Quantum Theory of DNA—- An Approach to Electron Transfer in DNA

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Inspired by Ikemura conjecture about electron transfer in DNA playing an important role in information exchanges, the field theoretical approach is applied to π-electrons and phonons inside DNA. Under some approximations, three-dimensional string action is derived. The DNA string model is applied to formulate the three phenomena – luminescence quenching, eletric current through DNA and absorption of light.

§1. Introduction

I have started working on this topic with H. Ikemura who is a biologist as well as my colleague of my university. I call his statement as Ikemura Conjecture,[1] which is, "Electron transfer in DNA plays an important role in information exchanges among various sections of DNA." Conventional knowledge of information transfer of DNA is that the transfer over various parts of DNA is done solely by protein. One protein gets attached to one part of DNA and then interacts with proteins attached to some other parts of DNA. They can communicate with each other, then information is transferred. Ikemura suspects that it may not be only source of the information exchange but some mechanism concerning electrons within DNA may play some role in exchanging information.

DNA has regulation regions, which we call RNA transcription, where DNA is transferred into RNA. Also, in DNA there is some region called enhancer, where RNA transcription is enhanced about 10^6 times. The enhancement is remarkably large amount, so it is hardly believable that such huge number of the transcription process is caused by proteins only. At this point, Ikemura conjecture seems to give a reasonable explanation. Here we will discuss his conjecture from an approach of quantum field theory.

§2. Quick review of DNA

In this section, we will quickly give an overview of the structure of DNA in Figs.1 and 2. DNA has double spiral structure, and its backbone is constructed by the unit of sugar(3')-phosphate-sugar(5'). In the cross section of DNA, there is some base pair attached to the backbone. The base pair is the combination of guanine (G) and cytosine (C) or the combination of adenine (A) and thymine (T). Larger area in the cross section separated by the base pair is called major groove, and smaller area is called minor groove. Proteins can attach to the base pair and cause interactions in DNA via the hydrogen bonding. If proteins get attached to minor groove, they take a form symmetric with respect to G and C (or A and T). So, one can not distinguish

G and C (or A and T). On the other hand, if proteins get attached to major groove, they are not symmetric. G and C (or A and T) can be distinguished.

