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物理研究所

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共軛高分子中的載子遷移率不對稱



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The Imbalance of Carrier Mobility in Conjugated Polymers

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摘要

在許多共軛高分子中，電子電洞的對稱不只是在能帶結構上會被發現，在因晶格缺陷所造成的失序結構中也同樣的被發現，但在實驗上卻被廣泛的看到電洞遷移率遠大於電子遷移率的現象。我們提出在空氣中存在着不可避免的氧吸附所造成的電子補捉來解釋此現象。在本文中，我們可以定量的計算出關於吸附以及電子電洞不對稱的許多性質，此外，也引入了一個用來估計原子之間跳越積分的方法。

The Imbalance of Carrier Mobility in Conjugated Polymers

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Electron-hole symmetry is found to exist not only the band structure but also the defect level caused by structure disorder. The commonly observed higher hole mobility is explained by the electron traps caused by oxygen molecule adsorption. We found that defects will enhance oxygen adsorption and this is a key to electron-hole symmetry breaking. In this paper, we calculate the adsorption and imbalance properties quantitatively . Besides, a method to estimate the hopping integral is also introduced.

謝 誌

一轉眼兩年就過去了，感覺還來不急留下些什麼，就要跟這裡說聲再見了。交大的兩年對我人格的養成是很重要的階段，除了學習到了科學研究的方法和基本的觀念，滿足了我對物理的著迷，更讓我有了很多難忘的回憶，和同學、老師、學長學弟妹之間的互動都是我年輕的證明。臨別匆匆，這兩年改變我最多的莫過於是指導我做論文的紀互學長，從他身上我真正接觸到了做研究是怎麼回事，我非常感謝他。另外我的指導教授孟心飛老師也讓我獲益匪淺，他精準的眼光，常常一語就到破了物理問題的核心，這點常讓我覺得要跟他學的還很多。除了研究，我想更要感謝的是我碩士班生活陪我走過酸甜苦辣的同學們：光胤、德明、瑞仁、翔瑞、孟老師實驗室的學長們，以及天天在所上搞笑的學弟妹們，要謝的人太多了。當然，最後一定不能忘記的是我的家人，還有我家的貓咪，如果沒有你們，我想這一切都不會存在，謝謝！

The imbalance of carrier mobility in conjugated polymers

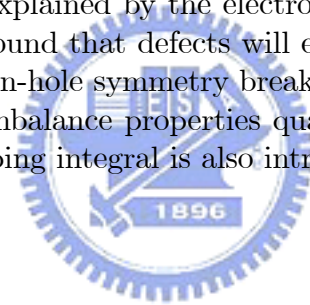


Shu-Ting Pi

2006. 6

Abstract

Electron-hole symmetry is found to exist not only the band structure but also the defect level caused by structure disorder. The commonly observed higher hole mobility is explained by the electron traps caused by oxygen molecule adsorption. We found that defects will enhance oxygen adsorption and this is a key to electron-hole symmetry breaking. In this paper, we calculate the adsorption and imbalance properties quantitatively . Besides, a method to estimate the hopping integral is also introduced.



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1. Introduction

1.1 Introduction to Conjugated Polymer

Recently, the research about new type semiconductor is a very hot topic. The rigorous process and expensive price always let people unsatisfied in traditional inorganic semiconductors like Si, Ge..., etc. In this point of view, conjugated polymer semiconductors can provide a new and possible future. [6] In the following, we will introduce some basic theory about this new material.

1.2 Transports in conjugate polymer

Conjugated polymers are constituted by organic elements which have a carbon backbone and some side chains. The backbone carbons are mainly bonded by sigma bonds and pi orbitals are weakly overlapped. In standard theory, because the sigma bonds are much tighter binding than pi bonds, the sigma band structure is much far away from the Fermi level than pi band structure. Therefore the pi band is the most important one and electrons are mainly transported in this band. [1]

(see fig.1.1 , molecular structure of polyacetylene)

In the above picture, we show how the pi orbital overlaps and electrons just hop in these molecular orbitals.

But there are more things we need to know about transport in conjugated polymer: quasi-particle, Peierls instability, missing n-type. In the following, we introduce quasi-particle and Peierls instability first.

As we know, the crystal is very soft in polymer, so there are strong electron-phonon interaction in this system. Electrons are actually transported in the form of polarons, solitons or bipolarons which are the quasi-particles of electron-phonon interaction and these quasi-particles have larger effective

mass than electrons.[?] No matter what results does polaron tell us, all we need to emphasize is that electron-phonon interaction is very important in conjugated polymers.[1]

In order to handle this electron-phonon interaction, a famous model called the "SSH Model" had already got many properties about the quasi-particle : soliton. But there are something more important than quasi-particle which appears in this model, i.e. Peierls instability.[5]

Peierls, an famous British physicist, had pointed out that: in a 1D chain, if every atom contribute one electron, the band structure should be no band gap which can easily obtain by tight-binding method. But, when there exist strong electron-phonon interaction, there should be still band gap because of the crystal deformation and the chain will not be metallic state. This result makes conjugated polymer looks like semi-conductor.

(see fig.1.2, pi band of polyacetylene)

In the above figure, when electron-phonon interaction vanish, the parameter t_1 will also vanish.

Beside electron-phonon interaction, the missing n-type also play important role in transport properties.

In most conjugated polymer, the polymer made FET are always p-type and the reason is unknown. Recently a paper, published in Nature, found that use of an appropriate hydroxyl-free gate dielectric—such as a divinyltetramethylsiloxane-bis(benzocyclobutene) derivative (BCB)—can yield n-channel FET conduction in most conjugated polymers. The reason why n-type behaviour has previously been so elusive is the trapping of electrons at the semiconductor-dielectric interface by hydroxyl groups, present in the form of silanols in the case of the commonly used SiO₂ dielectric. These findings should therefore open up new opportunities for organic complementary metal-oxide semiconductor (CMOS) circuits, in which both p-type and n-type behaviours are harnessed. [7]

Until now, some essentials of transport in polymer is known. In the next section, we will discuss a more intrinsic phenomenon: electron-hole imbalance.

1.3 Motivation

Although we have introduced many applications about conjugated polymer, there are still many problems need to be solved. one of them is electron-hole mobility imbalance. When making LED , it needs electrons and holes recombine in the emission layer. But in many polymer systems, the hole mobility is much higher than electron mobility and this makes the recombination in correct layer be difficult.

This problem is not only a challenge in application area but also a interesting puzzle in theoretic physics. Take PPV for example, PPV is also an P-type semiconductor but its Pi orbital band which is the transport orbital band has electron-hole symmetry structure. This means the electron and hole have the same effective mass , so they should have similar transport proprties. Some papers which caculate this problem by first-principle caculation even say that the electron and hole effective mass difference should be less than factor of 2.[11]

There are more things we need to be confused : the oxygen! In many papers, the experimantal results show the electron-hole mibility imbalance will be enhanced if polymers are exposed to oxygen gas. [14] This fact hints us the oxygen molucules must play an important role in this problem.

In next section, we will talk about oxygen more.

1.4 More on this problem

We have talked many things about the imbalance problem. But, in this section, we will talk about this more. In 1998, a paper which, published in Nature, says the electron-hole symmetry does exist in sloution by microwave experiments. [10] This result hints us the reasons which cause the imbalance shouldn't come from the essence of polymer structure. It should something interact with polymer in the air. Besides, in some papers, we found that oxygen can enhance the imbalance and this mechanism is totally reversible.[14] As we know, no matter how prefect vaccum you can make, there are always some oxygen molucules and they may form an unitentional doping in the bulk. According to the totally reversible process, we believe the oxygen doesn't actually bond with polymer chain. It should just be adsorptive. Furthermore, many papers which discuss about oxygen adsorption shows defects can enhance it. [15]

Therefore, our main topic may be transformed to explain what happens when polymers are exposed to oxygen gas if defects exist.

