Chapter 3

The Electronic Structure of Pentacene

3.1. Overview of pentacene

Pentacene (C_{22}H_{14}) is a flat organic molecule (D_{2h} - point group symmetry) consisting of five benzene rings, from which it derives its name. The organic molecular crystals and thin films comprised of these molecules received much attention in the past decade (see Fig. 3.1). The reason for this is that pentacene is an interesting organic semiconductor material suitable for practical applications. Therefore, it attracted considerable attention from the scientists working in the field of plastic electronics [2]. Among the acenes, similar to pentacene, like benzene, naphtalene, antracene, tetracene, hexacene, heptacene; pentacene has unique properties. The sublimation temperature increases with the number of acene rings, however, the band gap decreases with the number of acene rings. In particular pentacene is a good compromise: (not too big and not too small) between the values of the sublimation temperature and the band gap. The possibility of growing high quality thin films of pentacene from solution by self-assembling has been also considered [3, 4]. This is, in fact, the easiest and cheapest way of growing.

It is also worth mentioning the purity of the crystals since it plays a key role in the order of crystallinity. Chemical impurities and structural disorder are the main sources for lowering the overall performance of organic devices [5].

Small electronic devices such as field effect transistors (FET’s) [5–7] made of organic molecular crystals show very promising and interesting device characteristics. Particularly devices made of pentacene showed the highest mobility 35 (cm²/Vs) [8] among the organic materials. The higher the
Figure 3.2: Single crystal of pentacene viewed along [010] direction. The layered structure and herringbone arrangement of pentacene molecules in the layer are clearly seen. The shortest distance between the hydrogens and the nearest pentacene molecular planes is $\sim 2.2 \text{ Å}$.

Mobility the higher the speed of switching of a FET (on/off ratio).

Typically organic crystals and films have a very low space-group symmetry. The space group of solid pentacene is $P\overline{1}$. A closer examination of the crystal structure of pentacene shown in Fig. 3.2, reveals that it has a layered structure. Within the layer the pentacene molecules are arranged in the so called herringbone structure. There are two nonequivalent pentacene molecules in the unit cell which are not coplanar and are shifted with respect to each other along $c$ - the long molecular axis.

The herringbone structure originates from the electronic structure of a single molecule of pentacene. Although a pentacene molecule, due to its point group symmetry, doesn’t have a dipole moment, it has a quadrupole moment. The $p_z$ - electron system, which stretch out of the pentacene plane and participate in $\pi$-bonding, form a cloud above and below the pentacene plane, leaving the pentacene plane effectively positively charged. Due to this charge distribution two molecules of pentacene tend to orient perpendicularly to each other while the van der Waals interaction tends to orient them cofacially. The result of these two interactions leads to herringbone orientation within the crystal. It also follows from ab initio electronic structure calculations that the hydrogen atoms of one molecule interact with the $\pi$-system of carbons of the nearest pentacene molecule [7]. It is clear from Fig. 3.2 that there is some "empty space” in and between the layers of pentacene so that small molecules (N$_2$, O$_2$, H$_2$O) can diffuse into the material.

Depending on the growth condition pentacene can crystalize in several polymorphic phases [7,9]. Since there are several polymorphs of pentacene we will use the crystal structure for one at $T = 90 \text{ K}$ given in ref. [10] for the rest of this thesis. Particularly this polymorph has somewhat smaller volume of the unit cell compared to others [7] making computational efforts slightly less demanding.

The nature of charge transport in organic materials i.e. band-like (delocalized) or hopping-like (localized) is not very clear, particularly at room temperature. Several experimental investigations demonstrated band-like transport i.e. the mobility ($\mu$) decreases with an increase of temperature
3.2 Results on the isolated pentacene molecule.

[8, 11, 12]. This holds even up till room temperature. From the recent ESR measurements [13] it was concluded that at room temperature the injected charge carriers are delocalized over a range of about 10 pentacene molecules supporting the picture of delocalized transport. The nature of transport in organic materials like pentacene was studied theoretically [14, 15]. It poses a significant challenge for understanding mainly due to the weak van der Waals origin of the bonding. The weakness of such a bonding increases the coupling between charge carriers and lattice vibrations.

