Electronic properties of DNA

Written presentation for seminar II course

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Abstract

This seminar shortly reviews basic properties of DNA molecule in the beginning in order to understand the foundations of electronic conduction. It describes why and how DNA conducts charge carriers. I shall develop a simple model to show how \(\pi-\pi\) coupling influences the complex DNA conduction behavior. Two conduction mechanisms will be explained on rather empirical level. I will also try to find the background for such a variety of amazingly different experimental outcomes. A short review of experiment is covered at the end of the seminar.
1 Introduction

The DNA molecule, well known from biology for containing the genetic code of all living species, has recently caught the attention of chemists and physicists. A major reason for this interest is DNA’s potential use in nanoelectronic devices, both as a template for assembling nanocircuits and as an element of such circuits. DNA is a suitable candidate for use in molecular electronics because of highly specific binding between single strands of DNA, its related self-assembly property, and the ability to synthesize DNA in whatever sequence you want (versus the hit and miss control over, say, carbon nanotubes). Without question, a truly conducting form of DNA would have a major impact on developments in nanotechnology. It has also been suggested that extended electronic states of DNA could play an important role in biology, e.g., through the processes of DNA damage sensing or repair or through long-range charge transfer.

Motivated by these potential applications, numerous studies of charge transport in DNA have been carried out. However, although some consensus on the dominant mechanisms of single-electron transfer in DNA seems to be emerging [1], the nature of DNA’s intrinsic conductance properties remains highly controversial. Charge-transfer reactions and conductivity measurements show a large variety of possible electronic behavior, ranging from Anderson and band-gap insulators to effective molecular wires and induced superconductors. Indeed, understanding the conductance of a complicated polyelectrolytic aperiodic system is by itself a major scientific problem. In this seminar, I shall summarize the wide-ranging experimental and theoretical results and look for any consistencies between them. The seminar provides a quantitative overview of DNA’s electronic states, focusing on dependence on structure, molecular stretching and twisting, and water and counterions.

Heredity

I am the family face;
Flesh perishes, I live on,
Projecting trait and trace
Through time to times anon,
And leaping from place to place
Over oblivion.

The years–heired feature that can
In curve and voice and eye
Despise the human span
Of durance — that is I;
The eternal thing in man,
That heeds no call to die.

(by Thomas Hardy)
2 The structure of DNA

In order to adequately comprehend electronic properties of DNA\(^1\) some attention should be paid towards its structure and particular components.

The famous double–helix structure discovered by Watson and Crick 50 years ago consists of two strands of DNA wound around each other (see the figure on the frontpage). Each strand has a long polymer backbone built from repeating sugar molecules and phosphate groups (Figure 1). Each sugar group (deoxyribose) is covalently bound to one of four nucleobases. These four bases (planar heterocyclic molecules), guanine (G), cytosine (C), adenine (A) and thymine (T), form the genetic alphabet of the DNA, and their order or sequence along the molecule constitutes the genetic code.

In double–stranded DNA two polynucleotide chains associate through complementary hydrogen bonding. The chemical bonding is such that an A base only pairs with a T base, while a G is always paired with a C. It is of great importance that A\(·\)T base pairs associate via two hydrogen bonds, whereas C\(·\)G base pairs are joined by three hydrogen bonds (Figure 2). The base pairs look like the rungs of a helical ladder. Since the phosphate groups on the backbone are negatively charged, the DNA is always surrounded by positive counterions.

Figure 1: A single strand of DNA. This chain of DNA is composed of the bases T, A, C and G. Note that the nucleotides are linked through the phosphate groups connected between 5’ carbon and the 3’ carbon of adjacent deoxyribose sugar molecules. The chain of DNA has a negatively charged phosphate backbone with two chemically distinct ends. This sequence of DNA would be written TACG by the 5’ → 3’ convention.

Figure 2: Hydrogen bond is represented by single dashed line. C\(·\)G base pair (right) is strongly bonded than A\(·\)T base pair (left) due to an extra hydrogen bond.

\(^1\)Deoxyribonucleic acid
There are one hundred million base pairs in a chromosome. All of 46 human chromosomes make up a total length of the human DNA approximately 2 meters long. The existence of the tertiary structure enables a DNA molecule of such a length to be packed into a cell core of a few µm radius. The tertiary structure is governed by the special proteins call histones about which a DNA only 2 nm thick is wound. However, as one might have suspected, DNA is not a very pliable material. The length on which DNA behaves as a solid rod, the so called persistence length, can be estimated to about 60 nm which corresponds to approximately 200 base pairs. Due to the electrostatic forces the negatively charged outer skin of the DNA (the sugar–phosphate backbone) can be wound around the positively charged histone.

