DFT Approach to Calculate Electronic Transfer through a Segment of DNA Double Helix

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ABSTRACT: The electronic structures of an entire segment of a DNA molecule were calculated in its single-strand and double-helix cases using the DFT method with an overlapping dimer approximation and negative factor counting method. The hopping conductivity of the segment was calculated by the random walk theory from the results of energy levels and wave functions obtained. The results of the single-strand case show that the DFT method is quantitatively in agreement with that of the HF MP2 method. The results for the double helix are in good agreement with that of the experimental data. Therefore, the long-range electron transfer through the DNA molecule should be caused by hopping of electronic charge carriers among different energy levels whose corresponding wave functions are localized at different bases of the DNA molecule. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 1109–1117, 2000

Keywords: DFT method; calculating electronic transfer; DNA; hopping mechanism; charge-transfer

Introduction

Recently, it was experimentally found that DNA double helices can transfer electronic charges through long distance when the charge carrier is a hole.[1–8] This implies that DNA is not only a carrier of genetic information, but also a pathway to transfer charges in biological processes. However, the mechanism of such long-range electronic transfer remains unknown.[9–13] This is controversial by both experiments and theory.[14–24] Some recent researches in theory and experiments[15, 22, 23] suggested that the mechanism might be a multistep hopping of charge carriers.

The hopping mechanism of electron transfer through biological materials has been studied for decades.[25–31] Recently, Ladik and Ye[32–38] applied the random walk theory[39–45] to calculate electronic transfer rates through proteins and DNA segments,

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and pointed out that the proteins and DNA segments can transport electronic charges quickly by the hopping mechanism when they are doped. The holes, instead of electrons as charge carriers, can be easily transferred through these biological materials by the hopping mechanism.[32, 36–38]

In previous articles on the electronic transfer through DNA molecules[32, 37, 38] the calculations were performed in an HF scheme by which the correlation correction could not be included in the calculations on DNA with a double helix form. The correlation correction is important in the calculation of the electronic transfer through the DNA molecules.[32, 38] Therefore, in this article, the DFT method is applied to calculate the hopping conductivity through the DNA segment to include the influence of the correlation correction.

In this article we will report the theoretical results of hopping conductivity of a segment of DNA molecule calculated by the DFT method. The main formulae are briefly recalled in the second section. The third section presents the results for both single- and double-strand cases, and the last section presents the discussion and conclusions.

Methods

In this article we select the segment that has 28 base pairs[3] to be calculated, because it has fine defined experimental results that can be compared with the theoretical calculations. The sequence of the segment is 5′-CGCGA TATGG GCGCA TTAAC CAGAA TTC-3′.[3] Clementi's double ζ basis functions[46] are applied to all calculations presented in this article. The overlapping dimer approximation was applied to the calculations on the DNA segment as has been done in previous articles.[32, 37, 38] In this way, the 16 basic dimers shown in Figure 1 are calculated by the DFT method.

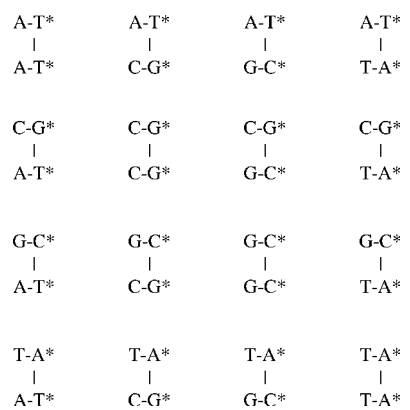

FIGURE 1. The 16 basic dimers of base pairs. The asterisk indicates the bases of the complemental strand.

The calculations are performed by the Gaussian94 DFT module, in which the potential functionals are B3LYP and B3PW91, which can be represented as:

$$A \times E_x^{\text{Slater}} + (1-A) \times E_x^{\text{HF}} + B \times \Delta E_x^{\text{Becke88}} + E_c^{\text{VWN}} + C \times \Delta E_c^{\text{nonlocal}} \quad (1)$$

Here, $\Delta E_c^{\text{nonlocal}}$ stands for the LYP gradient corrected form[47] in the P3LYP functional and the PW91 gradient corrected form in the B3PW91 functional,[48] respectively. $\Delta E_x^{\text{Becke88}}$ is Becke's gradient correction for the exchange energy.[49] The semiempirical coefficients A, B, and C are given by Becke[49] also.

