Energetics of holes trapped in DNA

Vadim Apalkov* and Tapash Chakraborty**†

*Department of Physics and Astronomy, University of Manitoba, Winnipeg, Canada R3T 2N2 and
**Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, USA

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We report on our study of the electronic properties of guanine traps in the DNA surrounded by adenines. We have shown that for a typical range of DNA parameters, formation of the bound state of two holes at the same guanine trap is possible for the GGG and GGGG traps if the hole-hole interaction is weak, which can be achieved for the DNA in solutions. The origin of the two-hole bound state is the competition between the Coulomb repulsion and the phonon mediated attraction between the holes. For the hole-phonon coupling constant $\approx 1$ two holes will be at the same trap if the on-site hole-hole repulsion energy is $\lesssim 0.9$ eV.

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The motion of a hole on DNA is usually studied by detecting its trapping at a series of guanine sites incorporated in the DNA [1]. The hole can be injected into DNA through oxidation process. Oxidation occurs under UV irradiation and in the presence of certain oxidants. Since the guanine has the lowest oxidation potential $E^0$ of the G-pair and the A-pair is about 0.1-0.5 eV [2, 3], which is also in the range of reported numerical estimates [4]. Finally, after the oxidation process takes place we get a guanine radical cation, or a hole injected into DNA at the G-pair. The next step then is the migration of the positive charge (hole) to the spots with lower energy [2, 5] which are the sequence of many guanines, e.g. GG or GGG. The importance of this migration is based on the fact that accumulation of holes at G-sequences makes these spots vulnerable to mutations.

There are a few established pictures of hole migration through DNA until it reaches the spot with the lowest energy: (i) Direct hole tunneling between G and GG (or GGG) spots. This transport mechanism works only when the distance between the G and GG pairs is small (a few base pairs). The transport rate then depends exponentially on the transport distance [2, 6]. (ii) Hole migration through subsequent tunneling: This picture is applicable when the distance between the G and GG spots is large (about 10-15 base pairs) and when between the G spot, where the hole was originally injected, and the GG (or GGG) spots, there are a few G-pairs. In this case the hole migration is via subsequent tunneling between the G-pairs [7]. Since this transport process is diffusive in nature, the transport rate has a power dependence on the distance between the G and GG spots. (iii) The polaronic hopping transport: This picture works when between the G and GG (GGG) spots there are only A-pairs. When the distance between G and GG is small the transport mechanism is again via tunneling (case (i)). However, for large distances, the hole at the G-spot tunnel into the nearest A base and then migrate via polaron hopping (diffusion) through the A…A sequence to the GG (or a GGG) spot [8]. The transport rate has a power dependence on the distance between G and GG.

Finally, the hole will be localized at the spots with the lowest energy, i.e. GG or GGG or GGGG (whichever is present in the DNA). A natural question that arises then is, if instead of a single hole many holes are injected into the DNA, what will be the final configuration of the system? Which positions of the holes will have the lowest energy? Can the GG, GGG, or GGGG spots trap two holes simultaneously? In this case such spots will be highly reactive and vulnerable to mutation. Formation of the bound state of two holes trapped by G-sites is analogous to bipolaron formation in the homogeneous 1D system [9]. In this paper, we report on the properties of the G-traps, surrounded by adenines. The main question we are addressing here is that under what condition the G-traps can accumulate multiple holes.

The Hamiltonian of the hole system consists of three parts: (i) the tight-binding Hamiltonian which includes the hole hopping between the nearest base pairs and on-site energies of a hole, (ii) the hole-hole interaction Hamiltonian, and (iii) the Holstein’s phonon Hamiltonian with diagonal hole-phonon interaction [10].