Figure 3: Structural parameters: The Watson–Crick double helix is composed of about 10.5 base pairs per helical turn. Since 360° constitutes one helical turn, there would be a 34.3° twist angle or rotation per residue between adjacent base pairs. The helix pitch or length per helical turn is 35.7 Å. The axial rise or distance between two planar base pairs is 3.4 Å. The base pair tilt or deviation from the horizontal plane of the bases is about −6°. The helix diameter or the width of the helix is about 20 Å.

Figure 4: (a) The double-helix structure of DNA consists of two linear strands with four bases: guanine (G), cytosine (C), adenine (A) and thymine (T). The A bases on one strand pair up with the complementary T bases on the other strand, while G pairs up with C. (b) Electron-transfer-rate experiments have been carried out on DNA molecules that have donor and acceptor groups added at each end. In electronic-transport experiments, the DNA molecules are sandwiched between two metal electrodes.
3 Why think of DNA as an electronic material?

As early as 1962, scientists suggested that the interbase hybridization of $\pi_z$ orbitals perpendicular to the planes of the stacked base pairs in double-stranded DNA (with the DNA helical axis parallel to the $z$ coordinate axis) could lead to conducting behavior. There are similar stacked aromatic crystals that are indeed metallic. The most famous of such materials are the Bechgaard salts (Figure 5). However, DNA also has important differences from these and conventional conductors.

![Figure 5: The Bechgaard salt (TMTSF)$_2$PF$_6$, a conducting molecular crystal.](image)

3.1 DNA, a highly dynamic and complex system

Most significantly, unlike crystals, biological DNA is not a periodic system. The largest ionization potential difference between two isolated bases is about 0.6 eV between guanine and thymine (see Figure 10), which exceeds the estimated electronic coupling between highest occupied molecular orbitals (HOMO) or lowest unoccupied molecular orbitals (LUMO) of neighboring base pairs (see Figure 11). This would lead to the expectation of random potential induced localization of the electronic states in the base pair stack.

In addition, the double helix of DNA acts to keep the hydrophobic bases out of water, and the acidity of DNA (negative phosphate groups on the backbone) requires a proximate condensation of positively charged counterions (normally Na$^+$ or Mg$^{2+}$) in the environment. The water molecules and counterions are, of course, polyelectrolyte, and exert non-negligible forces on the electrons in the base pair stack, which again contributes to an apparent random electronic environment. Hence it is insufficient to consider simply the molecule itself; one must also consider its surroundings.

The strong influence of molecular vibrations further complicate the study of DNA as an electronic material. In particular, the root-mean-square vibrational displacement of a base pair in DNA at room temperature is estimated to be about 0.3–0.4 Å, which is a tenth of the lattice constant and an order of magnitude higher than in crystals at room temperature. In effect, DNA is on the verge of melting, which of course is biologically useful in terms of facilitating replication or partial uncoiling (for genetic expression, regulation, or repair), but is technologically problematic, since one would prefer a more stable material!

Taken together, these structural, environmental, and vibrational properties make DNA a highly dynamic and complex system, and it is interesting to ask whether traditional concepts borrowed from solid-state physics might apply in understanding the diverse experimental results on this system.
3.2 The $\pi-\pi$ electronic coupling

$\pi-\pi$ interactions of stacked base pairs in double-stranded DNA could lead to conducting behavior. The reasoning behind this idea was that DNA’s bases are aromatic entities (i.e., organic compounds containing planar, unsaturated, benzene-type (Figure 6) ring structures) whose $p_z$ atomic orbitals (AOs) perpendicular to the plane of the base can form rather delocalized $\pi$ bonding and $\pi^*$ antibonding molecular orbitals (MOs) (Figure 7). These are separated by an energy gap of about 4 eV (Figure 10). If the coupling between the base pairs is strong enough, this could lead to extended states along the helical axis with a reduced DNA energy gap, due to level broadening. For a vanishing gap this could possibly lead to metallic DNA. On the other hand, even in the case of a nonvanishing gap, there is still the possibility of doping by either electrons or holes, in analogy to conventional doped semiconductors.

Figure 6: Benzene is a aromatic planar molecule, with 6 $sp^2$ hybridized C atoms, each having a $p_z$ AO perpendicular to the plane of the ring.