The Fock (and overlap) matrix $\mathbf{F}$ (and $\mathbf{S}$) of the whole molecular system of a DNA segment can be obtained after the 16 basic dimers have been worked out. The first step is to perform a rotation on the matrix $\mathbf{F}$ (and $\mathbf{S}$) of each dimer according to

$$\mathbf{F}' = \mathbf{R}\mathbf{F}\mathbf{R}^{-1} \quad (2)$$

in which

$$\mathbf{R} = \mathbf{R}_1 \oplus \mathbf{R}_2 \oplus \cdots \oplus \mathbf{R}_N \quad (3)$$

and

$$N = n_1 + n_2 \quad (4)$$

where N is the total number of atoms of the dimer in which the number of atoms in the first base pair is n_1, and that in the second one is n_2; $\mathbf{R}_i$ is the rotation matrix of the ith atom in the dimer. The Fock (and overlap) matrix $\mathbf{F}$ (and $\mathbf{S}$) of the whole molecular system of a DNA segmant can be constructed from the rotated matrices of the dimers according to the following formulae:

$$F_{ij}^{(S)}(n,n) = \frac{1}{m}\sum_{k=1}^{m} F_{ij}^{(d)}(n,n,k), \qquad m = 1,2 \quad (5)$$

$$F_{ij}^{(S)}(n,n+1) = F_{ij}^{(d)}(n,n+1) \quad (6)$$

in which $F_{ij}^{(S)}$ represents matrix elements of the Fock matrix of the whole molecular system, and $F_{ij}^{(d)}$ stands for the elements of the Fock matrices of the rotated basic dimers. The number n, which represents the numbering of base pairs in the DNA sequence to be calculated, runs from 1 to N in eq. (5) and from 1 to $N-1$ in eq. (6). The number m in eq. (5) is the number of the dimers in which the nth base pair is involved.

The eigenequation for the whole molecular system can be solved by the NFC method.[50–52] The ENFC program,[34] in which the NFC is a special case (the ENFC program can also solve the eigenequa-

tion with crosslinks such as in the case of proteins), is used in the calculations. The corresponding wave functions can be obtained by inverse iteration[53] after the energy levels are worked out. Gazdy et al.[54] have proven that the results obtained from the Fock matrix of a whole system constructed by local self-consistent calculations on these dimers would be similar to that calculated in a self-consistent field on the entire system.

It has been known that most of the frontier molecular orbitals (the highest filled and the lowest unfilled ones) of the DNA molecules are localized at one or two bases.[32, 37, 38] Therefore, the hopping mechanism can be applied to analyze electronic transfer through the DNA molecules. The formulae used in this article are the same as those developed by Ye and Ladik[33] to calculate the hopping conductivity of proteins. For the reader's sake, these formulae are briefly repeated here. The hopping conductivity can be determined by the Einstein relationship:

$$\sigma(\omega) = \frac{n_V e^2}{k_B T} D(\omega) \tag{7}$$

in which the n_V is the number density of charge carriers in the volume of a DNA segment; e is the charge of an electron; k_B is the Boltzmann constant; and T is the absolute temperature. The difussion constant $D(\omega)$ can be calculated by solving the following master equation:

$$\begin{aligned}\frac{\partial P[\mathbf{X}(n,j),t|\mathbf{X}(n_0,i_0),0]}{\partial t} &= -\Gamma_{\mathbf{X}(n,j)} P\big[\mathbf{X}(n,j),t\big|\mathbf{X}(n_0,i_0),0\big] \\ &\quad + \sum_{\mathbf{X}(n',j')\neq\mathbf{X}(n,j)} h_{\mathbf{X}(n',j')\to\mathbf{X}(n,j)} \\ &\quad \times P\big[\mathbf{X}(n',j'),t\big|\mathbf{X}(n_0,i_0),0\big]\end{aligned} \tag{8}$$

