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Modeling the bandstructures of B-DNA base stacks

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A pseudohelical approximation for the calculation of the bandstructures of DNA base homostacks in B conformation is introduced. It consists of choosing a unit cell of only two nucleobases with relative parallel displacement and twist that locally mimic the helical conformation. It is tested employing the extended Hückel method with a unique Wolfsberg-Helmholtz parameter. The resulting bandgaps and ionization potential trend agree well with the ones reported in the literature employing the full screw-axis symmetry and higher levels of theory. The electron and hole effective masses extracted from the bandstructures follow the same trends as the experimentally reported mobilities. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4803489]

I. INTRODUCTION

The exciting prospect that DNA could be an electronic conductor, due to the overlap between the π clouds of the constituent nucleobases,[1] has motivated a lot of experimental and theoretical efforts to characterize its electronic properties.[2] Although natural DNA is aperiodic, there are good reasons for studying long periodic strands of nucleotides: First, such strands can be synthesized;[3] second, the electronic structure of an extended system is much easier to calculate if it is periodic rather than aperiodic, thanks to Bloch's theorem;[4] and third, much can be learned from periodic strands than can be applied to the aperiodic ones.[5]

It has been shown that the bandstructure of a homopolynucleotide is, to a good approximation, the superposition of the bandstructures of the nucleobase stack (NS) and the sugar-phosphate chain (SPC).[6] This is fortunate because, for the determination of the properties relevant for the electronic conduction, one can focus on the electronic structure of the NS. The bandstructures of paired-base and single-base homostacks have been studied at a variety of semi-empirical,[2,7–14] *ab-initio*,[6,15–17] and density-functional-theory (DFT)[12,18–20] levels. The main conclusion of studies of this type is that short segments of the DNA double helix can exhibit a Bloch-type conduction of holes through the nucleobase stack, in combination with hopping and tunneling mechanisms.[5]

In the abovementioned reports, the full screw-axis symmetry of the stack is taken into account, which entails a unit cell of 10 nucleobases, making the computations demanding (or currently impossible if a very high level of theory is desired). However, in these systems, the overlap between basis functions located at different nucleobases is appreciable only if the latter are nearest neighbors, due to the relatively large separation between them.[16] This means that the bandstructure is largely determined by the *local* electronic environment around each nucleobase. One of the purposes of this paper is to exploit this observation for drastically simplifying the unit cell in bandstructure calculations. A second purpose is to show that, in conjunction with the previous approximation, the extended Hückel (EH) (tight-binding with overlap) method, with an appropriate calibration, can predict the same trends of the electronic properties as expensive higher-level calculations. Although these goals are rather modest, it is hoped that this methodology will constitute a useful tool for researchers needing economic, but reliable, estimates of the electronic properties of periodic or aperiodic DNA strands.

II. METHODOLOGY

To model the NS and the SPC separately, the bonds that connect these moieties are replaced by bonds to hydrogen atoms. Figure 1(a) shows a NS obtained in this way from a B-DNA single strand, where adjacent nucleobases are separated by a rise (interplanar distance) of 3.36 Å with a relative twist angle of 36°.[21] According to the discussion made in the Introduction, properties relevant for the electronic conduction should depend on the *local* geometry around each nucleobase. Hence, the model cell was defined with only two nucleobases arranged so as to preserve the parallel displacement, the rise [Fig. 1(b)] and the twist angle [Fig. 1(c)]. The resulting conformation of the NS, illustrated in Fig. 1(d), will be referred to as "pseudohelical," as it mimics locally the true helical conformation of Fig. 1(a). It is seen that this approximation introduces the error of making every other nucleobase turn in the wrong direction. However, this error is expected to be small, since a local-density approximation (LDA) study found that for a DNA NS the energies per unit cell with twist angles of 36° and −36° are close.[18] The stacks were built employing the HYPERCHEM software,[22] whose biomolecule database is taken from the protein data bank (PDB). The propagations of the unit cells were carried out using the periodic boundary conditions (PBC) module of the GAUSSVIEW 5 software.[23]

The bandstructures of the polyadenine (pA), polycytosine (pC), polyguanine (pG), and polythymine (pT) stacks were calculated at the EH, or tight-binding with overlap, level,[24] employing the BICON CEDiT package.[25] This