$$\mathcal{H} = \mathcal{H}_t + \mathcal{H}_i + \mathcal{H}_{ph},$$

where

$$\mathcal{H}_t = \sum_{i,\sigma} \epsilon_i a_{i,\sigma}^\dagger a_{i,\sigma} - t \sum_{i,\sigma} \left[ a_{i,\sigma}^\dagger a_{i+1,\sigma} + h.c. \right],$$

$$\mathcal{H}_i = \sum_{i,j,\sigma} V_{i,j} n_{i,\sigma} n_{j,-\sigma} + \sum_{i,j,\sigma} V_{i,j} n_{i,\sigma} n_{j,\sigma},$$

$$\mathcal{H}_{ph} = \hbar \omega \sum_i b_i^\dagger b_i + \chi \sum_{i,\sigma} a_{i,\sigma}^\dagger a_{i,\sigma} \left( b_i^\dagger + b_i \right),$$

where $a_{i,\sigma}$ is the annihilation operator of hole with spin $\sigma$ on site $i$, $\epsilon_i$ is the on-site energy of hole, $b_i$ is the annihilation operator of phonon on site $i$, $t$ is the hopping integral between the nearest base pairs (sites), $\omega$ is the
phonon frequency, $\chi$ is hole-phonon coupling constant, and $n_{i,\sigma} = a_{i,\sigma}^\dagger a_{i,\sigma}$. The Hamiltonian [Eq. (1)] without the $H_{ph}$ was studied earlier for a homogeneous system in Ref. [1].

In the tight-binding Hamiltonian [Eq. (2)], we assume that the site $i$ can be either a adenine or a guanine. We then take the energy of the hole on the A site as zero energy, i.e. $\epsilon_A = 0$, and the energy of the hole on the G-site to be negative, $\epsilon_G = -\Delta_{GA} < 0$. In the interaction Hamiltonian $H_i$, we take into account only the Hartree interaction between the holes. The first term in Eq. (3) describes the repulsion between the two holes with different spin. The holes can then occupy the same site. The second term in Eq. (3) corresponds to two holes with the same spin. To get the basic idea about the typical range of interaction parameters when many holes are trapped by the G-sites, we introduce a single-parameter interaction potential of the form

$$V_{i,j} = \frac{V_0}{\sqrt{(i-j)^2 + 1}},$$

(5)

where $V_0$ is the on-site repulsion between the two holes. The origin of the form of $V_{i,j}$ in Eq. (5) is the finite spreading of the hole on-site states. This spreading is about the distance between the nearest base pairs. Although the actual dependence of interaction potential on the separation between the holes is more complicated [12] than Eq. (5), this difference is not important for our analysis since only the on-site interaction plays the main role in formation of the bound state of two holes [13]. In the hole-phonon Hamiltonian $H_{ph}$, we include only the optical phonons [4] with diagonal hole-phonon interaction, and do not take into account acoustic phonons which results in non-diagonal hole-phonon interaction [13, 16] i.e. modify the tunneling integral. In Eqs. (2)–(5) we also assumed that the hopping integral $t$, the phonon frequency $\omega$, and the hole-phonon coupling constant $\chi$ do not depend on the type of the base pairs (A or G).

The form of the total Hamiltonian, Eqs. (1)–(4), leads to four dimensionless parameters which characterize the system: The nonadiabaticity parameter $\gamma = \hbar \omega / t$, the canonical hole-phonon coupling constant $\lambda = \chi^2 / (2 \hbar \omega t)$, dimensionless hole-hole interaction strength $V_0 / t$, and the dimensionless difference between on-site energies of G and A, $\delta_{GA} = \Delta_{GA} / t$.

We numerically determine the eigenfunctions and eigenvectors of the hole-phonon system by exactly diagonalizing the Hamiltonian Eqs. (1)–(4) for a finite size system consisting of six base pairs (sites). We also introduce limitations on the total number of phonons $N_{max}$, $\sum_i n_{ph,i} \leq N_{max}$, where $n_{ph,i}$ is the number of phonons on site $i$. To compare the energy spectrum of the systems with different number of holes, we keep the maximum number of phonons per hole the same for all systems. For the two-hole system the maximum number of phonons is $N_{max} = 16$ and for the one-hole system $N_{max} = 8$.

Our finite size system contains six sites which are originally adenines. We then introduce the G-traps with different number $N_G$ of guanines, G, GG, GGG, and GGGG, in the middle of the system. For example the system with two guanines is AAGGAA. For different traps we calculate the energy of the ground state of the systems with one and two holes. Denoting the corresponding energies as $E_{1,N_G}$ (for the one-hole system with $N_G$
guanines) and $E_{2,N_G}$ (for the two-hole system with $N_G$ guanines) we write the condition that the trap with $N_G$ guanines will accommodate two holes as

$$E_{2,N_G} < E_{1,N_G} + E_{1,1}. \quad (6)$$

The meaning of condition (6) is as follows: If two holes are injected into the DNA then the lowest energy of the system corresponds to the case when the holes are trapped by the same trap with $N_G$ guanines. The condition (6) will determine the critical value of the hole-hole interaction strength, $V^{cr}_0$. That means for $V_0 < V^{cr}_0$ two holes will be trapped by the same trap with $N_G$ guanines. For $V_0 > V^{cr}_0$ such a trapping is energetically unfavorable and two holes will be at different traps.

