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Important Structural Factors Controlling the Conductance of DNA Pairs in Molecular Junctions

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It has been demonstrated experimentally that DNA base pairs and sequences can be identified by measuring their current changes in metal junctions. We report here a first principles study on electron transport properties of DNA base pairs in gold metal junctions. It is found that the experimentally observed electrode-separation-width-dependent current changes of DNA base pairs are not due to the difference in number of hydrogen bonds involved in different base pairs as proposed in earlier experimental studies but caused by the difference in their stacking structures. It reveals that such an electronic read-out technique is not exact, but practically useful since the statistically favorable misaligned junctions do show distinct dependence on the character of the base pair.

The high costs of DNA sequencing have limited the wide use of a DNA technique in basic research and clinical medicine.¹ One noticeable development in this field is to take advantage of electron transport properties of DNA base pairs and sequences.^{2–6} The use of well-established electronic technology is expected to be an effective approach with great potential to lowering the costs. It has been shown that the hydrogen bonds between neighboring base pairs and the structural configurations of DNA strands can both affect electrical properties of DNA.^{9–12} Recently, a striking experimental finding is that with a scanning tunneling microscopy (STM) technique it is possible to identify the DNA base pairs by measuring the decay of their tunneling currents with respect to the distance between the substrate and the STM tip.^{7,8} The claimed underline mechanism is that the difference in the number of hydrogen bonds in the guanine–cytosine (G-C) and the adenine–thymine (A-T) pairs, (3 and 2, respectively), could result in different current–distance relationships.^{7,8} Moreover, it was found in the experiments that the hydrogen bonds can affect the current over a distance of 2 nm.⁸ These observations strongly challenge the basic intuition about the hydrogen bond. It is well-known that hydrogen bond is quite weak and localized because of its weak electrostatic nature.

We report in this paper our first principles studies on electron transport properties of a G-C or a A-T pair in a junction with gold electrodes following the experimental setup and measuring procedure given in the experiments.^{7,8} It is found that the hydrogen bonds have only a small and short-range effect on the current, while the impact of the stacking of two bases induced by shortening the distance between the electrodes is tremendous. The latter is a natural consequence of the experimental setup and was not discussed before. It also shows that for a perfectly hydrogen bonded base pair, the hydrogen bonding induced current disappears only after pulling the electrodes apart

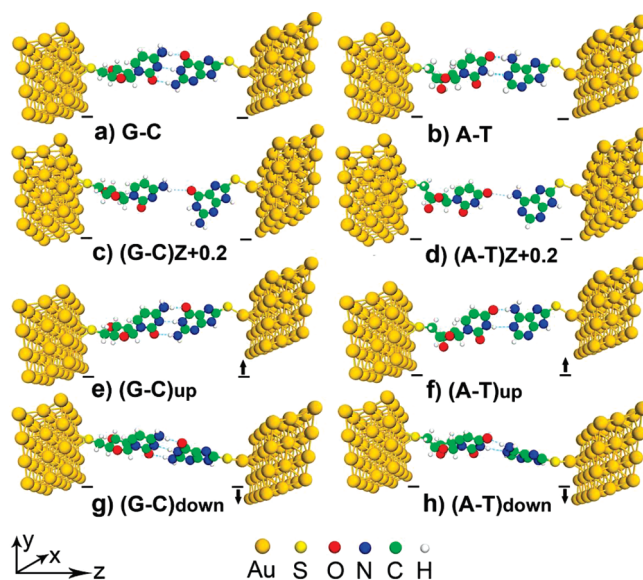


Figure 1. Configurations of molecular G-C and A-T pairs junctions with gold electrodes. (a) and (b) Perfectly aligned base pairs at equilibria. (c) and (d) Perfectly aligned base pairs after the right electrode pulling apart by 0.2 nm along the Z axis. Misaligned base pairs with the right electrode moving up (e and f) and down (g and h) by 0.3 nm.

for less than 0.3 nm, much shorter than what was claimed in the experiments.⁸

All the molecular junctions with either a G-C or an A-T pair sandwiched between two semi-infinite gold electrodes under investigation are illustrated in Figure 1. We have considered three cases taking into account the possible mutual spatial arrangements of two base molecules: perfectly aligned pairs and misaligned pairs with one electrode moving either up or down. The molecular structures of the base pairs are identical to the ones presented in the experiment.⁸ The base pairs are bonded to the gold electrode through the Au–S bond. The gold electrodes are constructed by three layers of an Au(111) slab,

