larger than a critical value, the chemical reaction rate is length independent. In the superexchange regime where the length of the molecule  $R$  is smaller than the critical value, the chemical reaction rate is proportional

to  $\exp(-\beta_s R)$ . The critical value depends on the relaxation and dephasing lengths. In spite of the fact that the rate constant is not rigorously related with the conductance and the electric current, our result may have some implications to these results. Our point here is that the temperature dependence of  $b$  where  $I \propto \sinh(bV)$  is a key variable to decide which regime our molecule belongs to. Because the inverse temperature dependence of  $b$  is closely related to the Marcus’s reorganization energy, the absence of the temperature dependence is suggestive that the reorganization energy is not relevant in the poly(dA)–poly(dT) molecule.

Yoo et al. used a similar formula with eq 25 to analyze the temperature independence of  $b$  observed in the poly(dA)–poly(dT) molecule. They introduced the temperature-dependent hopping distance  $a(T)$  and supposed that only the partial voltage drop that electron feels during a hop is relevant to the current density

$$I \propto \sinh\left( \frac{eaV}{2k_B Td} \right) \exp\left( -\frac{E_a}{k_B T} \right) \quad (26)$$

To explain the experimental results, they had to put  $a(T) \propto T$  without any significant reasons. The theory of variable range hopping<sup>33</sup> suggests that the linear temperature dependence of  $a(T)$  may not be likely. For simplicity, we assume  $V > 1$  and  $I \propto \exp(eaV/2k_B Td) \exp(-\beta_s a) \exp(-E_{vr}/k_B T) = \exp[-(\beta'_s a + E_{vr}/k_B T)]$  where  $\beta'_s = \beta_s - eV/2k_B Td$  and the tunneling factor  $\exp(-\beta_s a)$  between the hopping sites was introduced. The activation energy  $E_a$  was replaced with the local gap  $E_{vr}$ . The local density of state which can be accessed during a hop is  $2a(T)\rho(E_F)$  in the one dimension, where  $\rho(E_F)$  is the averaged local density of state per unit volume at the Fermi level. Then the interval of the energy spectrum of the localized states is given by  $E_{vr} = 1/(2a\rho(E_F))$ . The optimum hopping distance that maximizes the current would be  $a(T) = (2\beta'_s \rho(E_F)k_B T)^{-1/2}$ . The temperature independence of  $b$  in the poly(dA)–poly(dT) molecule was observed over such wide temperature range that the scenario proposed by Yoo et al. may not be an easy way to explain the temperature independence of  $b$ .

There are experimental evidences that show the Guanine (G) site is taking a major role in the hole transfer reaction.<sup>31,32,34</sup> The hole trapping at the G site and structural distortion around there were suggested by experiments. The G site may also be a source of dynamical perturbations. The site may randomize the phase and push the system into the incoherent regime. The absence of such site makes the poly(dA)–poly(dT) molecule quite different from the poly(dG)–poly(dC) molecule. The low ionization potential (IP) at clusters composed of G sites suggested by the molecular orbital calculation<sup>35</sup> may be the microscopic origin of the specific feature at the G site such like the easy response to dynamical perturbations. Although the poly(dG)–poly(dC) duplex may have potential application possibilities, the quasiquantum transport observed in the poly(dA)–poly(dT) duplex is interesting, because it provides an example of quasiquantum transport in such a floppy system. Our study implies supramolecules<sup>36</sup> as well as biological molecules may form a potential class of materials useful for nanobioelectronics, where the technological application may be closely related with scientific findings.

## Summary

We have studied the mechanism of electric conduction in the DNA molecule. We have adopted a tight binding small polaron model to study the mechanism. We used the Landauer



and the Kubo formalisms to calculate the molecular conductance both in the quasicohherent and the incoherent regimes. Our calculation shows that the mechanism of the electric conduction in the poly(dG)–poly(dC) and the poly(dA)–poly(dT) DNA molecules is quite different. Although the temperature dependence of the coefficient  $b$ ,  $I \propto \sinh(bV)$ , in the poly(dG)–poly(dC) molecule is derived similarly as one does the Marcus' reorganization energy, the temperature independence of  $b$  in the poly(dA)–poly(dT) molecule is derived exclusively from the phase coherence in the transmission coefficient. The latter is originated from the quasideagonal zero energy process of the small polaron hopping model. In the former case, Ohmic like inverse length dependence of the electric current was obtained, while the “superexchange” like length dependence  $\exp(-\beta_s R)$  was obtained in the latter case. Besides the temperature dependences of  $b$ , the length dependences of the electric current may have important implications for the future experiment.

**Acknowledgment.** The author appreciates Prof. Koichi Yamashita of the University of Tokyo for discussions on analogy between the theory of molecular conductance and the electron transfer reaction theory.