Organic materials like pentacene were extensively studied by ab initio methods [16–22]. In the following sections we will show the results on an isolated pentacene molecule and on solid pentacene.

3.2. Results on the isolated pentacene molecule.

Before studying the properties of bulk pentacene we first focus on some simple but relevant calculations. We calculated the bond lengths of the isolated pentacene molecule. First we relaxed very accurately the molecular structure starting from the typical carbon-carbon and carbon-hydrogen bond lengths. For an accurate relaxation we were using a conjugate gradient algorithm and a tolerance of 0.1 meV/Å on the interatomic forces. For these calculations we used a cubic box of $20 \times 20 \times 20$ Å$^3$ to ensure that the periodic images of pentacene do not interact and one k-point ($\Gamma$-point $(0, 0, 0)$) only. The energy cutoff for these calculations was chosen to be 400 eV. The further increase of the cutoff energy does not increase the accuracy of the calculations.

We performed the calculations both in LDA and GGA framework of density functional theory (DFT) [23] implemented in the VASP-code. The resulting optimized molecular structure of pentacene is shown in Table 3.1. As follows from the table our results are in excellent agreement with the experimental data. It also shows that LDA, which is believed to be a good approximation for slowly varying charge density systems, works well for pentacene. From the trends in the table we can see that the LDA results are systematically in better agreement with the experimental data than GGA. It can be noticed that LDA systematically leads to somewhat smaller bond lengths compared to GGA, showing over/under estimations of binding by the LDA/GGA approaches. The appreciable difference in total energies calculated with LDA and GGA is about 0.48 eV per atom. This also suggests overbinding of LDA compared to GGA.

It is also interesting to calculate the bond length and vibrational frequencies for the so called 6,13-pentacenequinone (C$_{22}$H$_{12}$O$_2$) C=O and 6,13-pentacene-endoperoxide (C$_{22}$H$_{14}$O$_2$) O−O. These molecules are the main chemical impurities in pentacene single crystals [5]. Vibrational frequencies were calculated using a finite difference method described in ref. [25]. It has an analogy with a classical harmonic oscillator. The force $F$, acting at mass $m$, is proportional to a displacement $\delta x$. 

Organic materials like pentacene were extensively studied by ab initio methods [16–22]. In the following sections we will show the results on an isolated pentacene molecule and on solid pentacene.
of the mass from the equilibrium position \( F=0 \). From this the force constant \( k (k = F/\delta x) \) and frequency of oscillation \( \omega (\omega = \sqrt{k/m}) \) can be defined. Applied to our system of interest it is a subject of much more cumbersome and complex mathematical formulas. Starting from the accurately relaxed structure, the atoms were displaced by 0.0025 Å and the forces were calculated via the Hellmann-Feynman method [26]. The force is proportional to the displacement where the coefficient of proportionality is the force constant. By considering all linearly independent displacements the full force constant matrix is obtained and the dynamical matrix is constructed. Further, by diagonalization of the dynamical matrix the vibrational frequencies are calculated. This method leads in general to quite reliable values of vibrational frequencies. The results of the calculations are shown in Table 3.2 and compared with the experimental values. The calculated values of the bond lengths and vibrational frequencies are in good agreement with the experimental values. This shows that the present DFT calculations, designed for solids, are accurate enough to describe single molecules.