Here $P[\mathbf{X}(n,j),t|\mathbf{X}(n_0,i_0),0]$ represents the probability that a carrier arrives at center $\mathbf{X}(n,j)$ at time t when it was at center $\mathbf{X}(n_0,i_0)$ at time $t=0$, and

$$\Gamma_{\mathbf{X}(n,j)} = \sum_{\mathbf{X}(n',j')\neq\mathbf{X}(n,j)} h_{\mathbf{X}(n,j)\to\mathbf{X}(n',j')} \tag{9}$$

In the master equation, the hopping frequency $h_{\mathbf{X}(n,i)\to\mathbf{X}(n',j)}$ can be calculated by the following formula from the electronic energy levels and corresponding wave functions obtained by the DFT calculations on the whole molecular system of the DNA segment:

$$h_{\mathbf{X}(n,i)\to\mathbf{X}(n',j)} = \begin{cases} \nu_{\text{phonon}}\left(\sum_{r\in n,\ s\in n'} C_r^{(i)} C_s^{(j)} \langle\phi_r(n)|\phi_s(n')\rangle\right)^2 \\ \quad \times \exp(-\Delta E_{ij}/k_B T), \qquad \Delta E_{ij} > 0 \\ \nu_{\text{phonon}}\left(\sum_{r\in n,\ s\in n'} C_r^{(i)} C_s^{(j)} \langle\phi_r(n)|\phi_s(n')\rangle\right)^2, \\ \qquad\qquad \Delta E_{ij} \le 0 \end{cases} \tag{10}$$

where $C_r^{(i)}$ and $C_s^{(j)}$ are the linear coefficients of the ith and jth molecular orbitals of the whole DNA segment; $\phi_r(n)$ and $\phi_s(n')$ are the basis functions of the molecular orbitals; r and s represent the numbering of the basis functions; and n, n' represent the numbering of base pairs. $\Delta E_{ij} = E_j - E_i$, is the difference between the jth and the ith energy levels. The ν_{phonon} is the acoustic phonon frequency, and is taken as 10^{12} s^{-1} as in ref. 33. The center of the ith molecular orbital in the nth base pair is defined as follows:

$$\mathbf{X}(n,i) = \frac{\sum_{A\in n} w_A(n,i)\mathbf{X}_A(n)}{\sum_{A\in n} w_A(n,i)} \tag{11}$$

where

$$w_A(n,i) = \sum_{r\in A} C_r^2(n,i) \tag{12}$$

in which A is an atom of the base pair.

The eq. (10) was first presented by Ladik et al.[55] It should be noted that the summation runs only over the basis functions of the nth and n'th bases (base pairs). This means that the wave functions are truncated, and the sum will be nonzero. [It will be zero when the summation runs over all bases (base pairs) of the DNA molecule because the wave functions are orthogonal for the entire molecular system.] Further, it will have the Marcus behavior because the basis functions are represented by exponential functions. Therefore, eq. (10) is a good approximation to calculate the hopping frequencies. One can also see Mott and Davis[40] for more details.

The diffusion constant in eq. (7) can be written in terms of the Laplace transform of the probability $P[\mathbf{X}(n,j),t|\mathbf{X}(n_0,i_0)]$ of eq. (8) as follows:

$$\begin{aligned}D(\omega) = -\frac{\omega^2}{2d} \sum_{\mathbf{X}(n_0,i_0)} \sum_{\mathbf{X}(n,j)} \big[\mathbf{X}(n,j) - \mathbf{X}(n_0,i_0)\big]^2 \\ \times \tilde{P}\big[\mathbf{X}(n,j),i\omega\big|\mathbf{X}(n_0,i_0)\big] f(E_{\mathbf{X}(n_0,i_0)})\end{aligned} \tag{13}$$