Fortunately, in carbon nanotube researches, they have the same problem like us.[16] In carbon nanotube, they also found the e-h symmetry breaking and this result doesn't match the symmetrical band structure. Further more, oxygen will enhance imbalance reversibly, too. All the researches about this problem in CNT refer this phenomenon is caused by oxygen adsorption. As we know, our problem is also made by carbon and oxygen. Thus, why not using the same ideas in our system ?

1.5 Oxygen molecule

since we have thought oxygen is the key to imbalance, some introductions to oxygen molecule is needed. The molecular energy level of oxygen is like the following figure:[4]

(see fig 1.3 , the oxygen level)

In this picture, we found the HOMO of oxygen is two unoccupied state and this is because of Hund's rule. This picture may tell us that adding an electron will not cost any energy. But in fact, the EA of oxygen molecule is around 1eV and IP is around 11 eV. This result tells us adding an electron to the HOMO needs about 10eV. This high energy difference mainly comes from the exchange effect and it will be important for us later.

Besides, the anti-bonding of HOMO is also important in the following.

As a result, two conclusions for oxygen molecule are essential:

- the exchange energy of oxygen HOMO is very high and this makes fill an electron to oxygen hard.
- anti-bonding of oxygen HOMO make coulomb interaction between oxygen HOMO and any single particle state become selective because of symmetry consideration.

1.6 Thesis Structure

Form last section , we know that the defects can induce oxygen adsorption and it may make the charge transfer form polymer to oxygen . Thus, we plan

to discuss our problem in four different parts.

1. *Crystal Defects*

In this part, we will analyse the energy and electron disturbance of defect states. What happens and what will be made when defects exist are our main topic in this chapter.

2. *Adsorption of Oxygen Molecules*

The adsorption of oxygen molecules is the main contributor that causes e-h imbalance. We will give a simple model to estimate the adsorption energy and adsorption distance.

3. *Hopping Integral*

When oxygen molecules are close to the defects, the interaction between polymer chains and oxygen is turned on. To construct this perturbation in the Hamiltonian is our main goal in this part. Besides, some discussions on molecular spatial symmetry are also included.

4. *Electron-hole Imbalance*

If we can get the perturbation term in the Hamiltonian, we can try to solve this Hamiltonian. We expect this slight perturbation could be the reason of electron-hole imbalance.

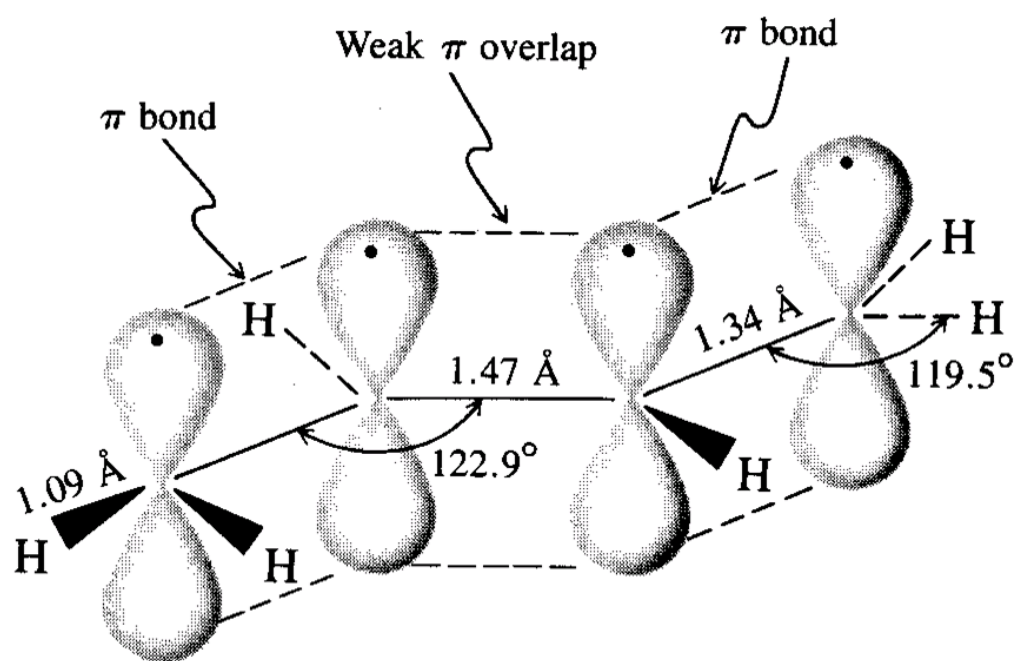


Figure 1.1: molecular structure of polyacetylene

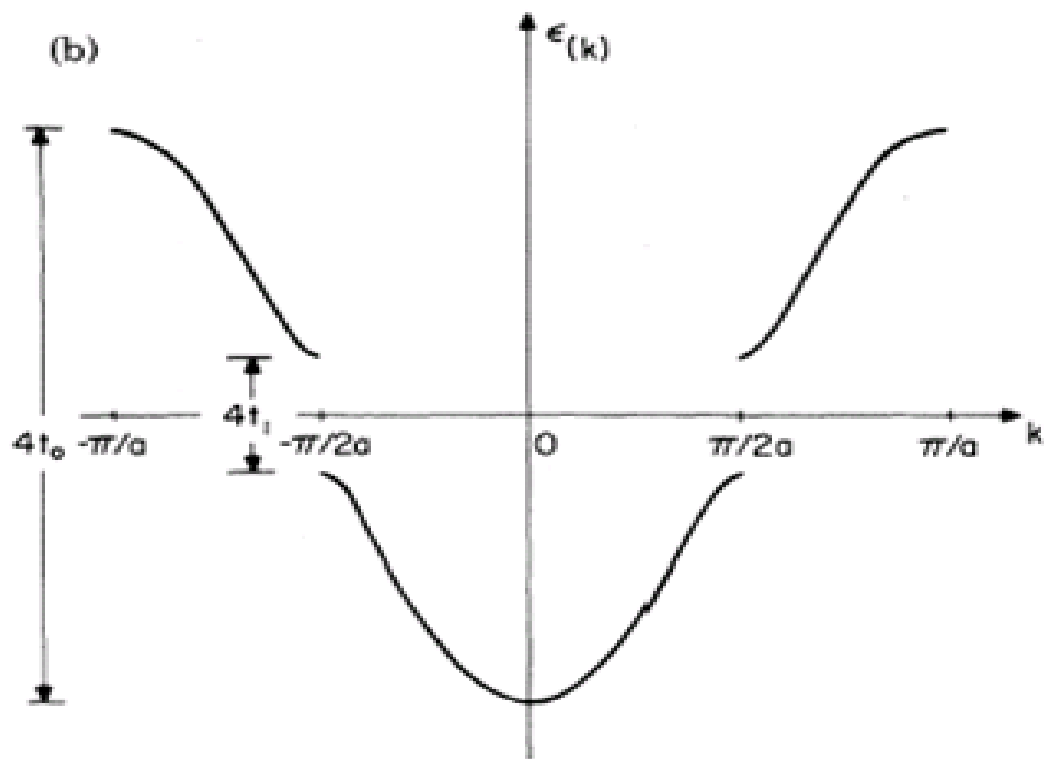


Figure 1.2: Pi band of polyacetylene.