Figure 7: Six different $\pi$ MOs can be made from the benzene $p_z$ AOs. While it is not shown on the figure, the energy of all six unhybridized AOs together is midway between the one–node and two–node orbitals. The ground state of benzene has the three lowest energy MOs doubly occupied.

In order to have extended, metallic states in DNA, the $\pi$ and $\pi^*$ states of the base pairs have to overlap sufficiently. This depends again on the twist angle and the separation of two successive base pairs. Since the $\pi$ and $\pi^*$ MOs are formed by the $p_z$ AOs perpendicular to the base pairs and pointing along the helical axis, one can also consider a simple Hückel model using just these. Two $p_z$ AOs from different base pairs, as shown in (Figure 8), couple by $pp\sigma$ and $pp\pi$ hybridization. These hybridization matrix elements have different signs due to the signs of the lobes of the $p_z$ AOs and may be modelled with the semiempirical Slater–Koster theory

$$V_{ppX} = \eta_{ppX} \frac{\hbar^2}{md^2} e^{-\frac{d}{\eta_e}}, \quad (1)$$

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where $\eta_{pp\sigma} > 0$ and $\eta_{pp\pi} < 0$. In Slater–Koster theory $d$ and $m$ are the distance between the AOs (see Figure 8) and electron mass. The exponential distance cutoff $R_c$ is additionally introduced to describe the exponential tails of the wave functions at large separations. The parameters $\eta$ and $R_c$ can be determined by matching to results of ab initio calculations.

Figure 8: The coupling between two $p_z$ AOs from parallel base pairs. The $pp\sigma$ and $pp\pi$ contributions have opposite signs and can cancel each other. Here, $d$ and $l$ are the distance between the two AOs and its projection on either base pair plane, respectively, and $z$ is the separation of the two base pairs.

The interatomic electron transfer matrix element between two stacking $p_z$ AOs on neighboring base pairs is then a combination of $pp\sigma$ and $pp\pi$ hybridization, which are given by

$$V = V_{pp\sigma} \sin^2 \phi + V_{pp\pi} \cos^2 \phi.$$  \hspace{1cm} (2)

According to this formula, complete annihilation of $V$ occurs when

$$\frac{l}{z} = \sqrt{\frac{\eta_{pp\sigma}}{|\eta_{pp\pi}|}} \approx 2.0,$$  \hspace{1cm} (3)

where $l$ and $z$ are defined in (Figure 8). Here, the value 2.0 on right–hand side of (Eq. 3) follows from a fit, and $z$ is about 3.4 Å for both A– and B–DNA (Figure 9). Hence, for a fixed base pair separation $z$, poor contacts between two AOs of adjacent base pairs reduce their electronic coupling contribution to the total electronic coupling between MOs on neighboring base pairs. A good contact is defined by $l \approx 0$ Å.

The electronic coupling between base pairs can be reduced for two reasons. First, the positive $pp\sigma$ and negative $pp\pi$ interaction between two interacting $p_z$ AOs can reduce or almost cancel each other, leading to a small net atomic pair interaction. Second, some rather large, predominantly $\sigma$ and $\pi$ pair interactions can reduce or cancel each other when added up to calculate the total base pair coupling. In other words, small base pair coupling can be caused by small individual atomic pair interactions or by an equal number of rather large positive and negative ones. This cancellation tendency is particularly important for A–DNA.

The resulting couplings exceed 1 eV for the $p_z$ AOs that are right on top of each other. But the actual couplings between base pairs are given by the overlap of the $\pi$ or $\pi^*$ MOs, which are extended in the plane of the base pair, and these are generally much smaller. In other words, the participation ratio for each single $p_z$ AO in the overall base pair MO is small. Approximating the MOs of different base pairs as being orthogonal to each other, one can describe the coupling between two successive base pairs by

$$t_{n,m} = \sum_{i} N_1 \sum_{j} N_2 V_{ij}^{12} c_{i}^{1,m} c_{j}^{2,m}.$$  \hspace{1cm} (4)
Three well-known (but highly idealized) forms of DNA: B and A are right-handed with 10 and 11 phosphates per helical turn, respectively, while Z is left-handed with 12 phosphates per turn. Real right-handed DNA in solution averages about 10.5 phosphates per turn, or halfway between B and A.

