

Study of HLGS AND Transfer Integrals OF DNA Bases for Investigating Charge Conduction

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Abstract: The scaling down of electron devices to achieve higher component density and speed is pushing electronics into the realm of molecular electronics. DNA is one of the foremost contenders for use as material in the futuristic molecular integrated circuits. In molecules charge conductivity is a function of energy of molecular orbitals. Due to the small size of molecules there are finite energy gaps between the two corresponding molecular orbitals. The transfer integrals and HOMO-LUMO gaps play a vital role in the charge conduction through molecules. In this paper the values of energy levels for occupied and unoccupied molecular orbitals of isolated DNA bases Adenine, Guanine, Thymine and Cytosine have been calculated using Hartee Fock method with STO-3G basis set in Gaussian 03 program. The transfer integrals for electron and hole transport through the DNA bases and HOMO-LUMO gaps of the four molecules are derived from the energy levels to study the electronic properties of the DNA bases. It is found that Guanine is most appropriate for hole transfer while cytosine is most probable for electron transfer. The HLGs for all the four bases are much larger than the room temperature thermal energy rendering all the four bases as suitable for use in nano-electronic devices.

Key Word: DNA, molecular electronics, transfer integrals, HOMO-LUMO Gap, nanoelectronic devices

I. Introduction

The development of electronics has been driven by scaling down of electronic devices. The scaling down of CMOSFETs which has been instrumental in enhancing the performance of integrated circuits is steering the devices into sub-50nm regime [1]. As the size of devices is reduced, the fundamental limits and technical capabilities of devices are challenged. Also the quantum effects make their presence felt in the nano-sized devices. Therefore to continue with the prodigious development of the integrated circuits it is essential to work on novel devices that are small and utilize the quantum effects. Molecules offer an excellent alternative for modeling of nano-scale electron devices. These new age devices would provide us with extremely high density integrating circuits with extremely low power consumption. Single electron devices are promising new class of nanoscale devices that can control and manipulate the flow of a single electron [2],[3],[4],[5],[6]. These devices lie at the intersection of two research trends, i.e. mesoscopic physics and miniaturization of electronic components, utilizing the quantum effects governing the flow of electrical current through an island. Coulomb blockade phenomenon and single electron charging form essential aspects of single electron devices. Study of these effects in DNA bases forms the basis of this paper.

II. DNA

DNA is a large bio-molecule, which sustains the genetic pattern of life. It is a long chain comprising of four monomers. Each of the four monomers is a unit called nucleotide. The nucleotide consists of a phosphate group, a 2-deoxyribose (5-carbon sugar), and one of the four bases namely Adenine, Thymine, Guanine and Cytosine. Adenine (A) and Guanine (G) are double ringed structure and are called Purines, while the single ringed bases Thymine (T) and Cytosine (C) are classified as pyrimidines. The molecular structure of the four bases is shown in Figure 1.