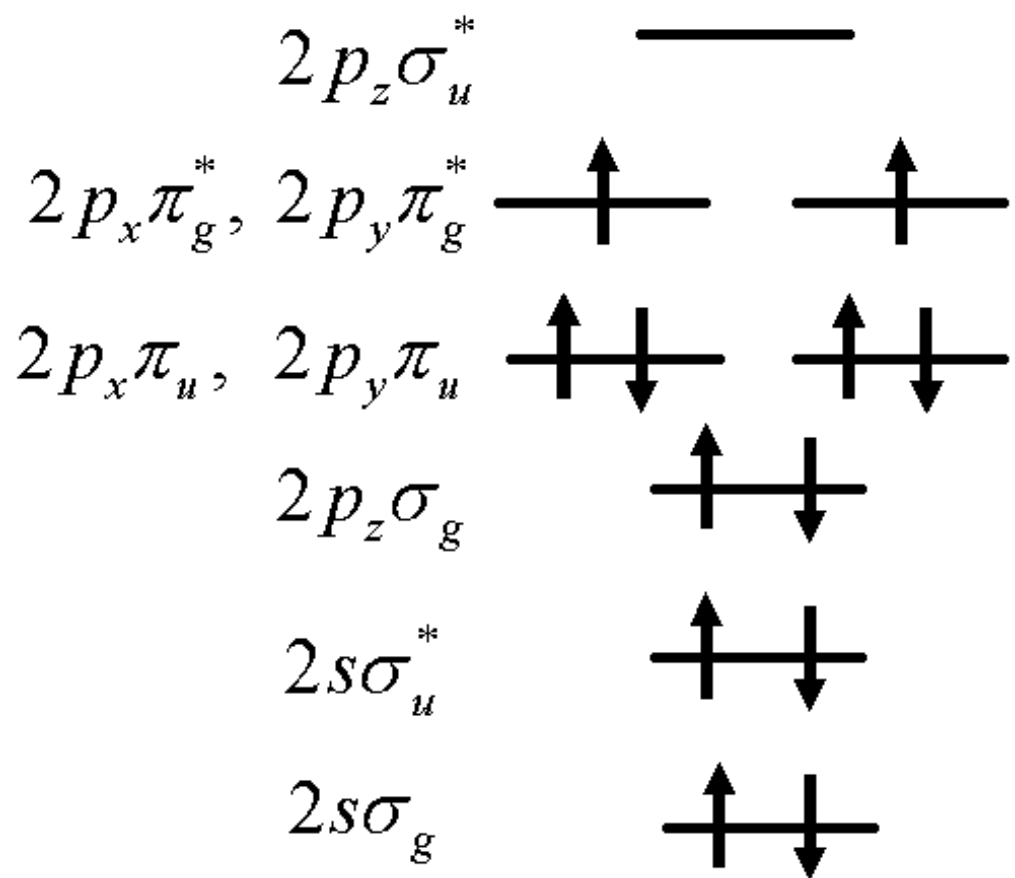


Figure 1.3: oxygen molecule levels

2. Crystal Defects

2.1 The Hamiltonian

In this chapter, we will focus on physical defects in polymer system. The "physical defects" means the defects which is made from crystal disorder like malposition or non-perfect bonding ,etc. For simplicity, we choose PPV (100 unit cell with perodic boundary condiction) as our model system to illustrate the effects when physical defects exist. The structure of PPV is :

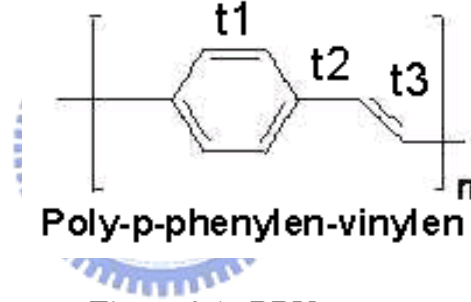


Figure 2.1: PPV surcuture

In tight binding model, we can use three tight binding parameter t_1, t_2 and t_3 to constructure the Hamiltonian :

$$\begin{aligned}
 H = & \sum_{n=1}^N \left[t_1 \left(\begin{array}{l} C_{8(n-1)+1}^+ C_{8(n-1)+2} + C_{8(n-1)+1}^+ C_{8(n-1)+3} \\ + C_{8(n-1)+2}^+ C_{8(n-1)+4} + C_{8(n-1)+3}^+ C_{8(n-1)+5} \\ + C_{8(n-1)+4}^+ C_{8(n-1)+6} + C_{8(n-1)+5}^+ C_{8(n-1)+6} \end{array} \right) \right] \\
 & + \sum_{n=1}^N \left[t_2 \left(C_{8(n-1)+6}^+ C_{8(n-1)+7} \right) + t_3 \left(C_{8(n-1)+7}^+ C_{8(n-1)+8} \right) \right] \\
 & + \sum_{n=1}^{8N} \varepsilon_n C_n^+ C_n + h.c. \tag{2.1}
 \end{aligned}$$

where the last term is on-site energy and we often set ε_n which is also the Fermi-energy be zero.

2.2 Band Structure

From some experimental papers, we can get $t_1=-3.1\text{eV}$, $t_2=-2.2\text{eV}$ and $t_3=-3.0\text{eV}$. [11] Thus, we can diagonalize the above Hamiltonian and get the band structure.

Furthermore, we can transform this equation to k-space by Fourier transformation. Thus, we have:

$$H = \sum_k \left\{ \begin{array}{l} t_1 [e^{ika \cos(\frac{\pi}{3})} (C_k^1 + C_k^2 + C_k^1 + C_k^3 + C_k^4 + C_k^6 + C_k^5 + C_k^6)] \\ + t_1 [e^{ika} (C_k^2 + C_k^4 + C_k^3 + C_k^5)] \\ + t_2 [e^{ika} (C_k^6 + C_k^7)] + t_3 [e^{ika} (C_k^7 + C_k^8)] \end{array} \right\} + h.c. \quad (2.2)$$

Where C_k^{n+} is the creation operator of the state which has wave number k in n-th band.

Thus, we can get the band structure in k-space by diagonalizing the above Hamiltonian:

(see fig 2.2, Band structure in k space)

When getting the band structure, we will discuss defects which are also the most interesting part in this chapter. As we know, there will be defect states if we change any tight binding parameter in any specified unit cell. But, what kinds of defects is the most important one? The answer is certainly "defects which can create levels in the forbidden band" because electrons which are close to the Fermi level (Here $E_F=0$) are the most active and dominating the system ones. From numerical tests, we found the only way to create levels in the forbidden band is to change t_3 in any specified cell and this conclusion also satisfies to experimental result. [12] In the following, we

change t_3 to -1.0eV for example, and plot the energy levels and density of states then. (take defect in 50th cell as our model)

(see fig 2.3, PPV energy level with defect)

(see fig 2.4, PPV density of states with defect)

In the following pages, we choose the t_3 bond in 50th cell as defect bond and this assumption will not affect any results. Thus, we can observe how the defect levels change with the value of t_3 by numerical calculation. In order to know how deep the defect is, we define a parameter called the "defect order parameter" :

$$\lambda = -\left(\frac{t_d - t_3}{t_3}\right) \quad (2.3)$$

Where t_d is the new tight binding parameter of t_3 in 50th cell.

Thus, when λ is zero there is no any defect. When λ is one there is a total broken chemical bond in t_3 -bond.

Also, we define a name called the "defect sites". This means the polymer chain atoms which are nearest to the changed t_3 bond.

As the results shown in fig 2.5, we found the upper and lower defect states will be more and more close to the Fermi level and they will become degenerate states when t_d is equal to zero. Besides, we can also observe how the wave function changes with t_d . From the following figures, we found the defect states will become more and more localized near the defect sites. When t_d is equal to zero, there will have maximum localization and 70% electrons in the lower defect will locate at the defect sites.