where $\tilde{P}[\mathbf{X}(n,j),i\omega|\mathbf{X}(n_0,i_0)]$ is the Laplace transform of the probability $P[\mathbf{X}(n,j),t|\mathbf{X}(n_0,i_0),0]$:

$$\tilde{P}\big[\mathbf{X}(n,j),i\omega\big|\mathbf{X}(n_0,i_0)\big] = \int_0^\infty e^{-i\omega t} P\big[\mathbf{X}(n,j),t\big|\mathbf{X}(n_0,i_0),0\big]\,dt \tag{14}$$

and $f(E_{\mathbf{X}(n,j)})$ is the equilibrium distribution function for the localized carriers and obeys the equation:

$$\sum_{\mathbf{X}(n',j') \neq \mathbf{X}(n,j)} h_{\mathbf{X}(n',j') \to \mathbf{X}(n,j)} f(E_{\mathbf{X}(n',j')}) = \sum_{\mathbf{X}(n',j') \neq \mathbf{X}(n,j)} h_{\mathbf{X}(n,j) \to \mathbf{X}(n',j')} f(E_{\mathbf{X}(n,j)}) \quad (15)$$

in which $E_{\mathbf{X}(n,j)}$ is the energy level of the carrier at center $\mathbf{X}(n,j)$.

Results

HOPPING CONDUCTIVITY AND LONG-RANGE ELECTRONIC TRANSFER RATE

The results for the single-strand case of the DNA segment are presented here to compare the performance between the DFT method and the HF MP2 calculations. Figure 2 displays the hopping conductivity of the DNA segment calculated by different methods. From the figure it can be seen that the result of the LYP functional is in good agreement with that of the HF MP2 method, while that of the PW91 functional is in a half order of magnitude lower than that of the HF MP2 method in the high-frequency range. The result of the HF method without the correlation correction is in about two orders of magnitude lower than that of the HF MP2 method. This means that the influence of the correlation correction is very important in the hopping conductive process. The performance of the LYP functional is better than that of the PW91 functional in these kind of calculations.

The results of the DNA segment in its double helix case are presented in Figure 3. In this figure, three curves are displayed. Two of them are the results of the hopping conductivity of the DNA segment calculated by the DFT method with the LYP and PW91 functionals, respectively. The third is the result calculated by the HF method without the correlation correction. From the figure it can be seen that the three curves agree with each other qualitatively. The result of the DFT method with the LYP functional has the highest value in the high-frequency range. It is in about a half order of magnitude higher than those by the DFT method with the PW91 functional and by the HF method without the correlation correction.

Table I presents the maximum values of the hopping conductivity of the DNA segment worked out by different quantum chemical methods. The experimental value of fresh quenching time was reported to be 150 ps.[3] The corresponding value of the conductivity to transfer a hole through the DNA segment can be estimated by the following formula:

$$|\sigma| = \frac{el}{\tau SU} \quad (16)$$

where e is the charge of an electron; τ is the time period of the transfer; l and S are the length and cross section of the DNA segment, respectively, and U is

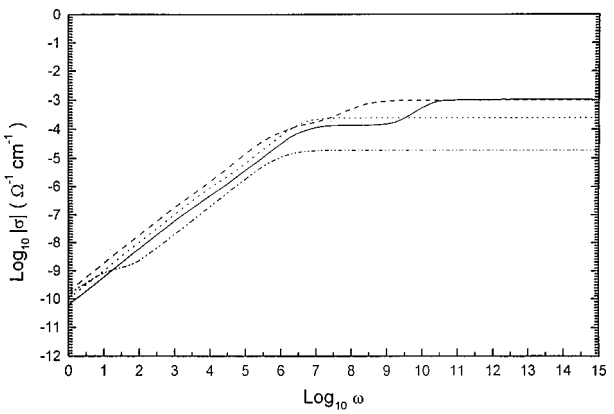

FIGURE 2. The absolute value of the hopping conductivity of the DNA segment in the single-strand case. The solid line (——) represents the results of the DFT method with the LYP functional; the dotted line (· · · · ·) stands for the results of the DFT method with the PW91 functional; the dashed line (- - - -) represents the results of the HF MP2 calculation, and the dashed and double dotted line (-··-··-) stands for the results of the HF calculation without the correlation correction.