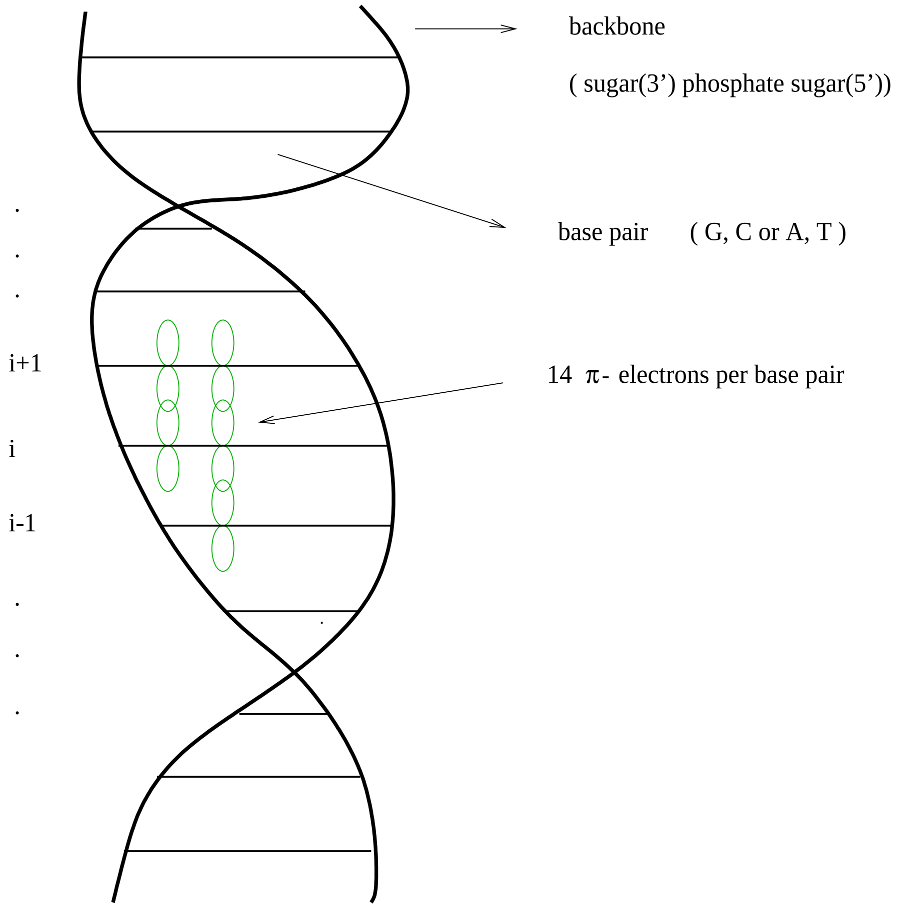

Fig. 1. A schematic figure of the structure of DNA. The green lines show the p-wave orbits of the wave functions of π-electrons in base pairs. The positions of base pairs are indicated by "$\cdots, i-1, i, i+1, \cdots$". Due to the overlap of the wave functions, electrons are transferred through DNA (in the vertical direction).

These base pairs carry a large amount of information. One repetition of the spiral contains approximately ten base pairs. Each base pair has fourteen π-electrons, whose wave functions describe the p-wave orbit. In discussing electron transfer in DNA, a crucial thing is overlap between the wave functions of π-electrons belonging to different base pairs. The overlap allows the electron transfer through the DNA.

§3. Field Theory Technique

In order to describe the property of π-electrons, we use a standard technique in particle physics and condensed matter theory, which may not be found in qunatum

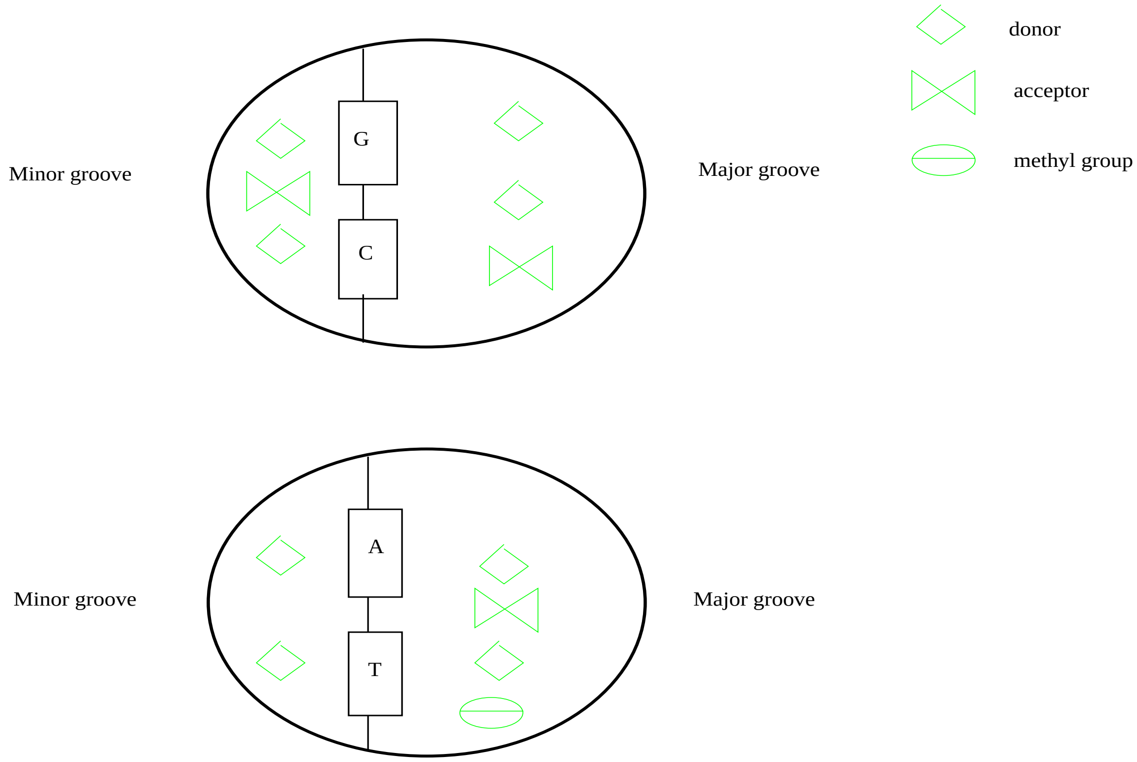

Fig. 2. A sketch of the cross sections of DNA. The base pair G and C (or A and T) is attached to the backbone of DNA. "Major groove" ("minor groove") means a larger region (smaller region) separated by the base pair. Proteins "donor", "acceptor" and "methyl group" are attached to the base pairs symmetrically in minor groove, but asymmetrically in major groove.