Here $i$ and $j$ run over the $N_1$ and $N_2$ $p_z$ AOs of base pairs 1 and 2, respectively. G–C has 19 while A–T has only 18 $p_z$ AOs. The $c_{i,j}^{n}$ is the $i$th LCAO (linear combination of atomic orbitals) coefficient of the $n$th MO of base pair 1. $V$ is the off-diagonal block matrix $(N_1 \times N_2)$ of the Hamiltonian matrix $(N_1 + N_2) \times (N_1 + N_2)$ describing the interaction between the states of the two base pairs.

Hence according to (Eq. 4) each interaction matrix element connecting two $p_z$ AOs from different base pairs is multiplied by two LCAO coefficients, whose product has a magnitude of order $1/m$. Hence each hybridization matrix element has only a small contribution to the inter–base–pair electronic coupling $t^{n,m}$. As one can see from (Eq. 2), the coupling $t^{n,m}$ will depend on how well the base pairs are stacked, i.e., on their relative twist angle and their separation. These variables are determined by the DNA structure, i.e., A–, B–, or Z-DNA (Figure 9). On the other hand, the dependence of $t^{n,m}$ on these variables is also important to understand, since at finite temperature the base pairs of DNA will oscillate about their equilibrium positions. This can affect the electronic coupling and hence the charge–transfer rate and conductivity.

Figure 9: Three well–known (but highly idealized) forms of DNA: B and A are right–handed with 10 and 11 phosphates per helical turn, respectively, while Z is left–handed with 12 phosphates per turn. Real right–handed DNA in solution averages about 10.5 phosphates per turn, or halfway between B and A.

Figure 10: Schematics of DNA energy levels. The DNA gap of 3.75 eV is taken from an optical absorption measurement, which also corresponds to the excitation energies of single bases. The excited–state energies of the bases are obtained from the single–base ionization energies by simply adding the gap size.
3.3 Coupling to vibrations

We shall discuss the effects of torsional modes on the electronic coupling $t_{n,m}$ by examining results from a numerical calculation\(^2\). On general grounds one would expect the single electron or hole transfer to be very sensitive to the motion of base pairs. One experiment finds time scale 75 ps in charge-transfer experiments. This presumably stems from a necessary reorientation of base pairs in order to make charge transfer possible. This is consistent with the extremely soft torsional acoustic modes ($\leq 20$ cm\(^{-1}\)) calculated theoretically and also seen in the dynamic Stokes shifts in fluorescence spectra.

In (Figure 11) we show the electronic coupling $t_{n,m}$ computed from DFT as a function of the twist angle about the helical axis. We disregard the influence of sequence upon base pair separation and relative twist here.

The different plots correspond to couplings between HOMOs (with energy corresponding to the ionization energy) and LUMOs (with energy corresponding to the electron affinity energy) between different base pair dimers. The coupling between HOMOs is important for hole transport, while the coupling between LUMOs is important for electron transport.

According to (Figure 11) there are sign changes of $t_{n,m}$ as a function of the twist angle. Interestingly, the sign changes occur near the equilibrium twist angle of A–DNA. The LCAO coefficients stay approximately constant during the rotation, so that the sign changes must stem from the interaction matrix elements $V_{ij}$, which depend strongly on the geometry of the base pair dimer. At room temperatures, the twist angle has a standard deviation of about 8°. In the interval of ±8° about the equilibrium it is possible that $t_{n,m}$ vanishes. One can easily imagine that base pair to base pair charge transport is limited by the low twisting frequencies, of order $10^{11}$–$10^{12}$ Hz, particularly in structures close to the A form. Separately at an angle of −36°, the base pairs are perfectly aligned (for identical base pairs) and parallel to each other. This leads to optimal $\sigma$ overlap and to a maximal $t_{n,m}$. At least for identical base pairs this can easily be rationalized, since we get approximately $t \approx \sum_i V_{ii}(c_i)^2 > 0$, where $V_{ii}$ are all positive due to $\sigma$ overlap and add up to give a large contribution. $V_{ij}$ with $i \neq j$ are typically very small.

The dependence of $t_{n,m}$ on the base pair separation is less dramatic.

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\(^2\)Theoretical approaches can be divided into two classes: model calculations and \textit{ab initio} (Hartree–Fock, DFT, and quantum molecular dynamics) calculations.
4 Charge migration mechanisms

The majority of the available experimental information on charge migration, separation, shift, and recombination in DNA pertains to hole (positive ion) transfer and/or transport in solution. Consider, for example, an extended molecule with a donor group at one end and an acceptor at the other end. Initially, DNA is doped\(^4\) by photoexciting a donor molecule which is bound to the DNA chain and supplies an additional charge to the DNA’s base pair. The base guanine is an easy target for many oxidizing agents. A hole placed in a guanine’s HOMO is only about 0.2 eV above the next lower occupied orbitals (of adenine; thymine and cytosine are even lower) and can begin to migrate through the DNA to find other easily oxidizable sites, like other guanines or sequences of guanines. In this scenario of hole transport DNA’s LUMO is not involved, because it is about 4 eV higher in energy. Extensive experimental and theoretical studies have shown that electron–transfer reactions within such a single molecule can occur by two principal mechanisms.