(Note: In fig.2.6, we plot how many electrons which belong to lower defect state are located in the defect sites)

(See fig 2.5, defect level and defect order parameter)

(See fig 2.6, electron density and defect order parameter)

2.3 Summary

In this chapter, we can conclude many things:

1. When defect is deeper, the defect levels will be closer to Fermi level.
2. When defect is deeper, the defect states will be more localized in defect sites.
3. Whether there exist defects or not, there will always have electron-hole symmetry. This means that defects can't be reasons for imbalance and this result also match experimental result.[13]



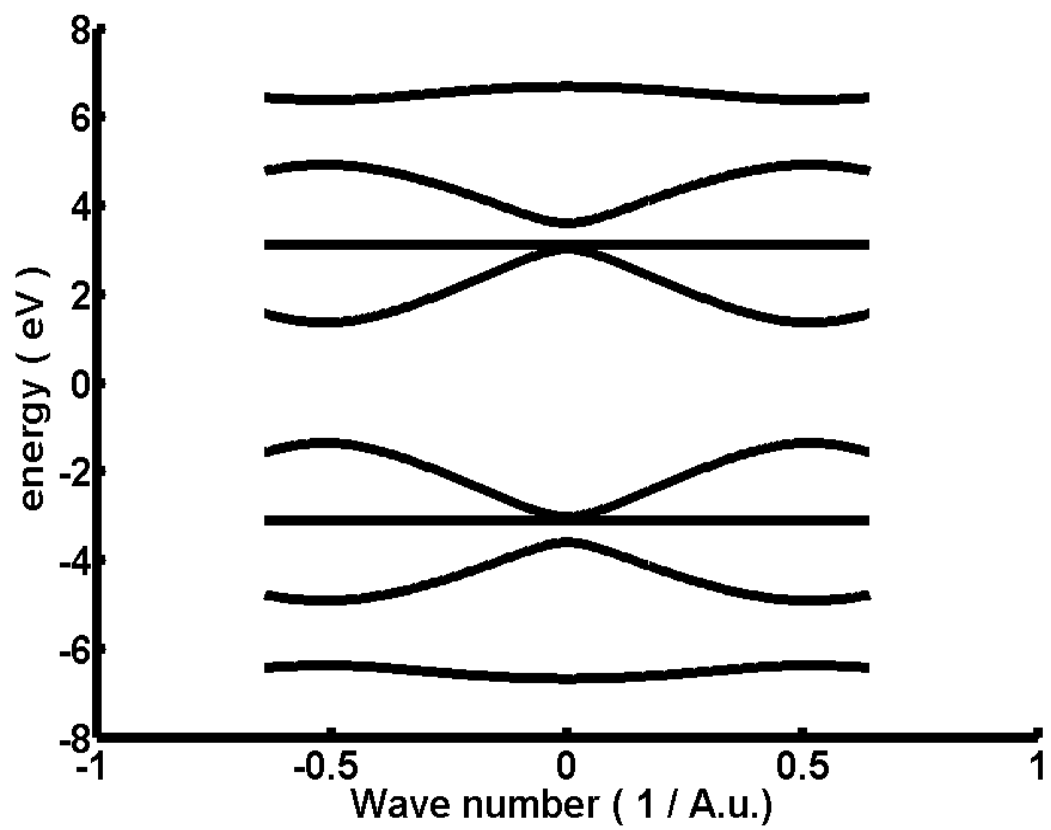


Figure 2.2: PPV band structure in k-space

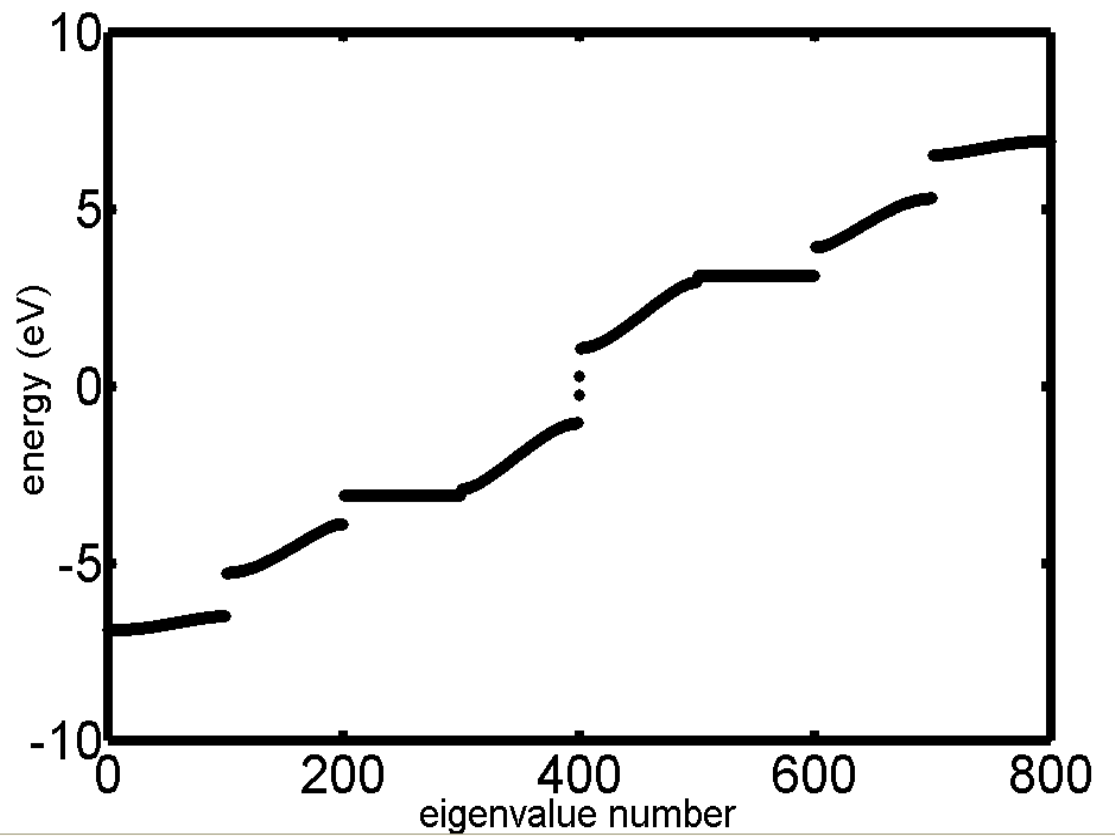


Figure 2.3: PPV energy level with defect ($\lambda = \frac{5}{6}$)