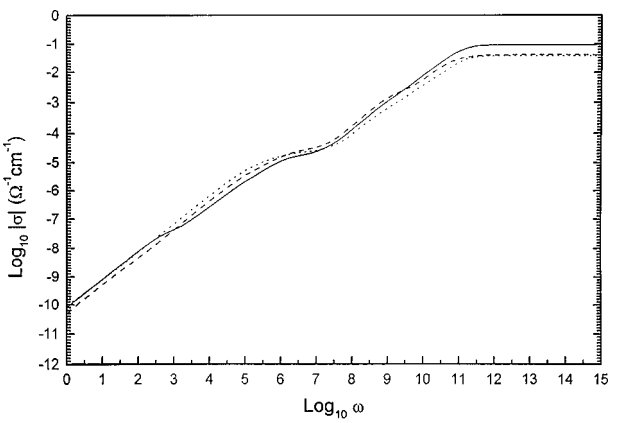

FIGURE 3. The absolute value of the hopping conductivity of the DNA segment in the double-helix case. The solid line (——) represents the results of the DFT method with the LYP functional; the dotted line (· · · · ·) stands for the results of the DFT method with the PW91 functional; the dashed line (- - - -) represents the results of the HF calculation without the correlation correction.

TABLE I.
Hopping Conductivity of the DNA Segment Worked Out by Different Methods.

Method	Basis set	Conductivity (Ω^{-1} cm^{-1})		Transfer rate (s^{-1})
		Double helix	Single strand	Double helix
B3LYP	DZ	9.30×10^{-2}	10.4×10^{-4}	9.20×10^{9}
B3PW91	DZ	3.77×10^{-2}	2.57×10^{-4}	3.74×10^{9}
HF MP2	DZ		9.92×10^{-4}	
HF	MB	1.57×10^{-2}		1.56×10^{9}
HF	DZ	4.04×10^{-2}	1.85×10^{-5}	4.00×10^{9}
Experiment (ref. 3)		6.72×10^{-2}		6.67×10^{9}

Clementi's basis sets (ref. 46) were applied to all of the calculations. (MB: minimal basis set; DZ: double ζ basis set.)

the voltage drop which was estimated for this DNA segment to be 0.8 V (see ref. 3). Using the same formulae, the conductivity can also be transformed to the time period τ that is needed to transfer a hole through the DNA molecule. The theoretical values of the charge transfer time are also displayed in the same table to be compared with the experimental one.

From the table, it can clearly be seen that all results of the conductivity of the single strand are lower than those values of the double strand by at least two orders of magnitude. Therefore, the single strand of the DNA molecule is not easy to transfer electronic charges because of its low conductivity. All the results of the hopping conductivities of the double helix of the DNA segment calculated by the different methods are in the same order of magnitude as that of the experimental value. This means that the electronic transfer through the DNA molecule is by the hopping mechanism, which is the dominant part of such kind of electronic charge transfer. The difference between the hopping conductivities of single-strand and double-helix cases of the DNA segment indicates that the complementary strand of a DNA double helices helps the DNA molecule to transfer electronic charges.