chemistry. The dynamics is governed by the Hamiltonian

$$H_{total} = H_{el} + H_{em} + H_{p-e} + H_{phonon}. \tag{3·1}$$

H_{el} is the Hamiltonian of electrons interacting with ions located at $\vec{R}_i$:

$$H_{el} = \int d^3x\, \psi^\dagger(x) \left(-\frac{\Delta}{2m} + \sum_i V(|\vec{x} - \vec{R}_i|) \right) \psi(x), \tag{3·2}$$

where $\psi(x)$ is a second quantized electron field, $V(x)$ is a potential made by the ions. Also, their electromagnetic interactions are written by using the gauge field $\vec{A}(x)$:

$$\begin{aligned} H_{em} &= \frac{ie}{2m} \int \vec{A}(\psi^\dagger \overleftrightarrow{\nabla} \psi)\, d^3x + \frac{e^2}{2m} \int \vec{A}^2 \psi^\dagger \psi\, d^3x \\ &\quad + \frac{e^2}{4\pi} \int \frac{\rho(x')\rho(x)}{|\vec{x}' - \vec{x}|}\, d^3x d^3x', \qquad (3·3) \\ \rho(x) &= \psi^\dagger(x)\psi(x). \qquad (3·4) \end{aligned}$$

We chose the Coulomb gauge which leads the four-electron interaction in the last term. Furthermore, interactions between electrons and phonons have to be taken into account. We expand the potential $V(|\vec{x}-\vec{R}_i|)$ around the equilibrium position of ions $\vec{R}_{i0}$ as

$$V(|\vec{x}-\vec{R}_i|) = V(|\vec{x}-\vec{R}_{i0}|) - \left.\frac{\partial V}{\partial r_i}\right| \vec{i}_i \vec{\varphi}_i + \cdots \tag{3·5}$$

with $\vec{i}_k = \frac{\vec{x}-\vec{R}_{k0}}{|\vec{x}-\vec{R}_{k0}|}$, $\vec{\varphi}_i = \vec{R}_i - \vec{R}_{i0}$ being the phonon field. The phonon - electron interactions are described as

$$H_{p-e} = \int \psi^\dagger \left(- \left.\frac{\partial V}{\partial r_i}\right| \vec{i}_i \right) \psi \vec{\varphi}_i \, d^3x, \tag{3·6}$$

and H_{phonon} in (3·1) is the Hamiltonian of phonons.

§4. Hartree approximations

To solve the system presented in the previous section, first we apply the Hartree approximation to the four-electron interactions in H_{em}:

$$\begin{aligned} &\frac{e^2}{4\pi} \int \frac{\rho(x')\rho(x)}{\vec{x}' - \vec{x}} \, d^3x d^3x' \\ &\to \frac{e^2}{4\pi} \int d^3x \psi^\dagger(x)\psi(x) \left\langle \int d^3x' \frac{\rho(x')}{|\vec{x}' - \vec{x}|} \right\rangle . \end{aligned} \tag{4·1}$$

It is convenient to incorporate it in the potential term of H_{el}. Then, the Hamiltonian we consider becomes

$$H_{el} = \int d^3x \, \psi^\dagger(x) \left(-\frac{\Delta}{2m} + \sum_i V_{eff} \right) \psi(x), \tag{4·2}$$

with the effective potential V_{eff} including the interaction (4·1) in addition to the original $V(x)$. $\psi(x)$ is expanded by a basis of the energy eigenfunctions $\chi_\mu(x)$ as $\psi(x) = \sum_\mu a_\mu \chi_\mu(x)$, with a_μ an annihilation operator of the quanta carrying the energy E_μ. It is however, convenient to use wave functions of the p-wave atomic orbit $\chi_i(x)$ rather than $\chi_\mu(x)$. Changing the basis as $\chi_\mu = \sum_i c^i_\mu \chi_i$, $a^i = \sum_\mu a_\mu c^i_\mu$, we assume the anti-commutation relation

$$[a^{\dagger i}, a^j]_+ = \delta_{ij} \left(\sum_\mu c^{\dagger i}_\mu c^j_\mu \right). \tag{4·3}$$