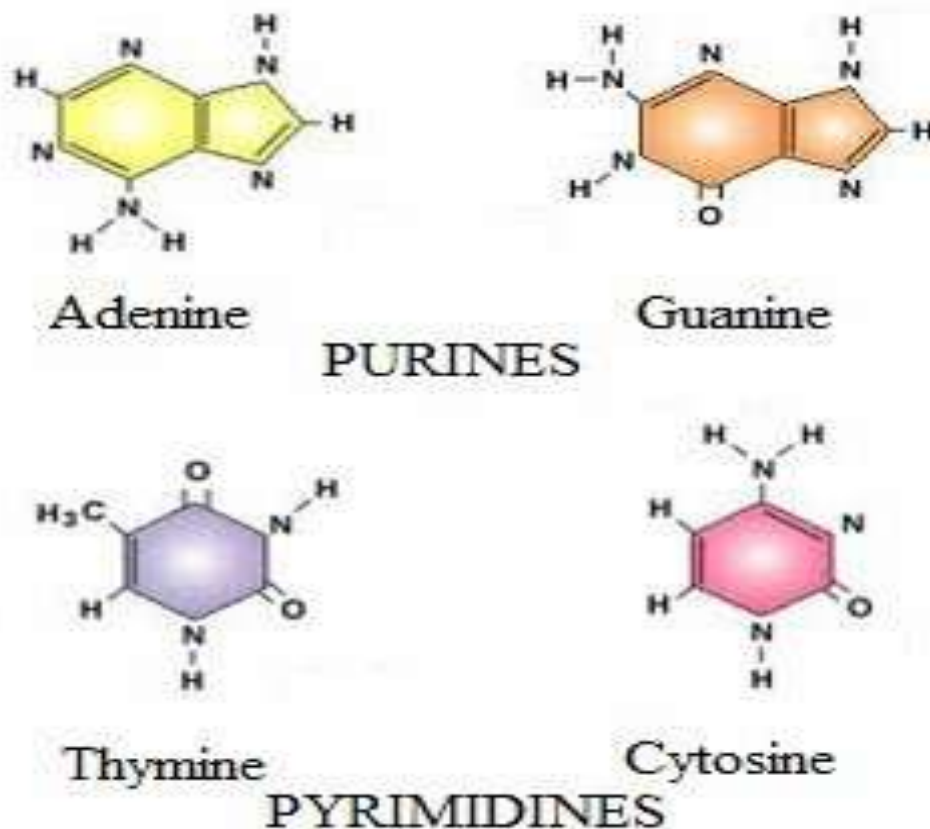


Figure 1 Bases of DNA Adenine, Thymine, Guanine and Cytosine

DNA exhibits unique property of recognition and self-assembly which can be utilized in molecular electronics. The fixed base pairing A-T and G-C render a unique self-recognition property to DNA. It describes the capability of the molecule to form selective bonds with other molecules or with substrates. This property of molecular recognition in DNA can be exploited to drive bottom-up fabrication of devices and integrated circuits from elementary blocks. The molecular electronic circuits can be constructed by joining various molecular electronic components based on the information stored in the structural features of the interacting molecules. The property forms the basis of molecular device integration. This property of self-recognition leads to self-assembly, which is capability of molecules to organize itself in supramolecular aggregates under suitable conditions [8]. Self-organization of structures due to property of self-recognition and self-assembly may occur in solution or solid state through hydrogen bonding, Vander Waals and dipolar interactions. The presence of selectivity approach in molecules while making choice of interacting partners reflects the information stored in the structure at the molecular level. These features in DNA molecules make them particularly suitable for use as active components for nanoscale devices [9]. Also by virtue of their sequence-specific recognition properties and related self-assembling capabilities, they might be employed to wire the electronic materials in a programmable way [10],[11],[12].

III. DNA Bases as Electronic Material

Electron transport through single molecules placed between two metal electrodes is expected to be very different from transport in bulk structures. This is mainly due to the inherent small size of the molecules. For very small islands, the quantum splitting between electron energy levels may become larger than E_c and $k_B T$. In this paper the focus is on studying the individual DNA bases rather than DNA strands for use in DNA based electronic circuits. As the charge transport through the molecules depends upon the placement of molecular orbitals in the energy spectrum, the energy values for the various occupied and unoccupied molecular orbitals of the four bases have been calculated.

3.1 Methodology:

Geometries of the four DNA bases Adenine , Guanine, Thymine and Cytosine were constructed using the templates for nucleic acids from the AMBER force field as implemented in HYPERCHEM7. The sugar-phosphate backbone was removed from the structures and hydrogen was added at standard bond lengths instead. The equilibrium energy levels of the molecular orbitals of the four molecules were calculated in Gaussian 03 program. The self consistent field method, Hartree Fock was used to minimize the energy of molecular orbitals utilizing the STO-3G basis set. The transfer integrals and HOMO-LUMO gaps were derived from the energy values of the various occupied and unoccupied molecular orbitals to predict the electronic properties of the four DNA bases.

Transfer Integrals

In molecules the charge conduction is portrayed as the intermolecular process in which charge hops between two molecules. The hole and electron transport process at the molecular level can be described as electron transfer or hole transfer reactions between the neighbouring molecules. The rate constant for electron transfer can be defined using the Marcus theory, [13]

$$k_{et} = 4[\pi^2/h (\pi/\lambda + k_b T)^{-1/2} \exp(-\lambda + / 4k_b T)] \quad (1)$$

Where t is the transfer integral/coupling matrix element between neighboring molecules, λ is the reorganization energy. The transfer integrals are related to the energetic splitting of frontier orbitals of the molecules and it can be calculated if coordinates of the interacting molecules are known. The transfer integrals can also be calculated using the direct coupling scheme or Koopman's theorem. [14],[15],[16].The splitting can be calculated using the energies of the HOMO, HOMO-1, LUMO and LUMO +1 of the molecules [17],[18] which can be obtained with the INDO Hamiltonian at the HF/STO-3G optimized geometry. The energy difference of the HOMO and HOMO-1 gives the energy splitting for the hole transport whereas the LUMO and LUMO+1 difference gives the energy splitting of the electron transport.