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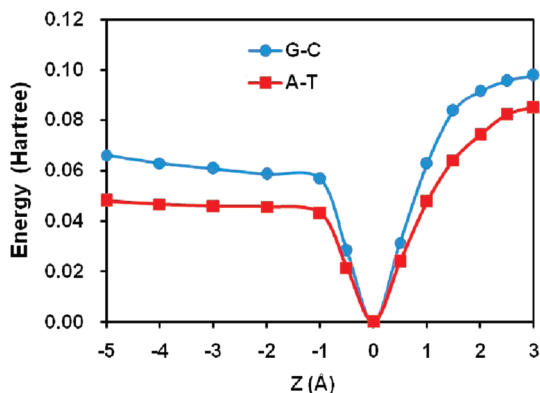


Figure 2. The change of the total energy for junctions of A-T and G-C pairs as a function of the moving distance of the right electrode.

which extends to 4×4 perpendicular to the transport direction. For the left electrode, the sulfur is on the hollow site of the gold surface with a bond distance of 2.86 Å. The right electrode, representing the movable STM tip in the experiments, is constructed by adding an extra gold atom on the top of the hollow site of the surface which connects to the terminal sulfur atom to ensure the flexibility of the junction. Geometry optimization has been performed with gold atoms fixed using density functional theory at hybrid B3LYP level with 6-31(d, p) basis sets for the light elements and Lanl2dz basis set for the gold atoms, as implemented in the Gaussian 03 package.¹³

The optimized structures for the perfectly aligned G-C and A-T junctions are shown in parts a and b of Figure 1. To simulate the experiments, the right electrode (STM tip) of each junction has been pulled out/in along Z axis step by step with an interval of 0.25 Å. At each step, the structure of the junction is always reoptimized. As examples, parts c and d of Figure 1 illustrate the optimized structures of the G-C and A-T junctions when the right electrode is pulled out by 0.2 nm. At this distance, only one hydrogen bond is presented in both junctions. Calculations have also shown that when the right electrode pulls out by 0.3 nm, the hydrogen bond is completely broken. The energy profiles of DNA pairs as the function of the distance between electrodes are shown in Figure 2. It can be seen that the hydrogen bond covers a very narrow region (± 0.1 nm) with an obvious energy dip. The compression of the electrodes introduces almost no energy changes, indicating that the DNA pairs are very soft.

It could be anticipated that in the experiment it would be difficult to perfectly align two bases simply due to the uncertainty in controlling the STM tip position and the actual molecular bonding site. To examine the possible effects of misalignment between two base pairs, we have considered two cases as shown in parts e and f of Figure 1, in which the cytosine and the thymine bases are moved up or down about 3.0 Å vertically (along the Y axis). For these types of junctions, we have also performed calculations to examine the effects of electrode pulling by adopting the same computational procedure as employed for the perfectly aligned junctions. It is worth mentioning that all the stepwise optimizations for different types of junctions are extremely time-consuming and can only be achieved with the help of massive parallel computing. For the misaligned junctions, we have also found that the hydrogen bond is broken after pulling out the right electrode by 0.3 nm. In the experiments, one of the electrodes, the STM tip, was pulled apart by as much as 2 nm, which is way beyond the effective region of hydrogen bonding. It might be possible that the initial

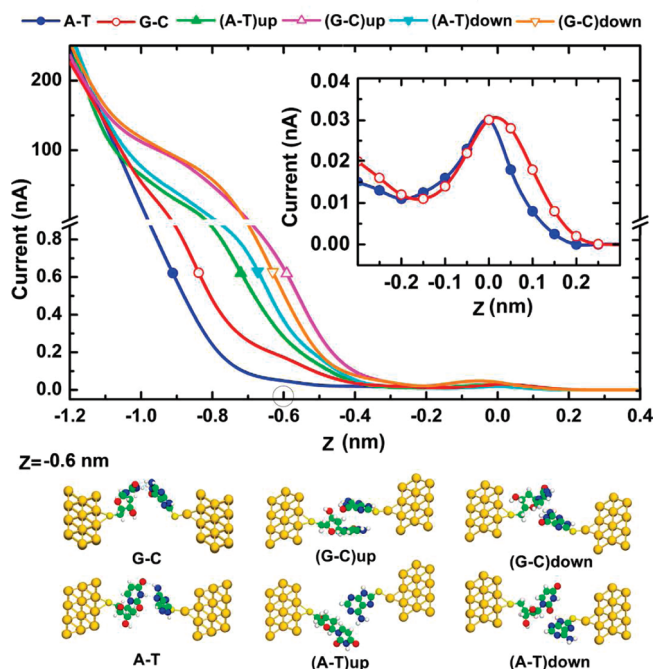


Figure 3. Current–distance relationships for different junctions. The equilibria of the base pairs are set to $Z = 0$. The right electrode can be pulled out (positive Z) and in (negative Z). Insert is for the region around $Z = 0$ for the perfectly aligned G-C and A-T pairs. The optimized configurations of the junctions at $Z = -0.6$ are given at the bottom.