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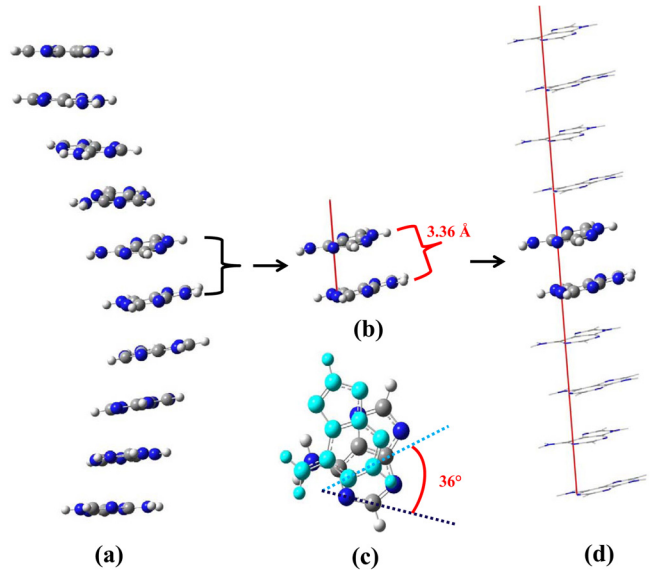

FIG. 1. (a) Lateral view of a stack of ten adenines with the B-DNA conformation. (b) Lateral view of the model unit cell, with the separation between the rings indicated. (c) Upper view of the model unit cell, with the relative twist angle between the bases indicated. For visualization purposes, all the atoms of the upper base are given the same color. (d) Propagation of the model unit cell.

package employs a basis set of atomic Slater-type orbitals (STOs), sets the diagonal elements (Coulomb or site integrals) of the Hamiltonian matrix (H_{ii}) equal to the ionization potentials (IPs) of the valence atomic orbitals, and offers a menu of Wolfsberg-Helmholtz formulas[26] for the evaluation of the off-diagonal elements (resonance or hopping integrals) of this matrix. This type of methodology has been applied successfully, for instance, to the study of the electronic structures of crystalline[27] and nanostructured[28] materials. In this work, the distance-independent Wolfsberg-Helmholtz formula

$$H_{ij} = \frac{K}{2}(H_{ii} + H_{jj})S_{ij} \tag{1}$$

was chosen, where S_{ij} is the overlap integral between basis STOs, which is calculated explicitly. The values of the Slater exponents were taken from the HYPERCHEM 7 package.[22] The empirical constant K was set to 2.2 in order to reproduce closely the "estimated real" gap of pC, as calculated by Ladik *et al.*[29]

Within the parabolic approximation, the effective mass of a charge carrier is determined from the $\epsilon - k$ dispersion by means of the familiar expression[4]

$$m^* = \frac{1}{\hbar^2}\left(\frac{d^2\epsilon}{dk^2}\right)_{k_0}, \tag{2}$$

where k_0 is the valence-band (VB) top or conduction-band (CB) bottom for holes or electrons, respectively.

III. RESULTS AND DISCUSSION

To determine the effect of the geometrical configuration on the electronic parameters, the bandstructures of the NSs in eclipsed configuration, i.e., neglecting the parallel displacement and twist angle but retaining the same rise and value of K, were also calculated. Tables I and II display these parameters for the pseudohelical and eclipsed configurations, respectively. E_{min} and E_{max} are the lower and upper edges of a band (Fig. 2) and $\delta E = E_{max} - E_{min}$ is the bandwidth. First of all, it is observed that the pseudohelical bands are very narrow, an aspect amply reported in the literature, which indicates that the electronic states remain highly localized around the unit cells. On the other hand, the eclipsed bands are up to two orders of magnitude wider, indicating that now the electronic states are much more delocalized across the stack, evidently because in this configuration the p_π atomic orbitals overlap head on, whereas in the pseudohelical configuration they overlap sideways.