Note that it is an approximated relation, because the basis χ_i is not exactly orthogonal. In terms of a^i, the Hamiltonian is expressed as

$$H_{el} = \sum_i \alpha_i a^\dagger_i a_i + \sum_{i,j} \beta_{ij} a^\dagger_i a_j, \qquad H_{p-e} = \sum_{i,j,k} \vec{\gamma}^k_{ij} \vec{\varphi}_k a^\dagger_i a_j, \tag{4·4}$$

$$\alpha_i = \int \chi^\dagger_i \left(-\frac{\Delta}{2m} + \sum_i V_{eff} \right) \chi_i \, d^3x, \tag{4·5}$$

$$\beta_{ij} = \int \chi_i^\dagger \left(-\frac{\Delta}{2m} + \sum_i V_{eff} \right) \chi_j \, d^3x, \tag{4·6}$$

$$\vec{\gamma}_{ij}^k = \int \chi_i^\dagger \left(-\frac{\partial V}{\partial r_k} \bigg| \, \vec{i}_k \right) \chi_j \, d^3x. \tag{4·7}$$

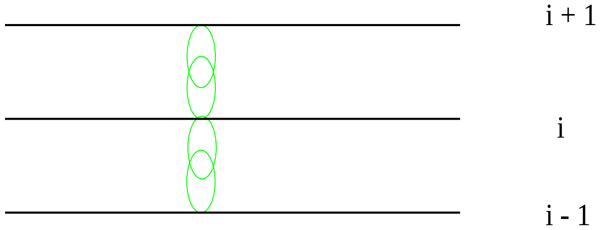

Fig. 3. Assumption for the wave functions to have overlaps only between neighboring sites.

We further assume that the orbital wave functions have overlaps between only nearest neighbors as in Fig. 3 to simplify the Hamiltonian as

$$\begin{aligned} H &= H_{el} + H_{p-e} \\ &= \sum_i \Big[\alpha_i a_i^\dagger a_i + \left(\beta_{i,i+1} + \vec{\gamma}^i_{i,i+1}(\vec{\varphi}_i - \vec{\varphi}_{i+1}) \right) a_i^\dagger a_{i+1} \\ &\qquad + \left(\beta_{i,i-1} + \vec{\gamma}^i_{i,i-1}(\vec{\varphi}_i - \vec{\varphi}_{i-1}) \right) a_i^\dagger a_{i-1} \Big] . \end{aligned} \tag{4·8}$$

In a special case that β, γ are constant and $\vec{\varphi}$ is longitudinal, this Hamiltonian reduces to so-called Su-Schrieffer-Heegger Hamiltonian.[2)]

Finally, we introduce the variable $\sigma = \kappa i$, where κ is a distance between the neighboring ions, and move to the continuous description $\kappa \sim 0$. α_i, $\beta_{i,i+1}$, $\beta_{i,i-1}$, $\vec{\gamma}^i_{i,i+1} \simeq \vec{\gamma}^i_{i,i-1}$ become functions of σ: $\alpha(\sigma)$, $\beta^+(\sigma)$, $\beta^-(\sigma)$, $\vec{\gamma}(\sigma)$, respectively. See Fig. 4. The quantum fields $\psi(\sigma)$ and $\vec{\varphi}(\sigma)$ satisfy the standard (anti)commutation relations

$$\left\{ \psi^\dagger(\sigma'), \psi(\sigma) \right\} = \delta(\sigma' - \sigma), \qquad \left[\varphi(\sigma'), \dot{\varphi}(\sigma) \right] = \frac{i}{M} \delta(\sigma' - \sigma). \tag{4·9}$$

Replacing the sum over the positions of ions i with the integral with respect to σ, we end up with the action

$$\begin{aligned} L = \frac{1}{\kappa} \int d\sigma dt \Big[& \psi^\dagger(\sigma) \left(-i \frac{\partial}{\partial t} \right) \psi(\sigma) - \psi^\dagger(\sigma) \{ \alpha(\sigma) + 2\lambda \} \psi(\sigma) \\ & - \kappa (\beta^+(\sigma) - \beta^-(\sigma)) \psi^\dagger(\sigma) \frac{\partial \psi}{\partial \sigma} - \kappa^2 \lambda \psi^\dagger(\sigma) \frac{\partial^2 \psi}{\partial \sigma^2} \\ & + \frac{M}{2} \left(\frac{\partial \vec{\varphi}}{\partial t} \right)^2 - a\kappa^2 \left(\frac{\partial \vec{\varphi}}{\partial \sigma} \right)^2 \Big], \end{aligned} \tag{4·10}$$

where $\lambda = \frac{1}{2}(\beta^+ + \beta^-) - \kappa \vec{\gamma} \frac{\partial \vec{\varphi}}{\partial \sigma}$. This can be seen as an action of strings which have bosonic and fermionic target space coordinates $\vec{\varphi}$ and ψ. Interestingly, DNA can be an object of string theory.