Another configuration of pentacene and oxygen, interesting to study, is the interaction of a flat pentacene molecule with a single oxygen molecule, on the top of central benzene ring, as shown in the upper inset in Fig.3.3. The calculations were performed with GGA. The result of these studies shows that a single oxygen molecule finds a stable position at \( z = 3.4 \) Å with a binding energy of 0.055 eV. This bound state has apparently a non-covalent origin. Evidently LDA results in somewhat stronger binding compared to GGA. In Fig.3.3 one can also see that the energy curve has a tendency to go up very steeply below 3 Å. This means that it is not likely for \( \text{O}_2 \) to come closer than 3 Å to the pentacene plane. This leads us to conclude that oxygen, diffused in bulk pentacene, occupies only a very limited number of sites because the typical distance between pentacene molecules in the crystal is less than 3 Å (see Fig.3.2). Hence, it follows that the entropy of oxygen in solid pentacene is much smaller than that in the gas phase. This conclusion will be a very crucial argument in the following chapter where we will study the phenomenon of \( p \)-doping of pentacene by diffused oxygen. For comparison we also put in Fig.3.3 the result for pentacene-endoperoxide with a binding energy of 0.71 eV and a shortest distance between oxygen bridge and pentacene of 1.22 Å. As will be discussed in the following chapter it is not likely for this stable defect to occur in bulk pentacene.
3.2 Results on the isolated pentacene molecule.

<table>
<thead>
<tr>
<th>C – C bonds</th>
<th>Theory (LDA)</th>
<th>Exp.</th>
<th>Theory (GGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 – C2</td>
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<tr>
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<td>C5 – C7</td>
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</tr>
</tbody>
</table>

Table 3.1: Calculated bond lengths (Å) for an isolated pentacene molecule (C\textsubscript{22}H\textsubscript{14}). The labeling of carbon atoms is shown in the figure above. The experimental values were taken from the Ref. [24].

Table 3.2: Calculated (LDA/GGA) bond lengths (Å) and vibrational frequencies (cm\textsuperscript{-1}) for isolated (a) 6,13-pentacenequinone (C\textsubscript{22}H\textsubscript{13}O\textsubscript{2}) and (b) 6,13-pentacene-endoperoxide (C\textsubscript{22}H\textsubscript{14}O\textsubscript{2}). The experimental values were taken from the Ref. [5].
Figure 3.3: The dependence of the GGA binding energy on the distance (z) between an oxygen molecule and a flat pentacene. The energy curve increases very steeply below 3 Å. The horizontal line below (at 0.71 eV) marks the binding energy for the pentacene-endoperoxide.

3.3. Results for bulk pentacene.

Since bulk pentacene is a genuine solid we check the convergence of the k-point mesh. We found that the difference in the total energy per unit cell calculated with the tetrahedron scheme for Brillouin Zone (BZ) integration for k-point mesh $8 \times 8 \times 4$ and $4 \times 4 \times 2$ is 0.086 meV. This indicates that the k-point mesh $4 \times 4 \times 2$ is sufficient. This is an important since in the next chapter we will deal with super cells of pentacene doubled in a and b directions ($2a \times 2b \times c$). For such a unit cell the k-point mesh must be two times smaller in the $k_x$ and $k_y$ directions so $2 \times 2 \times 2$ would be the optimal one. However, to increase the quality of density of states (DOS) we need to increase the k-point mesh. The $k_x$ and $k_y$ directions should be sampled better than $k_z$ since the interactions are mainly in the ab-plane of pentacene. Therefore we make the sampling finer (doubled) in the $k_x$ and $k_y$ directions. Calculations with a finer k-point meshes are computationally very demanding. Finally, for the supercell of pentacene we choose a $4 \times 4 \times 2$ k-point mesh.

We optimized the atomic positions using a conjugate gradient algorithm with a tolerance of 10 meV/Å on interatomic forces in the unit cell while keeping the cell parameters fixed. A very
important quantity is the cohesion energy ($E_{coh}$). Cohesion energy shows the gain in energy by bringing isolated pentacenes to form a crystal. It is expressed in a simple formula:

$$E_{coh} = -\left(\frac{E_{cryst} - 2E_{mol}}{2}\right),$$

where $E_{cryst}$ is ground state total energy per unit cell of pentacene and $E_{mol}$ is the total energy of a single isolated pentacene molecule. The calculated $E_{coh}$ with LDA gives $E_{coh}^{LDA} = 1.4$ eV which agrees with a previously calculated value of 1.3 eV [29]. It was a somewhat unexpected to find that GGA calculations give no bonding at all: $E_{cryst}^{GGA}$ is 0.1 eV above the energy of two isolated pentacenes. This result points that the overbinding in LDA can be interpreted as a van der Waals interaction while GGA does not. This observation lead us to conclude that for the total energy calculations for this system one should use the LDA rather than the GGA approximation to the exchange correlation potential.