According to Koopmans' theorem, IP $\approx -E_{max}$(VB) and EA $\approx -E_{min}$(CB), where IP and EA stand for the ionization potential and electron affinity, respectively (Fig. 2). For the pseudohelical NSs, it is seen that the IP follows the trend pT $\gtrsim$ pC > pA > pG, in accordance with the trend for nucleobase triads obtained by Voityuk *et al.*[30] at the semi-empirical NDDO-G level. The EA follows the trend pT > pC > pG > pA; a report for NSs with which to compare this trend was not found in the literature. Interestingly, for the eclipsed NSs, the IP and EA follow the same trends.

The pseudohelical bandgaps are observed to follow the trend pC > pT > pA > pG. It is noteworthy that this trend matches the one of the difference between the experimental EA[31] and IP[32,33] of the *individual* nucleobases. On the other hand, the eclipsed bandgaps follow the trend pC > pA > pG > pT. This observation, together with the abovementioned one about the IPs and EAs, suggest that the shift from the pseudohelical to the eclipsed configuration affects the NSs more or less in the same way, except for pT. This is likely due to the combination of the hyperconjugation between the $-CH_3$ group and the ring that is present in thymine and the increase in the overlap between orbitals located in neighboring $-CH_3$ groups that occurs in the eclipsed configuration.

TABLE I. Electronic parameters extracted from the bandstructures of the stacks in pseudohelical configuration. Energies in eV and effective masses in units of the normal electron mass.

	Valence band			Conduction band			Effective mass		
System	E_{min}	E_{max}	δE	E_{min}	E_{max}	δE	e^-	h^+	Energy gap
pA	−11.814	−11.809	0.005	−6.707	−6.606	0.101	0.911	−8.798	5.102
pC	−12.269	−12.254	0.015	−6.808	−6.805	0.003	45.711	−3.587	5.446
pG	−11.736	−11.628	0.108	−6.791	−6.744	0.047	1.603	−0.664	4.837
pT	−12.300	−12.295	0.005	−6.993	−6.982	0.011	3.866	−9.136	5.302

TABLE II. Electronic parameters extracted from the bandstructures of the stacks in eclipsed configuration. Energies in eV and effective masses in units of the normal electron mass.

	Valence band			Conduction band			Effective mass		
System	E_{min}	E_{max}	δE	E_{min}	E_{max}	δE	e^-	h^+	Energy gap
pA	−11.824	−11.592	0.232	−7.098	−6.197	0.901	0.309	−0.231	4.494
pC	−12.508	−12.022	0.486	−7.220	−6.232	0.988	0.279	−0.284	4.802
pG	−12.182	−11.388	0.794	−7.162	−6.218	0.944	0.299	−0.282	4.226
pT	−12.897	−11.829	1.068	−7.790	−6.706	1.084	0.261	−0.214	4.039

Figure 3 compares the bandgaps calculated by means of various approximations, including the present ones. It is well known that the Hartree-Fock (HF) method grossly overestimates the bandgaps.[5] Second-order perturbation corrections (HF + MP2) greatly improve the results, but a considerable overestimation persists.[16] However, according to Ladik *et al.*, an appropriate scaling derived from the quasi-particle correction (HF + QP) provides an estimate of the true bandgaps.[29] It is seen that these three methods predict the same trend and, in particular, that pG possesses the lowest bandgap, an observation widely accepted in the literature, since guanine is known to have the smallest IP of all the nucleobases [Fig. 2].[34–36]

The LDA implementation of DFT grossly underestimates the bandgaps, but predicts the same trend as HF + QP, except for pT.[37] The LDA to the exchange-correlation functional is known to underestimate the main gap of semiconductors and insulators by about 40%.[38] However, it has been suggested that a rigid shift in the LDA conduction band is enough to provide a reasonable agreement with the QP approximation,[39,40] which certainly holds in this case. The B3LYP exchange-correlation functional still notoriously underestimates the bandgaps, except for pG, and yields the wrong trend. This underestimation is caused by the well-known poor description of dispersion interactions provided by these functionals, which are of the utmost importance for $\pi - \pi$ stacked systems. However, there are functionals, such as PW91 (Ref. 41) and BHH,[42] which better account for long-range and dispersion interactions and, therefore, should probably provide much better bandgaps.

It is found that the present EH pseudohelical model predicts the same trend as HF + QP, except for the bandgap of pA which is underestimated. On the other hand, the EH eclipsed model underestimates all the bandgaps, for the same reason that it overestimates the bandwidths.