position of the STM tip was not at the perfect hydrogen bonding point but inserted into the molecular layer on the other electrode. If so, the stacking of two bases caused by the compression of the junction would become an important factor in controlling the current. In order to compare directly with experimental measurements, we have calculated the tunneling current in different junctions with different junction widths.

Electronic transport calculations have been performed by employing density functional theory (DFT) and the nonequilibrium Green's function technique implemented in ATK package¹⁴ with standard parameters. PBE gradient corrected density functional is used to describe the exchange-correlation interactions. Double ζ basis plus polarization (DZP) is employed for all the atoms except Au, which uses single ζ basis plus polarization (SZP) basis set. Here we only present the results at the bias voltage of 0.4 V to be consistent with the experimental results.⁸ The initial position of the electrode, $Z = 0$, is set at the energy minima of the base pair junctions. The calculated current–distance relationships for all junctions under investigation can be found in Figure 3. In general, the current shows roughly an exponential decay with respect to the pulling distance. At different distance, the current is controlled by different factors. Around $Z = 0$, the base pair is linearly connected by the hydrogen bond, which should be a major contributor to the current in this region. The hydrogen bonding induced current changes are clearly demonstrated by the results given in the insert of Figure 3 for perfectly aligned G-C and A-T pairs. It can be seen that the induced current is strongly correlated with the hydrogen bonding strength and only occurs within a narrow distance interval from -0.2 to $+0.2$ nm. It is noticed that the hydrogen bond effect of the G-C pair with 3 H-bonds extends over a slightly wider range, about 0.05 nm, than that of the A-T pairs with 2 H-bonds. But as clearly shown in the insert of Figure 3, the difference would be too small to be detected in the experiments. Our calculations can thus lead

to the conclusion that the experimentally observed distance dependent current changes over a 2 nm region can not only be a result of the hydrogen bond effect.

When the electrodes are pushed closer, the base pair intends to form a stacking structure. As examples, Figure 3 shows also the configurations of base pairs in different junctions at $Z = -0.6$ nm. At this distance, the two bases in the perfectly aligned G-C and A-T pairs are lifted up, while for misaligned junctions, they form a stacking structure. Under these conditions, the current is completely dominated by the through-space electron transport. In the misaligned molecular junctions, the stacking of two bases can be more easily achieved and their currents show much rapid increase with respect to the compression of the junction. It has been well demonstrated in previous studies that the stacking effect can significantly enhance the conductance of molecular junctions.^{9,12,15} The DNA pairs in compressed junctions give just another good example.

The current–distance relationship is sensitive to the mutual arrangement of two bases in the junction. It can be seen that the misaligned base pair junctions always result in larger current than those of perfectly aligned ones, due to a simple fact that the stacking of base pairs is more easily formed in misaligned junctions. This also indicates that the base pair stacking is a much more important factor than the hydrogen bond in controlling the current of the junctions. It is interesting to see that for the two sets of misaligned junctions the G-C pair seems always to have slower decay rate than that of the A-T pairs. When the base pair become perfectly aligned, the G-C pair still gives a lower decay rate than that of the A-T pair, but both are very different from the misaligned base pair junctions. Without knowing the exact alignment of the base pair inside the junction, it is in principle very difficult to distinguish the G-C and the A-T pairs. However, in the real experiments, one could image that from a statistic point of view, in most cases, the formed junctions could be misaligned. This explains the reported experimental results of Chang et al.,⁸ which showed that the G-C pair decays much slower than the A-T pair.

In summary, our first principles calculations have shown that the experimentally observed distance dependent current changes of DNA base pair junctions^{7,8} are determined by different

structural factors in different regions. Around the equilibrium point, where the base pair is linearly connected by the hydrogen bond, the current of the system is mainly controlled by the hydrogen bond. While at the compressed region, the current of the system is mainly controlled by the stacking structure. It is found that this electronic read-out technique is not exact for identifying DNA base pair but is probably practically useful since the statistically favorable misaligned junctions do show distinct dependence on the character of the base pair.

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