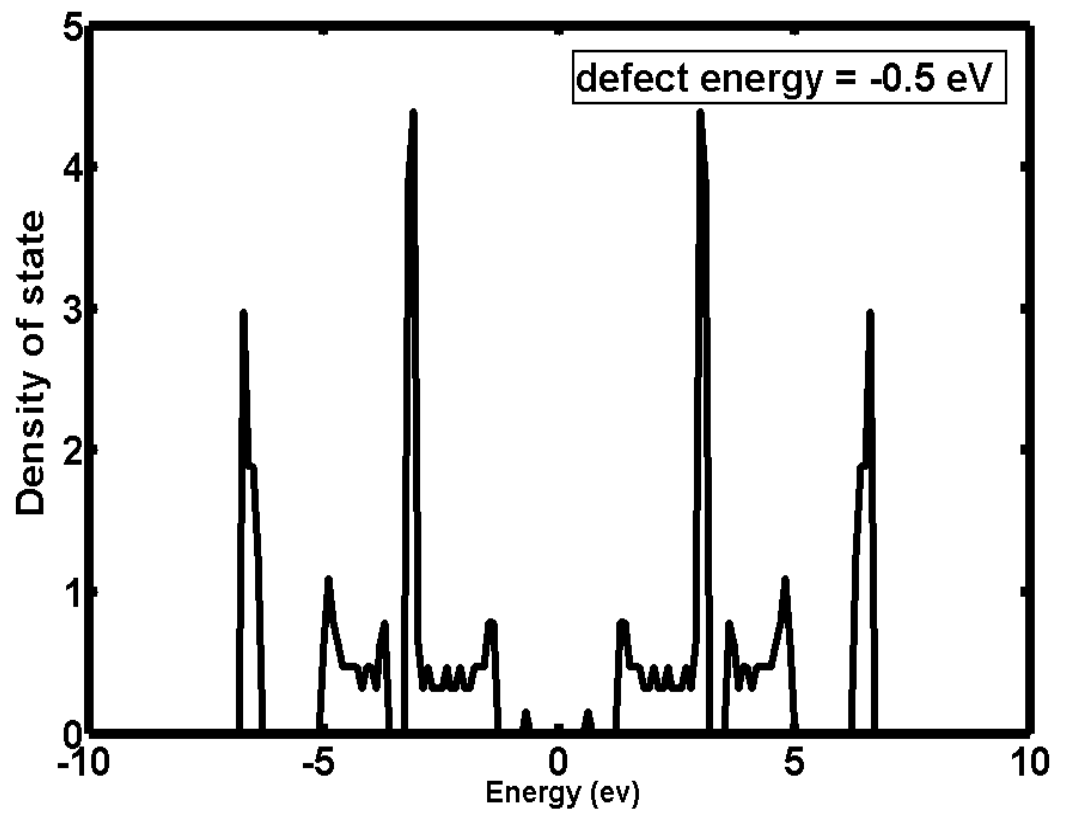


Figure 2.4: PPV density of state with defect ($\lambda = \frac{5}{6}$)

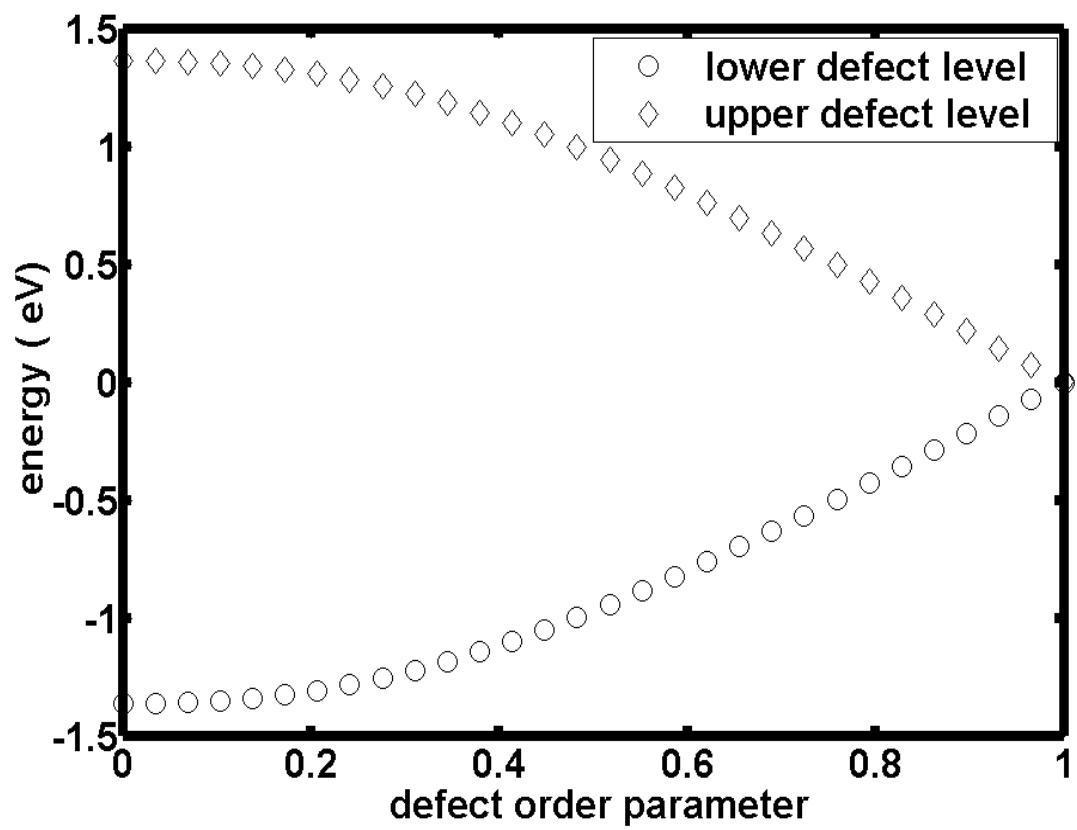


Figure 2.5: PPV defect levels and defect order parameter

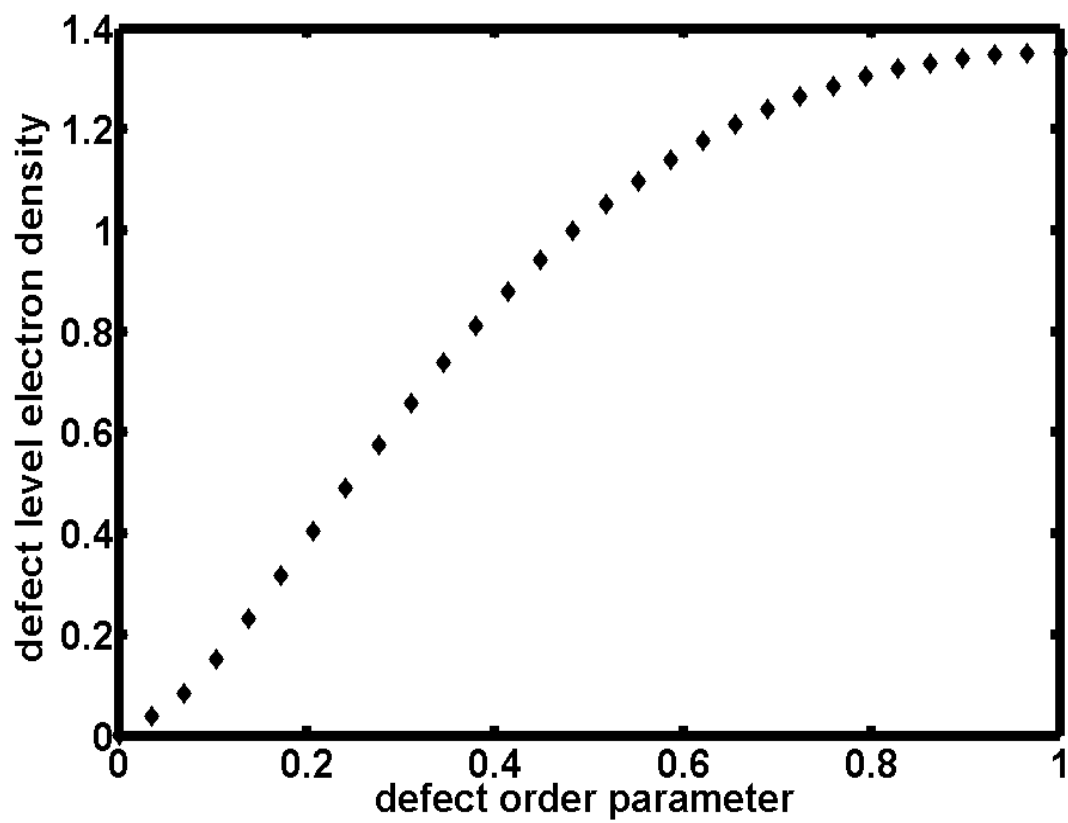


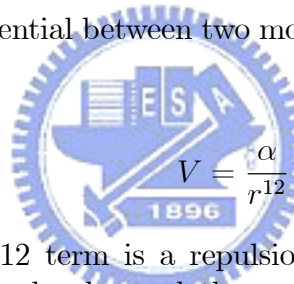
Figure 2.6: defect level electron density on defect sites

3. Adsorption of oxygen molecules

3.1 Lennard-Jones Potential

From the discussion in chapter zero, we know that oxygen molecules need to approach the defect sites when getting into the bulk or they will have no chance to interact. Therefore, giving an appropriate estimation to the adsorption energy and adsorption distance will help us to understand the process of oxygen adsorption. To solve this problem, we need to write down the potential between oxygen and carbon first.