The trajectory of interacting strings forms a two-dimensional surface of various topologies, which is called world sheet. The string of DNA has quite different world sheet structure compared to the case in ordinary string theory. There are two kind of basic interactions of DNA, i.e. RNA transcription and DNA replication. In the process of RNA transcription, the DNA string propagates and starts to creat short strings at certain points of world sheet time. The new strings go away from the original DNA. On the other hand, the situation of DNA replication is totally different. When the replication starts, the string splits at the positions of sugars (3') and (5'). There are many points, where such splitting occurs, making branch points in the string world sheet.

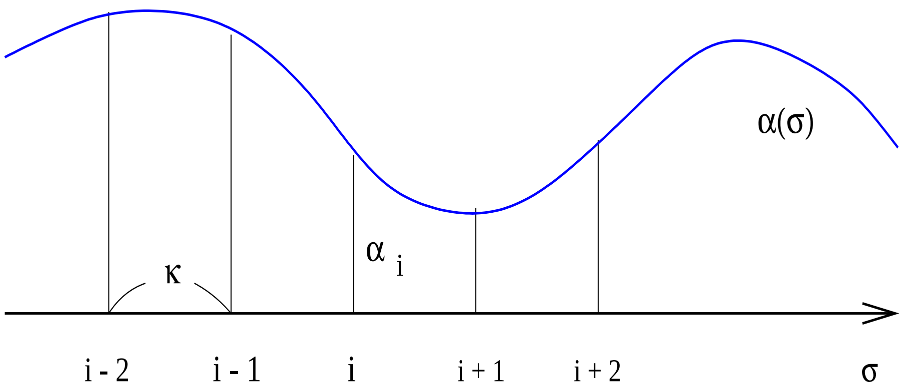

Fig. 4. In the limit $\kappa \to 0$, the discrete variables α_i are well approximated with the field $\alpha(\sigma)$. $\beta^{\pm}(\sigma)$, $\vec{\gamma}(\sigma)$ can also be defined in a similar way.

In order to understand the dynamics of the DNA string model (4·10), first let us consider classical and longitudinal oscillation for a simple case of the limit $\beta^{\pm}$, $\vec{\gamma} \to 0$. It corresponds to the tight binding approximation i.e. π-electrons of atomic orbits decoupled each other. In this case, the equation of motion becomes a simple form: $-i\frac{\partial}{\partial t}\psi - \alpha(\sigma)\psi = 0$, solved as

$$\psi(\sigma,t) = e^{i\alpha(\sigma)t}\psi(\sigma,0) = \int d\sigma_0 e^{i\alpha(\sigma_0)t}\delta(\sigma_0-\sigma)\psi(\sigma,0). \tag{4·11}$$

σ_0 signifies the position where the wave function is localized, and $\alpha(\sigma_0)$ means energy there. Back to the discrete description, it is written as $\psi(j,t) = \sum_i e^{i\alpha_i t}\delta_{ij}\psi(i,0)$.

Next we consider classical oscillation in a general case. The equation of motion is

$$\{E-(\alpha+2\lambda)\}\,\psi - \kappa(\beta^+ - \beta^-)\frac{\partial\psi}{\partial\sigma} - \kappa^2\lambda\frac{\partial^2\psi}{\partial\sigma^2} = 0. \tag{4·12}$$