The abovementioned flatness of the pseudohelical bands implies that the magnitudes of the hole and electron effective masses are relatively large (Table I), according to Eq. (2), which causes the charge carriers to have a low mobility. For electrons (e^-) and holes (h^+), these magnitudes follow the orderings pC > pT > pG > pA and pT > pA > pC > pG, respectively. In addition, for pA $m_h \gg m_e$, for pC $m_e \gg m_h$, for pG $m_e > m_h$, and for pT $m_h > m_e$. Since in a Watson-Crick double helix, the base pairings are A-T and C-G, these results predict that in pA · pT electrons are more mobile than holes, whereas in pC · pG, the situation is the opposite. Moreover, since pG has the lowest hole mass and the second to lowest electron mass, it is predicted that guanine-rich DNA strands should be the best conductors. These predictions are in agreement with observations reported in the literature.[30,43–47] On the other hand, the large bandwidths obtained for the eclipsed bands predict relatively small effective masses, and consequently, large mobilities. In addition, the magnitudes of these parameters turn out to be similar for all the eclipsed NSs.

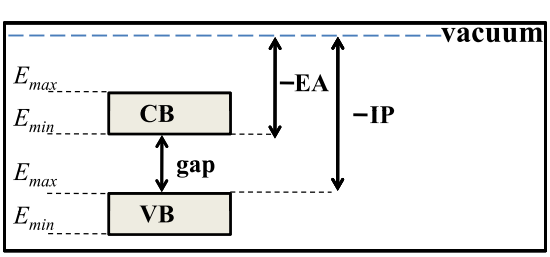

FIG. 2. Schematic definition of some of the electronic parameters calculated.

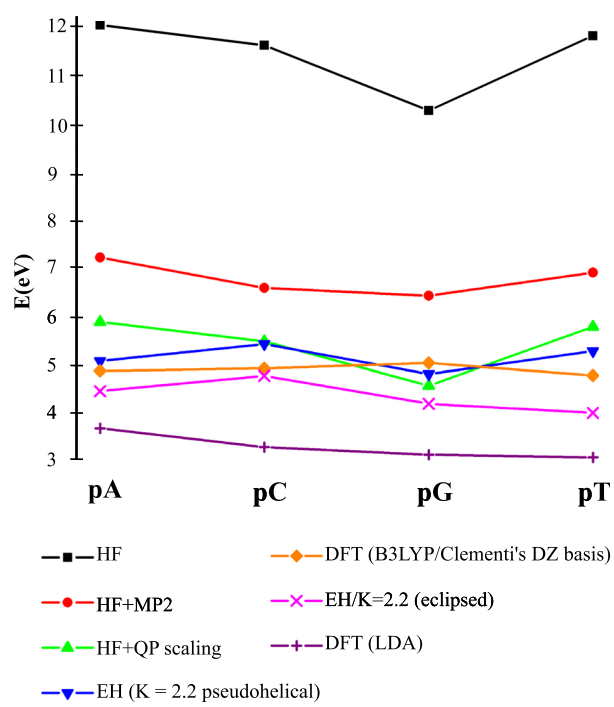

FIG. 3. Comparison of the NS bandgaps obtained by different methods. Squares: HF,[5] circles: HF with MP2 correction,[16] up triangles: HF with QP scaling,[29] down triangles: EH with K = 2.2 for pseudohelical model, diamonds: DFT with B3LYP functional and Clementi's DZ basis set,[20] X: EH with K = 2.2 for eclipsed model, +: DFT with LDA.[37]

IV. CONCLUSIONS

The pseudohelical conformation model seems to provide a good approximation for the calculation of the bandstructures of B-DNA nucleobase stacks, affording large computational savings, as the unit cell contains only two nucleotides, in contrast with the true helical conformation which contains ten nucleotides. The authors hope that this observation will prompt the application of such model to high-level calculations that are currently very difficult to perform employing the full screw-axis symmetry.

When coupled with the Extended Hückel, or tight-binding with overlap, method, the pseudohelical model provides a very cost-effective and reliable tool for the prediction of bandgaps and trends in ionization potentials, electron affinities, and charge-carrier effective masses.

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