In general, the potential between two molecules can be expressed as a Lennard-Jones potential:


$$V = \frac{\alpha}{r^{12}} - \frac{\beta}{r^6} \quad (3.1)$$

where the power 12 term is a repulsion force which comes from the core electrons of two molecules and the power 6 term comes from the dipole-dipole interaction (i.e. Van der Waals force) which is an attractive force. But, the question is how to estimate these two coefficients of r^6 and r^{12} term?

3.2 Physical Meaning of Lennard-Jones Coefficients

Before any estimation, we should talk about the physical meaning of these two coefficients. First, we know the r^{12} term mainly comes from core electron repulsion between two molecules. So, we believe the coefficient α should be only a function of what the two molecules are. In other words, it should be independent to the band structure or any other condensed matter effects.

Next, how about the r^6 term β ?

As we know the attractive potential of two molecules mainly comes from dipole-dipole interaction. Th dipole-dipole interaction is due to the electrons in one atom seeing the positive atomic nucleus in another atom, and there exist two dipole to interact each other therefore. In general, this interaction can be express as:[22]

$$V_{dip-dip} = \frac{e^2}{r^3} \{(\vec{p}_1 \cdot \vec{p}_2) - 3(\vec{p}_1 \cdot \hat{z})(\vec{p}_2 \cdot \hat{z})\} \quad (3.2)$$

where \vec{p}_1 and \vec{p}_2 are dipole moments of atom 1 and atom 2 and \hat{z} is the unit vector which is parallel to the connection axis.

Thus, we can get the second order perturbation:

$$E^{(2)}(r) = \frac{e^4}{r^6} \sum_{k \neq 0} \frac{|\langle k^{(0)} | V_{dip-dip} | 0^{(0)} \rangle|^2}{E_0^{(0)} - E_k^{(0)}} \quad (3.3)$$

Here, the energy $E_k^{(0)}$ is corresponding different single particle states of the isolated Hamiltonian (i.e. $H_{polymer} + H_{oxygen}$ without any interaction between them.) . In other words , the eigenstate are all costituted by $|\varepsilon_{polymer} \rangle \otimes |E_{oxygen} \rangle$, where the $|\varepsilon_{polymer} \rangle$ and $|E_{oxygen} \rangle$ are eigenstate of isolated polymer chain and isolated oxygen molecule. So, we should calculate eq.3.3 with all the electron filled in system. In order to simplify our calculation, we just extract the most important term in eq.3.3 and approximation will not affect our results if defect states energy are very close. Thus, we have:

$$E^{(2)}(r) \simeq \frac{e^4}{r^6} \frac{|\langle k^{(0)} | V_{dip-dip} | 0^{(0)} \rangle|^2}{(E_{lower-defect} - E_{upper-defect}) + (E_{\pi} - E_{\pi^*})} \quad (3.4)$$

$$\simeq \frac{e^4}{r^6} \frac{|\langle d_+, \pi^* | V_{dip-dip} | \pi, d_- \rangle|^2}{(\varepsilon_{d_+} - \varepsilon_{d_-}) + (E_{\pi^*} - E_{\pi})} \quad (3.5)$$

where, $|\pi, d_- \rangle = |\pi \rangle \otimes |d_- \rangle$ and $E_{\pi} - E_{\pi^*}$ is rough 4.3 eV.[20]

Therefore, the attractive term in Lennard-Jones potential:

$$\frac{\beta}{r^6} \simeq \frac{e^4 |\langle d_+, \pi^* | V_{dip-dip} | \pi, d_- \rangle|^2}{r^6 (\varepsilon_{d_+} - \varepsilon_{d_-}) + (E_{\pi^*} - E_{\pi})} \Rightarrow \beta = e^4 \cdot \frac{|\langle d_+, \pi^* | V_{dip-dip} | \pi, d_- \rangle|^2}{(\varepsilon_{d_+} - \varepsilon_{d_-}) + (E_{\pi^*} - E_{\pi})} \quad (3.6)$$

From the above equation, β is certainly different according to different band structures. For simplicity, we make an assumption further. That is the numerator can be seen as a constant, because the matrix element in denominator should be only dependent on what the two atoms are. From the previous discussion, all that we need to do is to search if there are any papers which have already obtained α and the numerator of β between carbon and oxygen in the Lennard-Jones and put them in our case. Fortunately, in carbon nanotube research, there already had many papers which discussed the interaction between carbon and oxygen. In the next section, we will calculate it.

3.3 Estimate Lennard-Jones Potential

From some calculations, we know that if we get the minimal energy and the its corresponding distance we can get a and b.

$$\begin{aligned} a &= V_{\min} * r_{\min}^{12} \\ b &= -2V_{\min} * r_{\min}^6 \end{aligned} \quad (3.7)$$

Here, we define a new parameter $\beta^* = e^4 \cdot |\langle d_+ | V_{dip-dip} | d_- \rangle|^2$ which is considered as a constant in our model.

Let's review two important papers about carbon nanotubes. In the first paper, we can get $\alpha=37500$, $\beta=193.7$ and pi band gap is 1.0eV (i.e. $\beta^*=193.7*(1.0+4.3)$).

In the second one, we can calculate α is 30000~40000 and β is around 300. All the adsorption distance are around 2.5~3 Å and adsorption energy is about 150 meV. We believe that in our system the order of α and β is close to these results.

Although the fluctuation of α is not small, but it does less affect the results of distance and energy because of its corresponding to a high order r term.

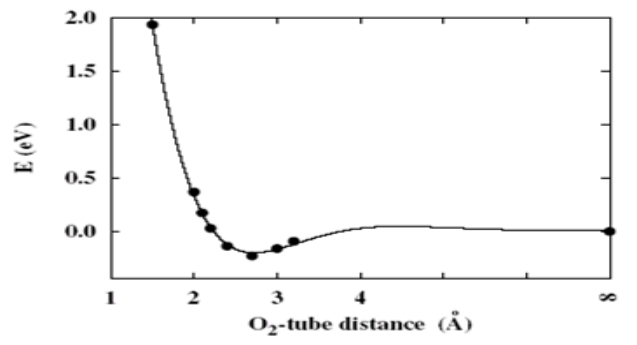


Figure 3.1: PRL 85 1710

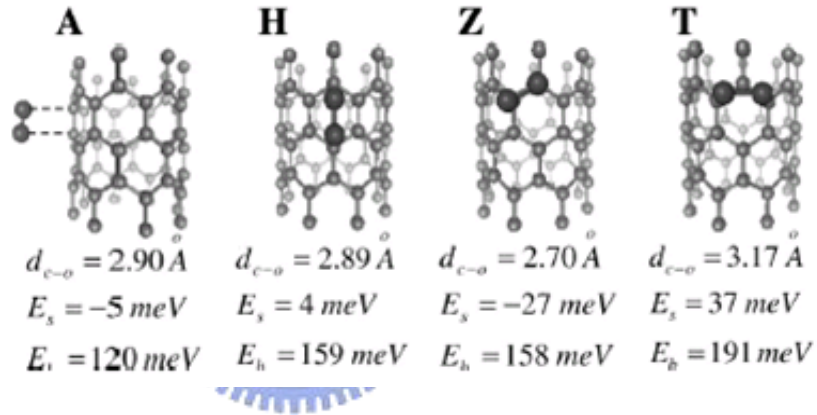


Figure 3.2: PRB 67 165424

All results in these two papers tell us: β is about 200~300 and α is about 20000~40000 . This means our assumption (i.e. α and β are almost constant) is quite reasonable. For simplicity, we just take the α and β^* in the first paper as our system parameter to help us estimate the adsorption properties qualitatively. Thus, we have:

$$V = \frac{37500}{r^{12}} - \frac{193.7 \times (4.3 + 1.0)}{r^6 \cdot [4.3 + (\varepsilon_{d+} - \varepsilon_{d-})]} \quad (3.8)$$

(See fig 3.3 , Lennard-Jones Potential and defect level gap)

Besides, we can also calculate the adsorption energy and adsorption distance

with different defect order parameter.