It can be solved under the WKB approximation as

$$\psi(\sigma,t) = \int \frac{d\sigma_0}{\kappa}\exp\left[\pm\int_{\sigma_0}^{\sigma}\left\{\sqrt{\alpha+2\lambda-E(\sigma_0)-\frac{\delta\beta^2}{\psi\lambda}}-\frac{\delta\beta}{2\kappa\lambda}\right\}d\sigma\right] \\ \times e^{iE(\sigma_0)t}\psi(\sigma_0,0) \tag{4·13}$$

with $\delta\beta = \beta^+ - \beta^-$. If we neglect the $\frac{\partial^2\psi}{\partial\sigma^2}$ term, it reduces to

$$\psi(\sigma,t) = \int \frac{d\sigma_0}{\kappa} e^{iE(\sigma_0)t} \exp\left[-\int_{\sigma_0}^{\sigma} \frac{\alpha + 2\lambda - E(\sigma_0)}{\kappa\delta\beta} d\sigma \right] \psi(\sigma_0, 0). \tag{4·14}$$

One can see that it depends on the sign of $\alpha + 2\lambda - E(\sigma_0)$ and of $\delta\beta$ whether the wave function is localized or not. Back to the discrete description, we have

$$\psi_i(j) = \exp\left[\sum_{k=i}^{j} \frac{E(i) - \alpha(k) + 2\lambda(k)}{\beta_{k,k+1} - \beta_{k,k-1}} \right] \tag{4·15}$$

with $\psi(j) = \sum_i e^{iE(i)t}\psi_i(j)a_i$. It is interesting to calculate physical or biological quantities using this wave function and to compare with experimental data.

§5. Applications[3)]

We discuss about applications of the result obtained in the previous section to the following three cases – luminescence quenching, eletric current and absorption of light.

5.1. *Luminescence quenching*

There is an experiment what we call "luminescence quenching".[4)] Preparing two metals Ru and Rh, one of them is intercalated at one end of DNA, and the other is intercalated at the other end. See Fig. 5. When Ru absorbs light and gets excited, electrons tend to go down to a certain level with luminescence in a life time of the excited state. At that level, however, other electrons from Rh at the other end are provided via transfer through the DNA. As a result, the luminescence is quenched due to the Paule principle. Note that the quenching occurs even when the metals are separated by DNA. It causes purely by the propagation of electrons inside DNA.

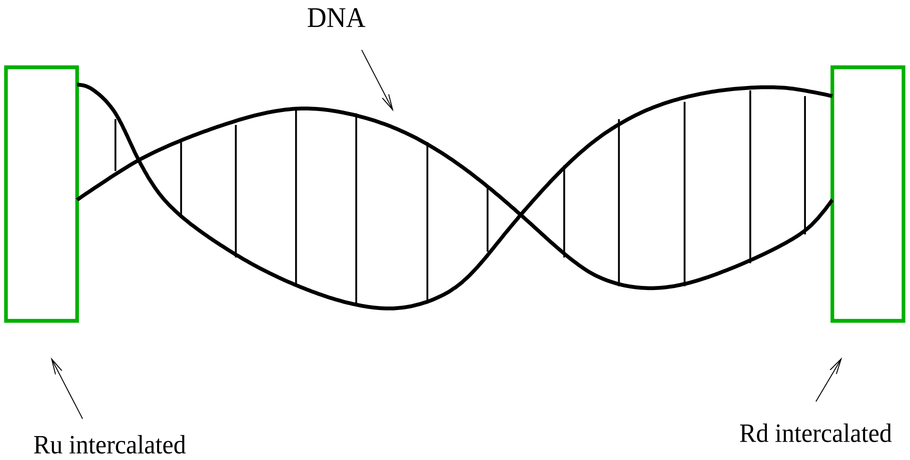

Fig. 5. The set up of an experiment of luminescence quenching.

For this application, we would like to notice some points. The DNA of prokariote, which is called "Genkaku-seibutsu" in Japanese, like bacteria, is interpreted as a closed string. On the other hand, the DNA of eukariote, which is "Shinkaku-seibutsu" in Japanese, like humankind, is an open string. Interestingly, we all have open strings. The open strings have telomere with certain protain at the ends, which makes the strings very stable. As we get aged, the telomere gets shorter and the strings become unstable.