As we shall see below the condition Eq. (6) is not the condition for formation of bound state of two holes within the trap containing $N_G$ guanines. The condition for formation of bound state of two holes should give different values for the critical hole-hole interaction strength, $V^{*cr}_0$. The values $V^{cr}_0$ and $V^{*cr}_0$ would coincide only for an infinite homogeneous system. In our case the system is finite, which results in an inequality $V^{cr}_0 < V^{*cr}_0$. The finite system in our problem is actually the finite number of guanine sites in the traps.

For our investigation of the system [Eqs. (1-3)], we consider the following typical DNA parameters: 0.1 eV < $t$ < 0.3 eV, 0.1 eV < $\Delta_{GA}$ < 0.5 eV, 10$^{-5}$ eV < $\hbar \omega$ < 0.1 eV. For the dimensionless canonical hole-phonon coupling constant we have taken the value $\lambda = 1$. For this coupling constant, the size of the polaron is about 2-3 base pairs. Our calculations show that the critical value $V^{cr}_0$ is very small ($V^{cr}_0 \approx 0.1$ eV) when two holes have the same spin and they can not occupy the same site. This small value of $V^{cr}_0$ also illustrate the fact that the phonon mediated attraction between the holes are largest when the holes occupy the same site. Therefore, in what follows we shall consider only the case of two holes with opposite spin.

In Fig. 1a the ground state energy of a single hole is plotted as a function of the hole-phonon coupling constant, $\lambda$, for different types of traps. For $\lambda \approx 1$ the difference between the bound state of a hole in G and GG traps is about 0.03 eV, which is smaller than the value (0.05 eV) obtained in Ref. [20]. The size of the polaron in our calculations is 2-3 base pairs depending on the values of $t$ and $\omega$. As a next step we calculate the ground state energy of two holes, $E_{1,N_G} + E_{1,1}$, one of which is bound at a G trap and another one at a GGG or GGGG trap. As an example, in Fig. 1b the ground state energy of two holes with the second hole bound by GGGG is plotted as a function of $\lambda$ for different values of the hopping integral, $t$.

In Fig. 2 the ground state energy $E_{2,N_G}$ of two holes bound in a single trap is plotted for $N_G = 3$ (Fig. 2a) and for $N_G = 4$ (Fig. 2b) as a function of the hole-hole interaction strength for different values of $\Delta_{GA}$ and $t$. Here we notice that at some critical value $V^{cr}_0$ of the hole-hole interaction strength, there is a change of slope in the $E_{2,N_G}(V_0)$ dependence. This critical value corresponds to the condition that the two holes are bound in the G-traps, forming a bipolaron. The illustration of this fact is given in Fig. 3. In Fig. 3a the average number of holes, $\langle n_h \rangle = \langle n_{1,\sigma} \rangle + \langle n_{1,-\sigma} \rangle$, is shown as a function of the base pair index for a GGGG trap and two different values of the hole-hole interaction strength, $V_0$. It is clearly seen that for $V_0 = 0.8$ eV < $V^{cr}_0$ the two holes are almost at the same G sites, while at $V_0 = 1.2$ eV > $V^{cr}_0$ the holes are away from each other. The corresponding distribution of

![FIG. 3: The average number of holes (a) and the average number of phonons (b) for a two hole system in a GGGG trap are shown as a function of the base index. The tunneling integral is $t = 0.3$ eV and the hole-phonon coupling is $\lambda = 1$. Dots and triangles corresponds to inter-hole interaction strength $V_0 = 0.8$ eV and 1.2 eV respectively.](image)