The first consists of a single–step electron–tunneling process\(^4\) from the donor localized site to the acceptor localized site involving intervening DNA–nucleobases as superexchange–mediators. This process is said to be coherent in the sense that the electron does not exchange any energy with the molecule during the transfer, and the electron is never localized. The rate of such reactions decreases exponentially (Table 5) with the distance between donor and acceptor. Therefore, for electron transfer over very long distances, one expects this coherent rate to be insignificant on any reasonable time scale (Figure 12).

The second possible mechanism for long–distance electron transfer is generally referred to as thermal hopping\(^5\). In this incoherent process, the electron is localized on the molecule and exchanges energy with it. Electron transfer proceeds in a multi–step fashion from donor to acceptor. Such hopping processes can transfer charge over far longer distances than the coherent tunneling process, and the motion can be thought of as diffusive, described in terms of a weak algebraic distance dependence. (Figure 12, Table 5)\(^6\).

\[
k_{CT} \propto e^{-\beta R_{DA}} \propto e^{-\eta n R_1} \quad \text{tunneling} \\
\beta \quad 0.6 - 1.4 \text{ Å}^{-1} \quad 0.01 - 0.1 \text{ Å}^{-1} \quad \text{hopping} \\
\eta \quad / \quad 1 - 2
\]

While this picture of coherent transfer and thermal hopping appears to describe the basics, it may not be the full story. Do the charge carriers have a polaron character: that is do they distort the neighboring DNA structure? What is the role of counterions:

\(^3\)in chemical terminology, oxidized or reduced
\(^4\)Synonyms: Unistep charge transfer, The superexchange mechanism
\(^5\)Synonyms: Multistep hopping–type charge transport, The hopping mechanism
\(^6\)\(k_{CT}\)…charge transfer rate, \(R_{DA}\)…donor–acceptor distance, \(n\)…number of base pairs in the bridge between donor and acceptor, \(R_1\)…the nearest distance of neighboring base pairs
could they possibly dope DNA in the way impurities contribute to the carrier density of a homogeneous semiconductor?

Figure 12: (a) Charge carriers hop along the length of the DNA molecule from one G·C base pair to the next. (b) The relative energies of G·C and A·T base pairs in this DNA sequence show that a positively charged hole has a lower energy on the G·C sites and moves from one G·C pair to the next by coherent tunnelling through the A·T sites.

Some of the pioneering work on photoinduced charge transfer shows a weak distance dependence, which led to suggestions that DNA could act as a molecular wire. However, later work using different donors and acceptors argued against the wire–like picture for DNA. The interpretation of some of these experiments may be even more uncertain, since it is not even clear if the reaction involves electron or hole transfer.

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7We note that the use of the term wire in the DNA charge–transfer literature is somewhat problematic, if not wholly ill defined. In this context we take wire to mean that injected holes or electrons can enjoy long range transport, i.e., over tens of angstroms, on fast time scales of picoseconds or less.
5 Conductivity

The question of whether DNA is intrinsically conducting is an unsolved problem. The experimental outcomes are amazingly different, covering all possible results: insulating, semiconducting, Ohmic, and even induced superconductivity. One difficulty is to make cleanly reproducible and easily interpreted experiments with nanoscale dimensions. The other difficulties have to do with the large number of variables (experimental conditions) on which the outcome of the experiments depend.

Assuming that the literature data are not artifacts and provide useful information about DNA conductivity, we can separate the sources of experimental uncertainties into two categories:

Contacts between the electrode and the DNA molecule: The contact is characterized by the work function of the electrode, as well as the nature of the tunneling barrier. Is there direct metal–π orbital contact or do charge carriers first have to tunnel through the backbone? If so, what is the size of the barrier? Unfortunately, only the work functions of metal electrodes are more or less known. In the important case of gold, it is not even clear if the Au work function is below or above the DNA LUMO.

Differences in the DNA molecules and their environments: There are many factors that influence DNA conductivity:

1) DNA sequence. Since each base has its own molecular energy level, a nonperiodic sequence will lead to disorder along the one-dimensional molecule (Figure 10).