DISTANCE DEPENDENT ELECTRONIC TRANSFER

There are numerous recent experimental studies that seem in conflict with the Barton rates. However, one can find that the conductivity of a DNA molecule will be exponentially decayed when the electronic charge is transfered by an elementary hopping process, which is the superexchange of electronic charge between the donor and acceptor, such as the results reported by Lewis and his coworkers.[16] In this case, the master equation (8) has a two-state behavior, and can be solved analytically, as have been done by Ye and Scheraga.[56] In this case, from equations (7)–(9) and (13)–(15), using the same method as in ref. 56, the hopping conductivity can be expressed as follows:

$$\sigma(\omega) = \frac{n_V e^2 l^2}{kT} \cdot \frac{h_{d\to a} \times h_{a\to d}}{h_{d\to a} + h_{a\to d}} \cdot \frac{\omega^2 + i\omega(h_{d\to a} + h_{a\to d})}{\omega^2 + (h_{d\to a} + h_{a\to d})^2} \tag{17}$$

in which l is the distance between the donor and acceptor, n_V is the number of effective charge carriers in the unit volume, and ω the external alternative electric field, which is suplied by the change of atomic positions of the molecular system during the biochemical reaction, for example, by vibration of the donor and acceptor. $h_{d\to a}$ and $h_{a\to d}$ are the hopping frequencies from donor to acceptor and from acceptor to doner, respectively. In the case of the two-state hopping, the number of charge carrier is 1. Therefore,

$$n_V = \frac{1}{lS} \tag{18}$$

where S is the cross section of the DNA segment. Substituting it into the eq. (16), it can be seen that

$$\left|\sigma(\omega)\right| = \frac{el}{\tau SU} = \frac{e^2 l^2}{lSkT} \cdot \frac{h_{d\to a} \times h_{a\to d}}{h_{d\to a} + h_{a\to d}} \cdot \left| \frac{\omega^2 + i\omega(h_{d\to a} + h_{a\to d})}{\omega^2 + (h_{d\to a} + h_{a\to d})^2} \right| \tag{19}$$

Therefore, the rate $1/\tau$ can be expressed as:

$$\frac{1}{\tau} = \frac{eU}{kT} \cdot \frac{h_{d\to a} \times h_{a\to d}}{h_{d\to a} + h_{a\to d}} \cdot \left| \frac{\omega^2 + i\omega(h_{d\to a} + h_{a\to d})}{\omega^2 + (h_{d\to a} + h_{a\to d})^2} \right| \tag{20}$$

that is,

$$\frac{1}{\tau} = \frac{eU}{kT} \cdot \frac{h_{d\to a} \times h_{a\to d}}{h_{d\to a} + h_{a\to d}} \cdot \frac{1}{\sqrt{1 + \left(\frac{h_{d\to a} + h_{a\to d}}{\omega}\right)^2}} \tag{21}$$

Equation (21) is the exact representation of the electronic transfer rate of the superexchange process in which only two electronic states are involved. It can be simplified to obtain the empirical formula used in the literature. When ω is larger than the elementary hopping frequencies $h_{d\to a}$ and $h_{a\to d}$, the above equation can be simplified as follows:

$$\frac{1}{\tau} = \frac{eU}{kT} \cdot \frac{h_{d\to a} \times h_{a\to d}}{h_{d\to a} + h_{a\to d}} \tag{22}$$

In the case that the electronic energy level of donor is higher than that of acceptor, $E_d > E_a$, that is, $\Delta E_{ad} = E_d - E_a > 0$, substituting eq. (10) into (22), it can be seen that

$$\frac{1}{\tau} = \frac{eU}{kT} \cdot \frac{\nu_{\text{phonon}} e^{-\Delta E_{ad}/kT}}{1 + e^{-\Delta E_{ad}/kT}} \cdot \left(\sum_{r\in d,\ s\in a} C_r^{(i)} C_s^{(j)} \langle \phi_r(d) | \phi_s(a) \rangle \right)^2 \tag{23}$$

The asymptotic behavior of the last term of the above equation is an exponential function of the distance between the donor and acceptor when the Slater-type basis functions are applied.[57] Therefore, the above equation can be simplified as follows:

$$\frac{1}{\tau} \approx \frac{eU}{kT} \cdot \frac{\nu_{\text{phonon}} e^{-\Delta E_{ad}/kT}}{1 + e^{-\Delta E_{ad}/kT}} \cdot \exp(-\beta R) \tag{24}$$