To calculate the transfer integrals in DNA bases for hole transport, values of HOMO- (HOMO-1) have been obtained from the energy levels of the occupied molecular orbitals. Similarly (LUMO+1) - LUMO have been obtained from the split energy levels that determine the transfer integrals for electron transfer. The values of the transfer integrals thus obtained for Adenine, Thymine, Guanine and Thymine are shown in Table 1.

Table 1 Transfer Integrals for holes [H-(H-1)] and electrons [(L+1)-(L)] in DNA bases where H is HOMO energy and L is LUMO energy

DNA Base	H-1 (eV)	H (eV)	H-(H-1) (eV)	L (eV)	L+1 (eV)	(L+1)-L (eV)
Adenine	-8.03	-6.61	1.41	6.15	7.05	0.89
Thymine	-8.24	-7.07	1.17	6.61	8.30	1.68
Guanine	-8.82	-6.18	2.64	6.45	7.51	1.06
Cytosine	-8.05	-6.42	1.63	6.37	8.33	1.96

The values of the transfer integrals for hole and electron transport for the four bases have been plotted in Figure 2. These values signify the probability of charge transfer through these molecules. It is observed that the transfer integral for hole transport is highest in Guanine while transfer integral for electrons transport is highest for Cytosine. Incidentally these bases are a natural complement for each other. The transfer integrals for hole transport are larger in the double ringed (pyrimidines) Adenine and Guanine as compared to their single ringed (purines) natural complements. Opposite is true for electron transport. The transfer integrals for electron transport are larger in Thymine and Cytosine than their natural complements Adenine and Guanine. This reflects that the pyrimidines will be a natural choice for hole localization while electrons will localize on the purines to facilitate charge transport through the DNA molecules.