## Appendix

We have assumed that the interatomic term is originated from the small polaron effect. Here we derive a formula of an averaged expectation value of squared interatomic coupling  $\langle \nu^2 \rangle_{av}$ . We start up with the following Hamiltonian:

$$H = t \sum_{j\delta} c_{j+\delta}^\dagger c_j + \sum_{\vec{q}} \omega_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{j\vec{q}} c_j^\dagger c_j e^{i\vec{q} \cdot \vec{R}_j} M_{\vec{q}} (a_{\vec{q}} + a_{-\vec{q}}^\dagger) \quad (\text{A1})$$

$c$  and  $a$  denote annihilation operators for electron and phonon.  $t$ ,  $\omega$ , and  $M$  denote the transfer integral for the electron, phonon frequency, and electron–phonon coupling constant, respectively. After the canonical transformation, the Hamiltonian reduces to

$$\tilde{H} = t \sum_{j\delta} c_{j+\delta}^\dagger c_j X_{j+\delta} X_j + \sum_{\vec{q}} \omega_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}} - \sum_j \Xi n_j \quad (\text{A2})$$

where

$$X_j = \exp \left[ \sum_{\vec{q}} \exp(i\vec{q} \cdot \vec{R}_j) \frac{M_{\vec{q}}}{\omega_{\vec{q}}} (a_{\vec{q}} - a_{\vec{q}}^\dagger) \right] \quad (\text{A3})$$

$$\Xi = \sum_{\vec{q}} \frac{M_{\vec{q}}^2}{\omega_{\vec{q}}} \quad (\text{A4})$$

If  $m_{\vec{q}}$  phonon is absorbed in each  $\vec{q}$  state during the hopping, the following expectation value may be a good estimate of  $\langle \nu^2 \rangle_{av}$ :

$$|\langle n + m | X_{j+\delta}^\dagger X_j | n \rangle|^2 = \prod_{\vec{q}} \exp\{-|u_{\vec{q}}|^2 (2N_{\vec{q}} + 1)\} \exp\left(\frac{m_{\vec{q}} \beta \omega_0}{2}\right) I_{m_{\vec{q}}} (2|u_{\vec{q}}|^2 [N_{\vec{q}} (N_{\vec{q}} + 1)]^{1/2}) \times 4^{m_{\vec{q}}} \quad (\text{A5})$$

where  $u_{\vec{q}} = M_{\vec{q}}/\omega_{\vec{q}}(1 - e^{i\vec{q} \cdot \delta})$  and we have assumed that  $\omega_{\vec{q}} = \omega_0$ . When the energy is conserved during the hopping, the total number of phonons does not change  $\sum_{\vec{q}} m_{\vec{q}} = 0$ . If we remind the additive property of the Bessel functions,  $\sum_m I_m(\xi_1) I_{n-m}(\xi_2) = I_n(\xi_1 + \xi_2)$ , the energy-conserved

average of the squared expectation value is now given as follows:

$$|\langle n + m | X_{j+\delta}^\dagger X_j | n \rangle|_{av}^2 = \exp(-2S_T) I_0(\xi) \cong \frac{1}{(2\pi\xi)^{1/2}} \exp(-2S_T + \xi) \quad (\text{A6})$$

where

$$2S_T = \sum_{\vec{q}} |u_{\vec{q}}|^2 (2N_{\vec{q}} + 1) \quad (\text{A7})$$

$$\xi = \sum_{\vec{q}} 2|u_{\vec{q}}|^2 [N_{\vec{q}} (N_{\vec{q}} + 1)]^{1/2} \quad (\text{A8})$$

We have assumed in eq A6 that  $|\xi| > 1$  and hence  $I_0(x) \cong 1/\sqrt{2\pi\xi} \exp(\xi)$ .

It should be noted that eq A6 is independent of  $m_{\vec{q}}$  and the site index. The average is uniform over the sites. Because  $2N_{\vec{q}} + 1 = \coth(\beta\omega_{\vec{q}}/2)$ , it is not difficult to find that

$$2S_T - \xi = \sum_{\vec{q}} |u_{\vec{q}}|^2 \tanh(\beta\omega_{\vec{q}}/4) \quad (\text{A9})$$

If we denote

$$\Delta = k_B T \sum_{\vec{q}} |u_{\vec{q}}|^2 \tanh(\beta\omega_{\vec{q}}/4) \quad (\text{A10.a})$$

the expectation value is finally given as follows:

$$|\langle n + m | X_{j+\delta}^\dagger X_j | n \rangle|_{av}^2 \propto \exp\left(-\frac{\Delta}{k_B T}\right) \quad (\text{A10.b})$$

Here we have neglected the factor  $(2\pi\xi)^{-1/2}$  in eq A6, which might be phenomenologically incorporated into  $\Delta$ . Taking into account of the electronic part

$$\langle \nu^2 \rangle_{av} = t^2 \exp\left(-\frac{\Delta}{k_B T}\right) \quad (\text{A11})$$

The case of energy-conserved nondiagonal transition considered here may be between the two limiting cases of the diagonal and the nondiagonal transitions. Although it exhibits activation type temperature dependence, it may preserve quasi-coherence of electrons.

**Note Added after Print Publication.** Equation 20a was published with a typographical error. The term published as  $(e/\hbar)$  should read  $(e/\hbar)^2$ . This paper was published on the Web on 4/19/2003 and in Vol. 107, No. 19, May 15, 2003, pp 4647–4652. The electronic version of this paper was corrected and reposted on 7/16/2003. An Addition and Correction appears in Vol. 107, No. 32, (August 14, 2003).

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