(See fig 3.4 , adsorption energy and defect order parameter)

(See fig 3.4 , adsorption distance and defect order parameter)

3.4 Summary

To sum up this chapter, we can conclude:

1. Deeper defect induces higher adsorption energy and shorter adsorption distance.
2. Defects can enhance adsorption actually.
3. In other words, deeper defect induces strong interaction between oxygen and polymer chain.
4. Futhermore, we can assert the oxygen must be adsorptive near defect sites because the attractive trem is mainly contributed by the defect levels.



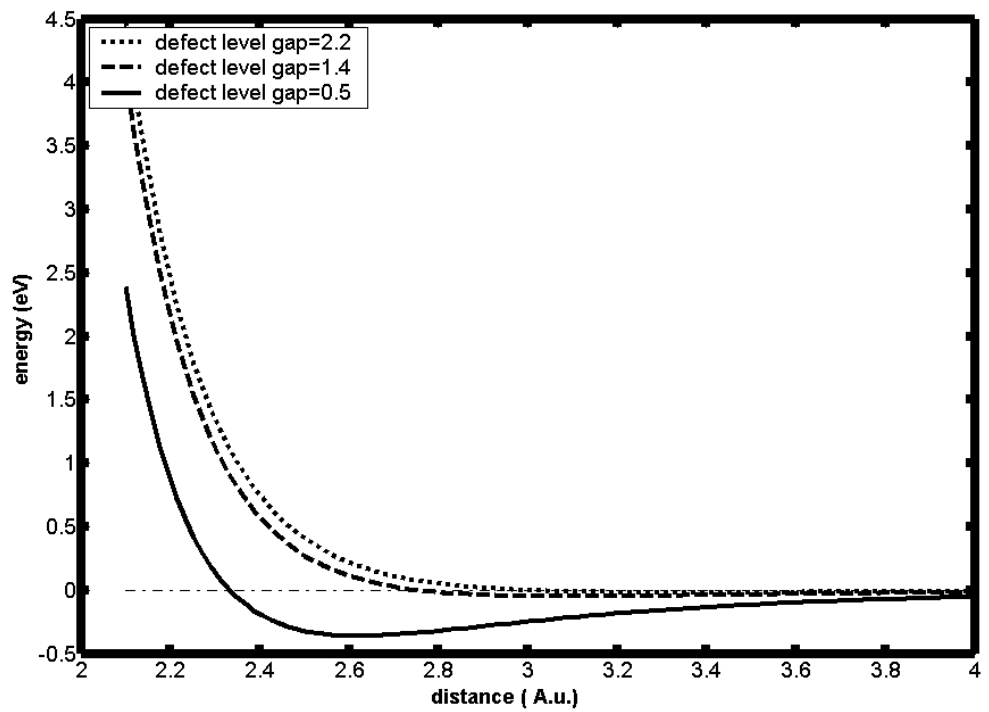


Figure 3.3: Lennard-Jones Potential

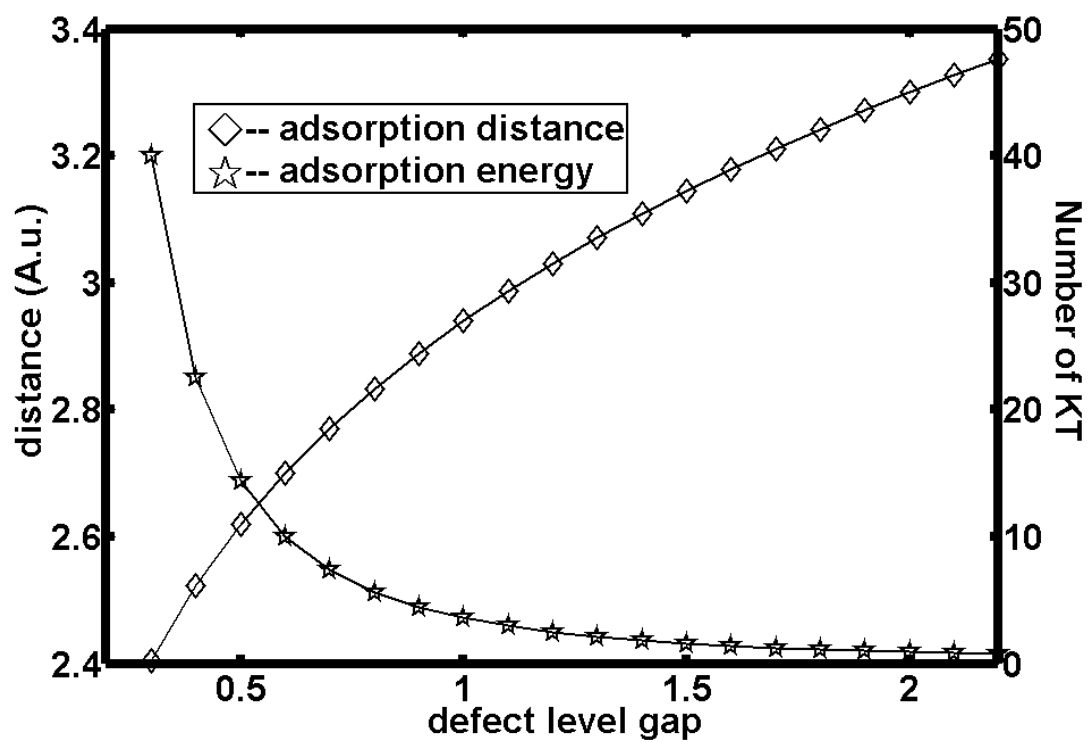


Figure 3.4: adsorption energy and distance

4. Hopping integral

4.1 Hamiltonian

According to the analysis in last chapter, we know that defects can induce oxygen adsorption near the defect sites. When oxygen molecule is close to polymer chain, the interaction between oxygen molecule and polymer chain will turn on. Thus, the total Hamiltonian can be written as:

$$H = H_{polymer} + H_{oxygen} + V_{int} \quad (4.1)$$

where, V_{int} is the perturbation term.

$$H_{polymer} = \text{eq 2.1} \quad (4.2)$$

$$H_{oxygen} = [\varepsilon(n_{\pi_1^*} + n_{\pi_2^*}) + \frac{U}{2}(n_{\pi_1^*} - 1)(n_{\pi_2^*} - 1)] - \frac{J}{2} \vec{S}_{\pi_1^*} \cdot \vec{S}_{\pi_2^*} \quad (4.3)$$

$n_{\pi_1^*} = C_{\pi_1^*}^+ C_{\pi_1^*}$ and $n_{\pi_2^*} = C_{\pi_2^*}^+ C_{\pi_2^*}$ is charge number operator of oxygen π_z^* , π_x^* . $\vec{S}_{\pi_1^*} \cdot \vec{S}_{\pi_2^*}$ is spin coupling operator and that why the ground state of oxygen is triplet. Here, we choose the axis which connects two oxygen atom as y axis. (Note: the highest occupied molecular orbitals [HOMO] are degenerate). ε_o is the onsite energy of oxygen HOMO state and U is exchange energy of this orbital. When charges transfer to oxygen and make it be negative, the total energy of oxygen molecule will rise because of its coulomb exchange effects. So, U should be a positive number.

On the other hand, the interaction V_{int} can be represented as a perturbation term in the Hamiltonian like this:

$$V_{int} = t(C_{d_1}^+ C_{o_{1z}} + C_{d_2}^+ C_{o_{2z}}) + h.c. \quad (4.4)$$

(reason for this term is in fig 4.2)

where $C_{d_1}^+$ and $C_{d_2}^+$ are creation operators of the two defect site atoms and $C_{o_1}^+$ and $C_{o_2}^+$ are creation operators of the two oxygen atoms.