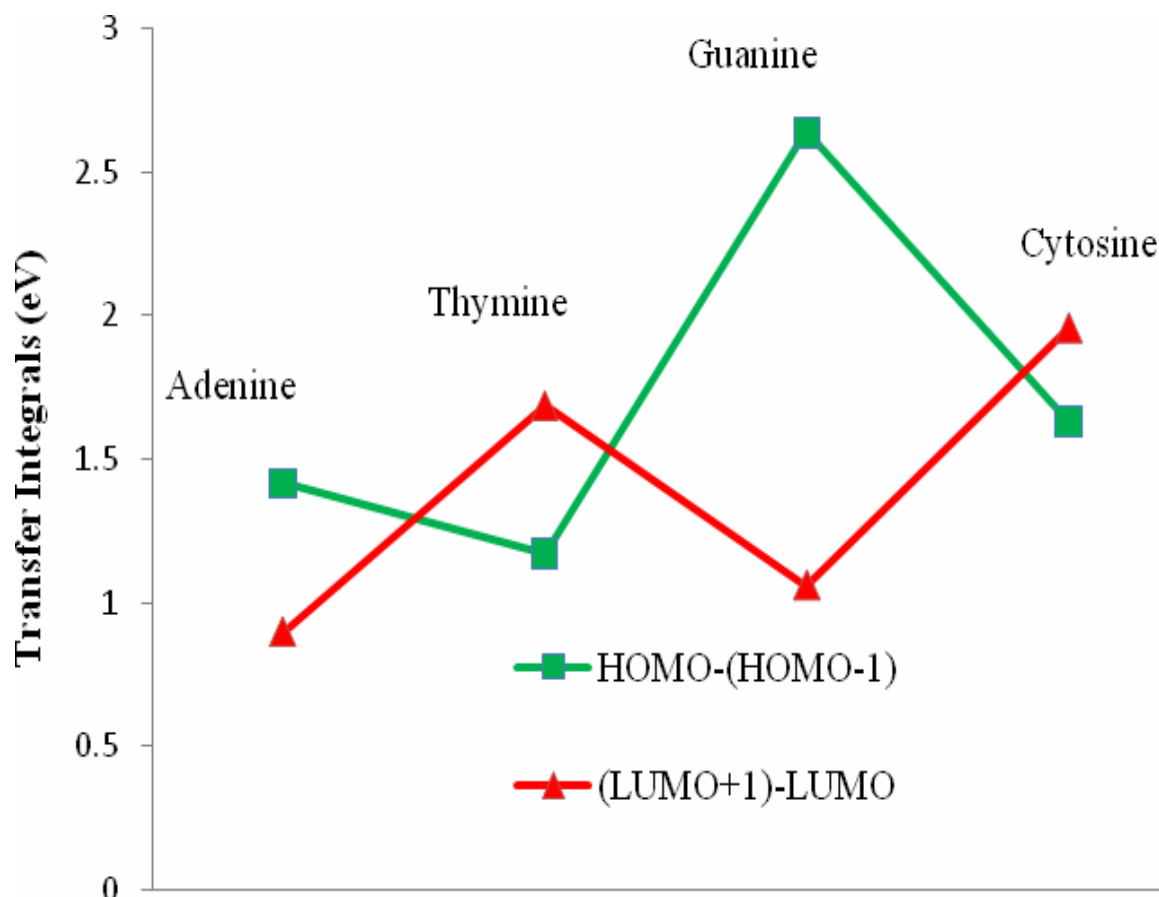


Figure 2 Transfer integrals of the DNA Bases

3.2 HOMO-LUMO Gaps

Molecular orbitals are energy levels present in a molecule which can be occupied by electrons. The occupancy of these orbitals is defined by the energetic of electrons revolving around the nucleus. The orbitals closer to the nucleus are occupied by electrons. In molecules these orbitals are separated by a substantial energy gap virtue the inherent small size of molecules. The occupied orbitals are surrounded by empty orbitals called unoccupied orbitals. The gap between occupied and unoccupied orbitals is called HOMO-LUMO Gap that describes the hardness of a molecule. HOMO is the Highest Occupied molecular orbital which can be similarised to the valence orbital of the organic semiconductor. LUMO (Lowest Unoccupied Molecular Orbital) is the energy level next to HOMO and signifies an energy level that can be occupied on addition of an extra electron. The energy gap between the HOMO and LUMO represents the charging energy which can also be treated like band gap energy between valence and conduction band. This gap may serve as a measure of excitability of a molecule where smaller gap means that the molecule can be easily excited. So the value of HLG basically signifies the thermal stability of the molecule which is essential feature for room temperature electronics.

Temperature can play havoc in the performance of electron devices. The thermal energy can very easily affect the flow of current in the devices and can definitely smear the performance of single electron devices, which are essentially the driving force behind nanoelectronics. The single electron devices are basically based on handling of singular electronic charge for propagation of charge through the devices. The charging energy (energy required to add on an electron onto the molecule or to remove an electron from the molecule) is crucial in the operation of a molecular single electron device. The single electron effects are possible subject to the condition that the HLG of molecules is larger than the thermal energy at the operating temperature so that the electrons do not jump from valence (HOMO) to conducting orbital (LUMO) due to thermal energy. At room temperature (300K) thermal energy is calculated to be equal to 0.026 eV.

The first step in understanding the operation of any inhomogeneous such as molecular device is to draw an equilibrium energy level diagram assuming that there is no voltage applied between the metallic contacts

across the molecule. So the values of equilibrium energy levels of the various DNA base molecules were converted into energy level diagram as shown in the Figure 3 where dark lines represent the occupied and the gray lines represent the unoccupied molecular orbitals. The HLG of the four bases were calculated from the values of energy levels of molecular orbitals and are tabulated in Table 2.