Let us use our theory to compute the probability of the quenching. The interactions to the metals are described by the following terms:

$$H_{int} = \sum_{\vec{k}} U_{\vec{k}} \left(\xi^\dagger(\sigma_L, \vec{k})\psi(\sigma_L) + \xi^\dagger(\sigma_H, \vec{k})\psi(\sigma_H) \right) + \text{h.c.}, \tag{5·1}$$

where $\xi^\dagger$ is a creation operator of electrons on the metals, and σ_H (σ_L) means the higher (lower) end signifying the position of each of the metals. Amplitude of the transfer of electrons is calculated as

$$\begin{aligned} A &= \int \langle f|T(L_{int}(t_H)L_{int}(t_L))|i\rangle \, dt_H dt_L \\ &= 2\pi\delta(E_i - E_f)U_{k'}U_k^* \int dt \, \Delta(t, \sigma_H - \sigma_L) \, e^{iE_i t}. \end{aligned} \tag{5·2}$$

$\Delta(t,\sigma)$ represents the propagator of ψ, which is given by

$$\begin{aligned} \Delta_{ji}(E) &= i\int e^{iEt}\, \Delta_{ji}(t)\, dt = \sum_k \frac{\psi_k(j)\psi_k(i)}{E - E_k - i\varepsilon} \\ &= \sum_k \frac{1}{(E - E_k - i\varepsilon)N_k} e^{\sum_{l=k}^{j} \frac{E_l - E_k}{\delta\beta_l}} e^{\sum_{l=k}^{i} \frac{E_l - E_k}{\delta\beta_l}}. \end{aligned} \tag{5·3}$$

Thus, we obtain the probability

$$R = |A|^2 = 2\pi \frac{dn}{dE} E_i |U_i U_j^*|^2 \left| \sum_k \frac{1}{(E_l - E_k)N_k} e^{\sum_{l=k}^{j} \frac{E_l - E_k}{\delta\beta_l}} e^{\sum_{l=k}^{i} \frac{E_l - E_k}{\delta\beta_l}} \right|^2, \tag{5·4}$$

where $\frac{dn}{dE}$ stands for the density of electrons in the metal Rh.

5.2. *Electric current in DNA*

When each end of DNA is attached to an electrode and voltage is given between the two electrodes, one can see various profiles of electric current in DNA against the voltage.[5)] (See Fig. 6.)

In our theory, the rate of electrons is given by

$$R = 2\pi\delta(E_i - E_f)|U_i U_f^*|^2 \left| \sum_k \frac{1}{(E_i - E_k - i\varepsilon)N_k} e^{\sum_{l=k}^{f} \frac{E_l - E_k}{\delta\beta_l}} e^{\sum_{l=k}^{i} \frac{E_l - E_k}{\delta\beta_l}} \right|^2, \tag{5·5}$$

then the current under the voltage V is computed as

$$I = e\int R \frac{d^3k_i}{(2\pi)^3} \frac{d^3k_f}{(2\pi)^3} (n_f(k_f) - n_i(k_i))$$

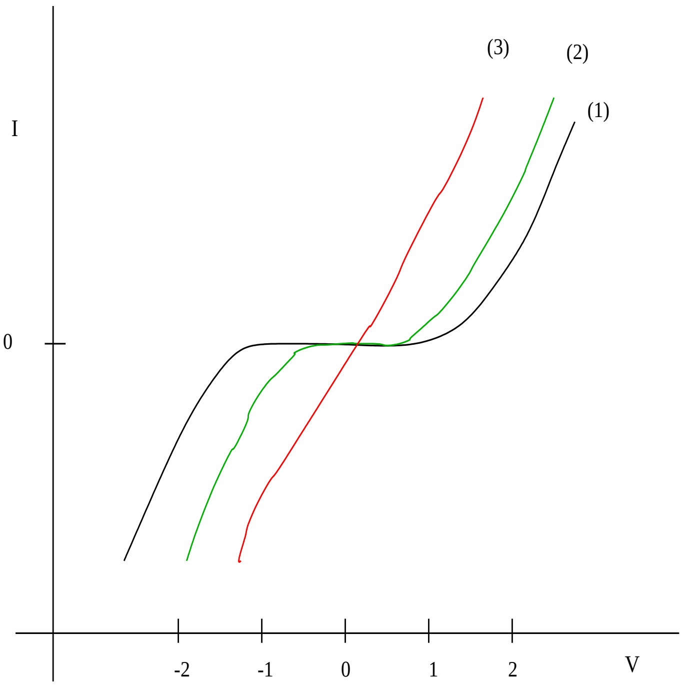

Fig. 6. A schematic plot of the profiles of electric current in DNA. The current exhibits various behaviors like the three curves (1), (2), (3).