In the case that the electronic energy level of donor is lower than that of acceptor, $\Delta E_{da} = E_a - E_d > 0$, it can be obtained that

$$\frac{1}{\tau} \approx \frac{eU}{kT} \cdot \frac{\nu_{\text{phonon}} e^{-\Delta E_{da}/kT}}{1 + e^{-\Delta E_{da}/kT}} \cdot \exp(-\beta R) \tag{25}$$

From eqs. (24) and (25), it is obvious that the transfer rate is distance dependent in the superexchange cases. When the temperature is taken as a constant, they become the empirical equation:

$$\frac{1}{\tau} = A \exp(-\beta R) \tag{26}$$

From the above analysis, it can be seen that the physical meaning of the β parameter in eq. (26) is the interaction between the electronic charge transfered and the atomic groups of the donor and acceptor. The larger the value of the β parameter, the stronger the interaction.

ELECTRONIC STRUCTURE OF A NATIVE DNA SEGMENT

The electronic structure of a native DNA segment[37] is presented in this subsection to answer the question of why the random walk theory is applied to calculate the hopping conductivity. In this calculation, all atoms consisting of the DNA segment, including the phosphate backbone and sugar rings, are considered. The calculation was performed by HF method in *ab initio* scheme with Clementi's minimal basis set.

The coordinates of the operator,[58] a segment of native DNA molecule that dominates genetic expression in living cells, is obtained from the Brookheaven Protein Data Bank (pdb1trr.ent). There are four single chains that consists of 16 bases in each segment in the B conformation. The sequence is 5′-AGCGTACTAGTACGCT-3′ for each chain. Only one segment, chain C in the data set, is taken into the calculation. There was no hydrogen atom in the original data set. All of the coordinates of hydrogen atoms are added to the data set theoretically. The number of atoms in the DNA segment is 507, including hydrogen atoms. One thousand eight hundred sixty-seven basis functions should be used when Clementi's minimal basis set is applied to the quantum chemical calculation on the entire segment.

Table II shows the rates of distributions of wave functions of different energy levels on the nucleotides of the molecule. The component of a wave function localized at the nth nucleotide, $a(n)$, is estimated by the following formula:

$$a(n) = \frac{\sum_{j=1}^{m_n} C_j^2(n)}{\sum_{n=1}^{N} \sum_{j=1}^{m_n} C_j^2(n)} \tag{27}$$

in which the m_n is the number of the basis functions in the nth nucleotide and $C_j(n)$ is the coefficient of the jth basis function in the nth nucleotide. N is the total number of the nucleotides. Those nucleotides are neglected when the components of a wave function localized at it are less than 0.05. The energy bands are divided by the numbering of the molecular orbitals to calculate the rates of distributions. From the table, one can clearly see that at the edges of both bands the molecular orbitals are localized at one or two nucleotides. The more inside the bands, the more delocalized the molecular orbitals. Therefore, the mechanism of electronic transport through a native DNA molecule should be dominated by hopping among different localized molecular orbitals instead of Bloch-type transport through delocalized ones.

The energy gap between the valence band and conduction band is estimated to be 10.807 eV. It is too large to allow intrinsic conductivity in the native DNA molecule. The DNA molecule should be an insulator in ordinary conditions because thermal energy is not enough to pump electrons from the filled valence bands region to the empty conduction band region. The DNA molecule could transport

TABLE II.
The Distribution Rates of Energy Levels of the Operator.