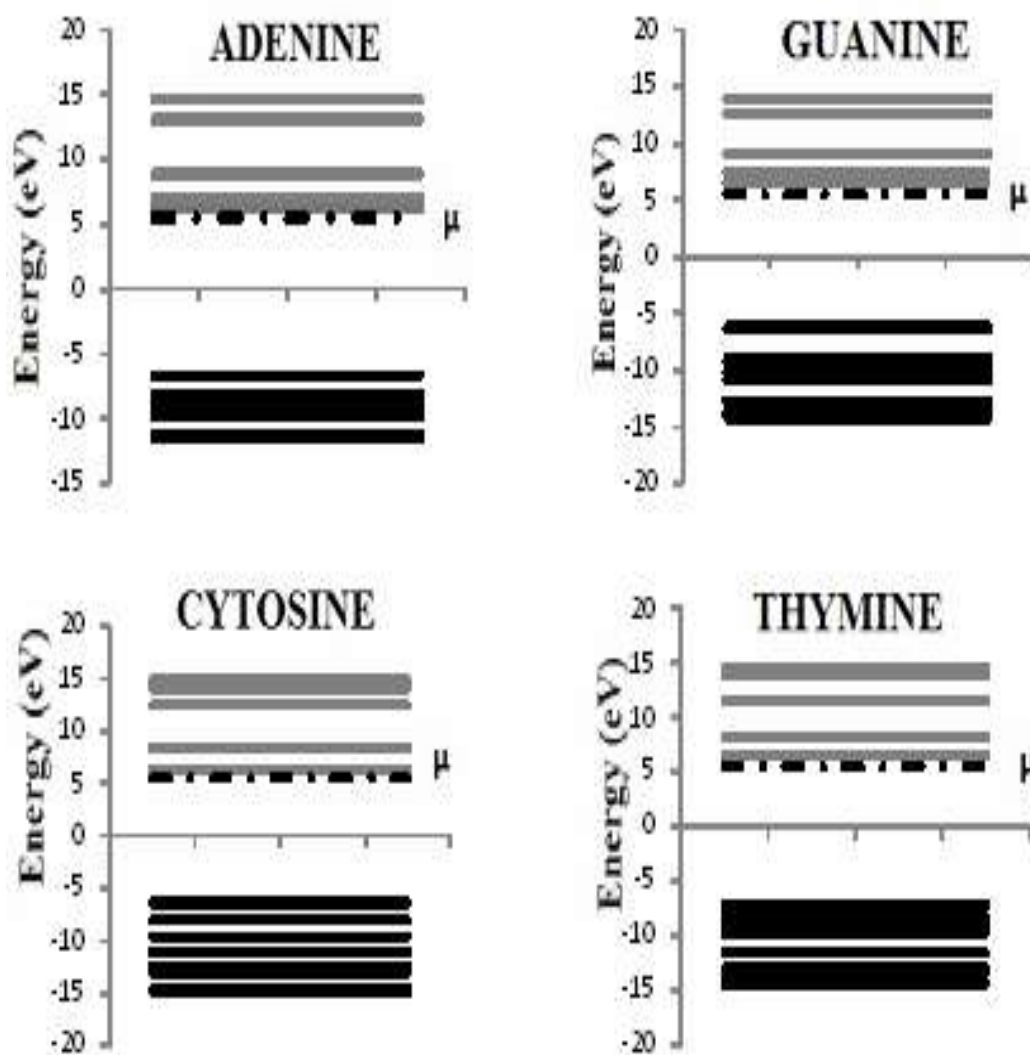


Figure 3 Equilibrium Energy Levels of the DNA Bases Adenine, Guanine, Cytosine and Thymine. The dark lines represent occupied orbitals and the gray lines represent unoccupied orbitals.

Table 2 HUMO-LUMO Gaps for DNA bases Thymine (T), Cytosine (C), Adenine (A), Guanine (G)

DNA Base	HOMO (eV)	LUMO (eV)	HLG (eV)
Guanine	-6.17	6.44	12.62
Adenine	-6.61	6.15	12.76
Cytosine	-6.42	6.36	12.78
Thymine	-7.07	6.61	13.68

It is observed that Guanine (G) offers lowest HLG of 12.62 eV, while the other DNA bases are listed in increasing order of HLG as A (12.76 eV) < C (12.78 eV) < T (13.68 eV). All the HLG values are much larger than the thermal energy value. This renders all the four DNA bases as suitable for use in room temperature single electron devices. The HLGs also depict the barrier for conductivity of charge carriers through the molecules. This barrier represents the charging energy required for an electron to enter the conduction orbital so as to propagate through the molecule. The charging energy also represents the presence of coulomb blockade in the DNA bases that is an integral ingredient of the single electron devices.

IV. Conclusion

DNA molecules are strong contenders for use in nanoelectronic devices. In this paper the four DNA bases Adenine, Guanine, Thymine and Cytosine have been studied for probable use in electronic devices. The equilibrium energy levels of a molecule represent the blueprint of a molecule. The same were drawn for the four DNA bases to study the charge conductivity probability. Transfer integrals and HLGs were calculated to verify the suitability of these molecules. It was seen that hole transfer will be more likely in the double ringed DNA bases Adenine and Guanine as compared to their natural complementary bases Thymine and Cytosine. The transfer integrals for electron transport are larger for pyrimidines than their complementary purines. All the four bases display large HLGs that depict the temperature stability of the molecules. As the HLGs represent coulomb blockade, they also satisfy the charging energy criterion for observing single electron effects.

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