![FIG. 4: Energies $E_{1,1} + E_{1,4}$ and $E_{2,4}$ of a two-hole system are shown as a function of hole-phonon coupling, $\lambda$, by dashed and solid lines, respectively. Tunneling integral is $t = 0.3$ eV and $\Delta_{GA} = 0.3$ eV.](image)
the average number of phonons \( \langle n_{ph} \rangle \), is shown in Fig. 3b. Another critical value of \( V_0 \) is introduced by equation Eq. 10. The competition between \( E_{1,1} + E_{1,N_G} \) and \( E_{2,N_G} \) for \( \lambda = 1 \) and different values of \( t \), \( \Delta_{GA} \), and \( \omega \) one can determine \( V_0^{cr} \). The result is summarized in Table 1 for the GGG trap. The corresponding results for the GGG trap is about 0.1 eV smaller values for \( V_0^{cr} \), [7] 4.6 The dimensionless parameters, \( \gamma \), \( \delta_{GA} \), and \( V_0^{cr}/t \), are also given in Table 1. From this data we can conclude that within the present range of parameters the dependence of \( V_0^{cr} \) on \( \Delta_{GA} \) is weak, and \( V_0^{cr}/t \) depends mainly on \( \gamma \). This dependence can be approximated by a linear function as

\[
V_0^{cr} \approx 3\gamma t + 1.6t \approx 3\hbar\omega + 1.6t. \tag{7}
\]

We see from these data that depending on the parameters of DNA, the critical hole-hole interaction strength, \( V_0^{cr} \) can range from 0.4 eV to 0.8 eV. Numerical analysis of the electron correlations in different types of DNA [12] shows that the hole-hole interaction strength is around 0.9 eV for A-DNA and 1.5 eV for B-DNA. Additional suppression of the inter-hole interaction by a factor of \( \approx 0.7 \) can occur for DNA in solution, when hole-hole interaction is screened by polar solvent molecules and mobile counterions. Under this condition trapping of two holes by GG and GGGG traps would be possible.

In conclusion, we have shown that for a typical range of DNA parameters, formation of bound state of two holes at the same guanine trap is possible for GG and GGGG traps if the hole-hole interaction is sufficiently weak, which can be achieved for DNA in solutions. Formation of the two-hole bound state results in double positive charge of G-traps, which should modify their chemical properties and increase the reactivity of these traps. Experimental study of the two-hole states in G-traps should also give additional insight on the hole-phonon interaction strength. Formation of the bound state of two holes at the G-traps requires a strong hole-phonon interaction, which should overcome the hole-hole Coulomb repulsion. In our calculations the hole-phonon coupling constant was \( \lambda = 1 \) which is larger than the experimentally reported \( \lambda \approx 0.2 \) in Ref. [22]. Hence, experimental observation of the two-hole bound state should give an additional estimate for the strength of hole-phonon interaction.

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\begin{array}{cccccc}
\text{Table I: Calculated values of } V_0^{cr} \text{ for various values of the dimensionless DNA parameters} \\
\hline
\text{t (eV)} & \hbar\omega (eV) & \Delta_{GA} (eV) & V_0^{cr} (eV) & \gamma & \delta_{GA} V_0^{cr}/t \\
\hline
0.1 & 0.1 & 0.1 & 0.42 & 1.00 & 1.00 & 4.2 \\
0.1 & 0.1 & 0.3 & 0.45 & 1.00 & 3.00 & 4.5 \\
0.1 & 0.1 & 0.5 & 0.46 & 1.00 & 5.00 & 4.6 \\
0.1 & 0.05 & 0.1 & 0.36 & 0.50 & 1.00 & 3.6 \\
0.2 & 0.1 & 0.1 & 0.42 & 0.50 & 0.50 & 3.25 \\
0.2 & 0.1 & 0.3 & 0.59 & 0.50 & 1.50 & 2.95 \\
0.2 & 0.1 & 0.5 & 0.62 & 0.50 & 2.50 & 3.1 \\
0.3 & 0.1 & 0.1 & 0.82 & 0.33 & 0.33 & 2.7 \\
0.3 & 0.1 & 0.3 & 0.78 & 0.33 & 1.00 & 2.6 \\
0.3 & 0.1 & 0.5 & 0.82 & 0.33 & 1.67 & 2.7 \\
0.3 & 0.05 & 0.3 & 0.60 & 0.17 & 1.00 & 1.97 \\
0.3 & 0.05 & 0.5 & 0.62 & 0.17 & 1.67 & 2.07 \\
\end{array}
\]