The density of states is shown in the Fig.3.4. The DFT band gap is 0.68 eV. The experimental value is 2.2 eV [30]. This discrepancy is due to the well known limitation of DFT to calculate the band gap [23, 27] correctly. Better agreement with the experimental band gap can be obtained with the GW - method [28]. We calculated the partial density of states for C and H which is shown in Fig.3.5. For these calculations we defined spheres of radii 0.85 and 1.00 Å around the carbon and hydrogen atoms respectively. The partial $s, p$ - density of states for carbon and hydrogen were evaluated in these spheres. The radius for hydrogen was somewhat exaggerated compared to the atomic radius but it gives an idea about the contribution of the hydrogens to the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital) states. The main contribution to the HOMO and the LUMO are from the $p$-electrons of the carbon atoms as shown in the Fig.3.5, however the $p$ contribution from hydrogen can not be neglected. This shows that the hydrogens of one pentacene molecule interact with the carbons of the neighboring molecule within the crystal and thus contributing to the width of the valence and conduction bands.

We also calculated the band structure of pentacene. The band structure of the valence and the conduction bands is shown in Fig.3.6. The width of the HOMO is 0.52 eV and the width of the LUMO is 0.63 eV, which are in agreement with previous calculations [28]. This results implies that pentacene might be a very useful material for making ambipolar FETs, as follows from discussions in the previous chapter. Ambipolar pentacene FETs indeed were realized [31]. From the calculated band structure the anisotropy of the interaction in the main crystallographic directions can be clearly observed, implying also the anisotropy for a mobility of charge carriers measured along the corresponding directions. By fitting the tight binding model to the band structure the overlap integrals can be found [16].
Figure 3.4: Density of states (DOS) in states per eV per unit cell as function of the energy. Fermi energy is chosen on the top of valence band (at zero). IDOS is the integrated DOS in electrons per unit cell. It was calculated using a $4 \times 4 \times 2$ k-point mesh.

Figure 3.5: The partial density of states per s and p states of carbon and hydrogen atoms contributing to the total DOS. Fermi energy (at zero energy) was chosen at the top of valence band.
3.3 Results for bulk pentacene.

Figure 3.6: The band structure of solid pentacene. The valence and conduction bands appear in pairs since there are two pentacene molecules in the unit cell. The Fermi energy is chosen at the top of the valence band. The energies are plotted along the lines in the first Brillouin zone connecting the following points: $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $M = (a^*/2, b^*/2, 0)$, $Y = (0, b^*/2, 0)$, $Z = (0, 0, c^*/2)$, $N = (0, b^*/2, c^*/2)$, $H = (a^*/2, b^*/2, c^*/2)$, $O = (a^*/2, 0, c^*/2)$. 
3.4. Conclusions

In this chapter we reviewed the main results on pentacene and validated the methods of calculation both for a separate molecule as well as for bulk pentacene. Our calculations are based on the DFT (LDA/GGA) approach implemented in the VASP code. This is a full potential method that does not make any approximation to the shape of the potential. This is very important because organic semiconductors usually possess lower symmetry as compared to traditional solids. We tested and performed numerical DFT calculations on a single isolated molecule of pentacene and the pentacene solid. For the total energy calculations in this systems it is better to use the LDA than the GGA approximation to the exchange correlation potential. Computational methods we are using are appropriate and accurate enough to work with both molecular and solid pentacene. Therefore the same approach is employed in the study of the effect of oxygen in the bulk of pentacene which is the subject of the following chapter.
[1] This histogram was generated from the web of science (www.apps.isiknowledge.com) on 30.11.08 by selecting articles with an appropriate subject.