Numbering of energy levels	Percentage of distributions				
	1–2	3–4	5–6	7–8	9–10
			The conduction band		
1826–1867	97.6%	2.4%	0.0%	0.0%	0.0%
1746–1825	81.2%	17.5%	1.2%	0.0%	0.0%
1666–1745	23.8%	53.8%	20.0%	2.5%	0.0%
1586–1665	6.2%	51.2%	35.0%	6.2%	1.2%
1506–1585	6.2%	57.5%	31.2%	5.0%	0.0%
1426–1505	8.8%	40.0%	36.2%	11.2%	3.8%
1346–1425	15.0%	52.5%	22.5%	8.8%	1.2%
1266–1345	71.2%	22.5%	5.0%	1.2%	0.0%
			The valence band		
1186–1265	80.0%	20.0%	0.0%	0.0%	0.0%
1106–1185	15.0%	56.2%	25.0%	3.8%	0.0%
1026–1105	21.2%	47.5%	25.0%	6.2%	0.0%
946–1025	22.5%	42.5%	28.8%	5.0%	1.2%
866–945	11.2%	42.5%	36.2%	8.8%	1.2%
786–865	6.2%	50.0%	30.0%	11.2%	2.5%
706–785	11.2%	52.5%	28.8%	7.5%	0.0%
626–705	50.0%	35.0%	12.5%	2.5%	0.0%
546–625	75.0%	18.8%	5.0%	1.2%	0.0%
466–545	98.8%	1.2%	0.0%	0.0%	0.0%
386–465	67.5%	31.2%	1.2%	0.0%	0.0%

electrons only when it is doped, that is, when it is acted by photoexcitation such as radiation or bound by other molecules such as proteins and other chemicals. In the former, the electrons in the valence band region are pumped to the conduction band region to create free charge carriers, while in the latter, the biochemical reactions take electrons from the valence band region or put electrons to the conduction band region to create free charge carriers.

Discussion and Conclusions

The electronic transfer through the DNA segment is very fast, as measured experimentally. It is in the range of 10^{-10} s. The transfer is irreversible. This is equivalent to a half period of high-frequency alternating current. Therefore, the treatment of a high-frequency electric current can be used as an approximation to describe such processes. This is the reason why our interests are focused on the high-frequency range of ac conductivity.

All the results calculated by different quantum chemical methods are in the same order of magnitude as that measured experimentally. The results of this article clearly pointed out that the long-range electron transfer through DNA double helices is caused by the hopping mechanism. Besides hopping among energy levels at different bases, there are many other channels for electronic charge transfer through the DNA molecule such as multichannel tunnelling and electron transport coupled to ions and protons. However, they do not seem to be the dominant factors in the long-range electronic charge transfer through a DNA double helix. For example, the multichannel tunnelling through DNA molecules has been worked out by Beratan and coworkers.[15] The results showed that it is much weaker than the experimental value measured.

From the results presented above, it can be seen that the single strand of the DNA molecule cannot transfer electronic charges easily. The conductivities of the single strand of the DNA segment calculated by different methods are lower than those of double helix by two orders of magnitude. Therefore, the complementary strand plays an important role in the electronic transfer through DNA molecules. It helps the electron transfer through the double strand case by the fine structures of the distribution of energy levels and corresponding wave

functions.[32, 37] The interference on the DNA double helices strongly influence their conductivity, as has been observed experimentally by Hall and Barton.[5]

From the results presented previously, it can also be seen that the better basis set applied, the higher the value of conductivity obtained. The highest value of conductivity is obtained when the correlation correction is obtained by the DFT method. These are in good agreement with the conclusions drawn by Ladik and Ye,[32] that DNA can be good conductors to transfer holes in the biological process. The value of conductivity obtained by the DFT method with the LYP functional is higher than that experimentally measured. This implys that the electronic transfer through the DNA double helix might be somewhat faster than what has been observed.

It should be noted that the hopping mechanism presented in this article happens in the valence band region instead of between the valence and conduction band region. That is, the hoppings happen among the energy levels that consist of the valence band. As pointed out by Beratan,[15] hopping is not energetically accessible when the energy gap between the valence band and the conduction band is large. Therefore, one of the necessary conditions that can make DNA transfer electronic charges is that the molecule should be doped. That is, to create electronic charge carriers through photoexcitation or biochemical reaction or both of them. Only in these cases can the electronic charge be transported through the molecule by the carriers hopping among the energy levels in a band instead of between two bands.

In summary, all of the results presented in this article show that a DNA molecule can transfer electronic charges through its double helix by hopping of charge carriers among different energy levels whose corresponding wave functions are localized at different bases of the DNA molecule.

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