2) Length of the DNA molecule.

3) Character of the DNA molecule (e.g., ropes vs single molecules).

4) Environment of DNA (influence of water and counterions). Here, for example, the number of water molecules is critical in influencing structure: for 5–10 water molecules per base pair, DNA obtains the A structure while for more than 13 water molecules per base the B structure is preferred.

5) Microstructure of DNA (dependent upon humidity, stretching, or combing preparation conditions).

6) Interfacial character (e.g., free-standing molecules, surface-bound DNA on, say, CaF$_2$ windows).

7) Preparation and detection protocols (drying of DNA via flowing N$_2$ gas, which tends to provide 2–3 water molecules per nucleotide; detection of single molecules by scanning probe microscopies or electron microscopies, which can dope the molecules).

Some of the above-mentioned variables are hard to control, e.g., the nature of the contact and the actual structure of DNA. A key experimental challenge in measuring DNA conductance lies in the attachment of a DNA bundle or single molecule to two electrodes. This has been made possible largely due to advancements in nanotechnology. Electron-beam lithography is used to fabricate nanoelectrodes, atomic force microscopy (AFM) and low energy electron point source (LEEPS) microscopy are used to image the sample, and scanning tunneling microscopies (STM) can be utilized to induce a tunneling current.
6 Experimental results

The experimental results from different groups can be clearly seen to vary widely. Again, assuming the results not to be artifacts, we can examine them to see if they can be explained consistently owing to the large number of factors mentioned above. To do so, we divide the results into the following four classes:

- **Class 1:** DNA is an insulator at room temperature, as found by Braun et al. [8], de Pablo et al. [9], Storm et al. [5], and Zhang et al. [10]. These samples show I–V characteristics with essentially no discernible conductance out to ±10 V bias, consistent with completely localized states.

- **Class 2:** DNA is a true wide-band-gap semiconductor at all temperatures, as measured by Porath et al. [4] and (for B–DNA oligomers) by Rakitin et al. [11].

- **Class 3:** DNA is Ohmic or nearly Ohmic at room temperature (it may show a small activation gap of less than 0.2 eV) and is insulating at low temperatures, as found in experiments by Fink and Schönenberger [3], Cai et al. [12], Tran et al. [13], Rakitin et al. [11] (dried B–DNA droplets), Yoo et al. [14], and Hartzell et al. [15], [16].

- **Class 4:** DNA is truly metallic down to low temperatures requiring extended molecular energy bands, as suggested by Kasumov et al. [6]. This isolated case is the hardest to account for. Since, to my knowledge, there has been no independent verification of this result, it is the least reliable one.
7 DNA nanotechnology

The self-assembly properties of the DNA double helix can be exploited to make a variety of structures. In this case (left), the bases on one molecule (red) bind together with the fragments of two other molecules (green and blue) that have complementary bases. When a fourth fragment is added (black), the result is a cross. Three-dimensional structures, such as cubes (right), have been already built, using this principle.

DNA chips are patterned with many short snippets of single-strand DNA, each with a different sequence of bases. When DNA has been extracted from a cell, for example, and labelled with a fluorescent marker, it will only bind to the fragments that have exactly the right genetic code. Currently the chips are read out optically by searching for the fluorescent markers, but the electronic properties of DNA might soon be exploited for this purpose.

Figure 13: (a) 2D and 3D DNA structures. (b) DNA sequencer.

8 Conclusion

In this seminar I have presented an elementary introduction to the electronic properties of DNA. We began by discussing its similarities to certain charge transfer molecular metals. We then summarized recent experimental and some theoretical studies of electron transport in DNA. For migration of a single hole in DNA, a general theoretical consensus appears to be emerging. However, the conductance behavior of DNA remains poorly understood. Nevertheless, insights from \textit{ab initio} methods do help explain some of the conflicting experimental outcomes. It appears that drying DNA, as is usually done prior to measuring the conductance, can lead to DNA conformations with localized electronic $\pi$ states, although hole doping of the backbone by counterions might be possible. On the other hand, wet DNA may support electrical current, partly due to solvent impurity states sitting in the large $\pi-\pi^*$ energy gap. In the case of divalent magnesium counterions, these might even dope unoccupied $\pi^*$ states with electrons. Whether the molecule of life can also lead us into a second industrial revolution cannot yet be said. We are just at the beginning. The first DNA field-effect transistor has been built, and more DNA-based molecular electronic devices will likely follow.
References