$$= \frac{em^2}{2\pi^3} \int dE\, k^2 |U_k|^4 \left| \sum_k \frac{1}{(E_i - E_k - i\varepsilon)N_k} e^{\sum_{l=k}^{f} \frac{E_l - E_k}{\delta\beta_l}} e^{\sum_{l=k}^{i} \frac{E_l - E_k}{\delta\beta_l}} \right|^2$$
$$\times (n_f(k) - n_i(k)), \tag{5·6}$$

where n_f, n_i are distributions of electrons at both ends given by

$$n_{f,i} = \left[\exp\left(\frac{E - \mu_{f,i}}{kT} \right) + 1 \right]^{-1}, \tag{5·7}$$

$$\mu_f = E_F + \frac{1}{2}eV, \qquad \mu_i = E_F - \frac{1}{2}eV. \tag{5·8}$$

E_F is the Fermi energy. In the case of the temperature quite low $T \to 0$, the energy E_k in the intermediate state in (5·5) must fall into the band $[E_F - \frac{1}{2}eV, E_F + \frac{1}{2}eV]$ to give a nonzero contribution to the current I. When E_k is within the band for infinitesimal V, the current I grows always linearly as the voltage V increases. It exhibits a metal-like behavior. On the other hand, in the case that E_k is outside the band for small V, the current is not observed until V exceeds some value V_0, and then linearly grows for $V > V_0$. Its behavior is semi-conductor-like. In this way, the computation from our theory seems to reproduce somewhat similar tendency with the experimental result.

5.3. *Optical absorption*

According to Sarukura's proposal, it is possible that as a nano-size material, DNA absorbs light and electrons are excited from the ground band to an excited band.

Relevant to such process is the electromagnetic interaction in our theory. The interaction term reads

$$\begin{aligned} L_{int} &= \frac{-ie}{2m}\int \vec{A}(\psi^\dagger \overleftrightarrow{\nabla}\psi)\, d^3x dt \\ &= \frac{-ie}{2m}\int \frac{d^3k}{(2\pi)^3\sqrt{2\omega_k}} C^\mu(k)\vec{\varepsilon}_\mu \int d\sigma\, \psi^\dagger(\sigma,t)\psi(\sigma,t)\vec{V}(\sigma,\vec{k})\, e^{i\omega_k t}, \end{aligned} \tag{5·9}$$

where $\vec{V}$ is an analog of the vertex operator of vector fields in ordinary string theory:

$$\vec{V} = \frac{1}{\kappa}\int e^{i\vec{k}\vec{x}} \left(\chi_i^\dagger \overleftrightarrow{\nabla}\chi_{i+1} - \chi_i^\dagger \overleftrightarrow{\nabla}\chi_{i-1} + \chi_i^\dagger \overleftrightarrow{\nabla}\chi_i\right) d^3x. \tag{5·10}$$

The computation of the absorption rate leads to the result

$$R = \frac{e^2}{4m^2}(2\pi)^5\frac{1}{2\omega_k}\sum_\mu \left|\sum_k \varepsilon_\mu^{(i)} V^{(i)}(k,\vec{k})\frac{1}{\sqrt{N_i N_f}}\, e^{\sum_{l=i}^k \frac{E_l - E_i}{\delta\beta_l}}\, e^{\sum_{l=f}^k \frac{E'_l - E'_f}{\delta\beta'_l}}\right|^2. \tag{5·11}$$

§6. Conclusion

We derived three-dimensional string action starting from a system of π-electrons and phonons in DNA under some approximations. It can be solved for the wave functions of π-electrons approximately, and some property of electron transfer inside DNA was seen. Furthermore, applications to luminescence quenching, electric current through DNA and optical absorption are formulated in the theory.

We have lots of problems remaining. First one is to compare our result with direct experiments, which has not been done yet. Second one is a treatment of proteins in our theory. The most important aspect of DNA is an interaction with proteins. How to describe this interaction and the way to understand it are still unclear. Sometimes we can put into the interaction only as a formal background, just like a background of string theory. But sometimes we may have to describe proteins themselves dynamically, because proteins are products of RNA which is a product of DNA.

Thirdly, we have treated the phonon classically, not yet quantized. Some people claim that the phonon-electron interaction maybe leads some new state which makes a behavior of DNA semi-conductor-like.

Finally, further improvement of the approximation is needed. So far we have done analysis only by the Hartree approximation. Some constancies are probably important and further approximation may be important.

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