The relation between $C_{d_1}^+$, $C_{d_2}^+$, $C_{\pi_1^*}^+$ and $C_{\pi_2^*}^+$ is:

$$C_{\pi_1^*}^+ = \frac{1}{\sqrt{2}}(C_{o_{1Z}}^+ - C_{o_{2Z}}^+) \quad (4.5)$$

$$C_{\pi_2^*}^+ = \frac{1}{\sqrt{2}}(C_{o_{2X}}^+ - C_{o_{1X}}^+) \quad (4.6)$$

Here, $C_{o_{nX}}^+$ and $C_{o_{nZ}}^+$ are the creation operators of $2P_x$ and $2P_z$ molecular orbital of n_{th} oxygen atom.

Our main problem is what the value of U , ε and t is?

From some experimental results, the EA (electron affinity) and IP (ionization potential) of oxygen molecule is -0.45eV and -12eV in gas phase.(here, the minus means we set vacuum is 0) As we know the HOMO of oxygen are degenerate states. Thus, we can define EA and IP by:

$$(2\varepsilon - \frac{J}{2}) + IP = \varepsilon \text{ and } (3\varepsilon + U) + EA = 2\varepsilon - \frac{J}{2}$$

from experimental result: $J=1\text{eV}$. So, $U = IP - EA - J = 10.6\text{eV}$

In solid state system, EA and IP should be closer to the Fermi level but U is still not too small , because EA of oxygen in solid may be higher than gas phase value significantly due to solid state polarization effects and structural relaxation.[2] Even though we don't know the exact value of EA and IP in solid state, we can still handle our problem. In next chapter, we will show that only EA is important and it should range between -0.45 and -3.5 eV.

4.2 Estimate the Hopping Integral

Next, we will estimate t . In general, we can replace t by a single particle matrix element. Here, we assume t is:

$$t \simeq \langle 1s(a) | \frac{1}{4\pi\epsilon r} | 1s(b) \rangle \quad (4.7)$$

where $|1s(a)\rangle$ and $|1s(b)\rangle$ are the effective 1S orbital of carbon and oxygen. So, if we can find the effective Bohr radius of these two atoms, we can get the matrix element.

This matrix element with different Bohr radius is:

$$\langle 1s(a) | \frac{1}{4\pi\epsilon r} | 1s(b) \rangle = \frac{4\left(\frac{1}{a_1 a_2}\right)^{\frac{3}{2}} a_1^2 a_2^2 \times \left[e^{-\frac{r}{a_1}} (r a_1^2 - r a_2^2) + 2 a_1 a_2^2 (e^{-\frac{r}{a_2}} - e^{-\frac{r}{a_1}}) \right]}{4\pi\epsilon \times r (a_1^2 - a_2^2)} \quad (4.8)$$

where a_1 and a_2 are the Bohr radius of carbon and oxygen.

In CRC Handbook, we can find that the effective Bohr radius of carbon and oxygen is 0.77 \AA and 0.65 \AA . The dielectric constant ϵ in polymer is 3.

Thus, we can get the following figure:

(see fig 4.1 , Hopping integral and distance)

When distance is around $1.2 \sim 1.3 \text{ \AA}$, the integral is around $2.5 \sim 3.5 \text{ eV}$. This result is quite reasonable.

4.3 Hopping Integral in Energy Basis

In order to specify our problem, we need to build a geometry relation of oxygen and defect sites. In many papers which discuss about adsorption of oxygen and carbon think the bond of oxygen is parallel to the polymer plane.[17] [18] Besides, there are also little paper think the bond of oxygen is normal to the bond of carbon.[19] In our problem, we believe the actual picture should be like the first status. (i.e. the bond of oxygen molecule is parallel to the polymer plane). Thus, we will assume the adsorption is like fig 4.2 and we will also give a reason of why this status is more possible later.

(see fig 4.2 , Geometry of asorption)

As a result of this geometry, the main contributor of Carbon-Oxygen overlap is certainly π_z^* orbital because this wave function is combined by $2P_z$ orbital and its space distribution overlap with carbon highly. Therefore, in order to reduce our symbols, we will replace π_z^* by just π^* .

Furthermore, we can also calculate single particle states hopping. As we know, when we diagonal the Hamiltonian of polymer chain, we can get all the single particle levels and there are only site $|d_1\rangle$ and $|d_2\rangle$ exist hopping intergal with oxygen atoms. So, for every single particle state, we have:

$$|\varepsilon_n\rangle = \sum_{n=1}^{8N} a_n |n\rangle \Rightarrow t_{\varepsilon_n - \pi^*} = \langle \varepsilon_n | V_{int} | \pi^* \rangle = \sum_{n=1}^{8N} a_n \langle n | V_{int} | \pi^* \rangle$$

Because, $|\pi^*\rangle = \frac{1}{\sqrt{2}}(|O_1\rangle - |O_2\rangle)$. Thus,

$$\begin{aligned} t_{\varepsilon_n - \pi^*} &= \frac{1}{\sqrt{2}} \sum_{n=1}^{8N} a_n (\langle n | V_{int} | O_1 \rangle - \langle n | V_{int} | O_2 \rangle) \\ &= \frac{t}{\sqrt{2}} \sum_{n=1}^{8N} a_n \left\{ \begin{array}{l} + \langle n | (C_{d_1}^+ C_{o_1} + C_{d_2}^+ C_{o_2}) + h.c. | O_1 \rangle \\ - \langle n | (C_{d_1}^+ C_{o_1} + C_{d_2}^+ C_{o_2}) + h.c. | O_2 \rangle \end{array} \right\} \\ &= \frac{t}{\sqrt{2}} \sum_{n=1}^{8N} a_n \left\{ \begin{array}{l} + \langle n | C_{d_1}^+ C_{o_1} | O_1 \rangle + \langle n | C_{o_1}^+ C_{d_1} | O_1 \rangle \\ + \langle n | C_{d_2}^+ C_{o_2} | O_1 \rangle + \langle n | C_{o_2}^+ C_{d_2} | O_1 \rangle \\ - \langle n | C_{d_1}^+ C_{o_1} | O_2 \rangle - \langle n | C_{o_1}^+ C_{d_1} | O_2 \rangle \\ - \langle n | C_{d_2}^+ C_{o_2} | O_2 \rangle - \langle n | C_{o_2}^+ C_{d_2} | O_2 \rangle \end{array} \right\} \\ &= \frac{t}{\sqrt{2}} (a_{d_1} - a_{d_2}) \end{aligned}$$

where $|n\rangle$ is polymer site basis, $|O_n\rangle$ is oxygen site basis, $|\varepsilon_n\rangle$ is polymer energy site basis and $|\pi^*\rangle$ is oxygen molecule energy basis.

So, we can caculate all the single particle energy hopping integral with oxygen molecule.

(see fig 4.3 , single particle energy level hopping integral)

4.4 About Symmetry

As a result in last section, we found the hopping integrals of single particle energy levels are maximum at upper defect level and almost zero at lower defect level. It is totally because the upper defect is highly localized and anti-bonding at the defect sites just like the oxygen is anti-bonding, too. If we assume the oxygen molecule is normal to the polymer plane, the maximum will occur in the lower defect level.

In our system, we wish to construct an electron trap to explain electron-hole imbalance. So, let the upper defect level have larger hopping integral is better and we will show this in the next chapter.

4.5 Summary

In this chapter, we have already gotten some important things:

1. We build a standard process to estimate the hopping integral by using a semi-empirical method and get reasonable results.
2. We calculate the hopping integral between different polymer single particle energy levels and oxygen energy level.
3. Whether the Oxygen molecule is normal or parallel to the polymer plane, symmetry is always an important property which is deeply affect the hopping integral. In our system, we prefer the parallel case and it will be explained in the next chapter.

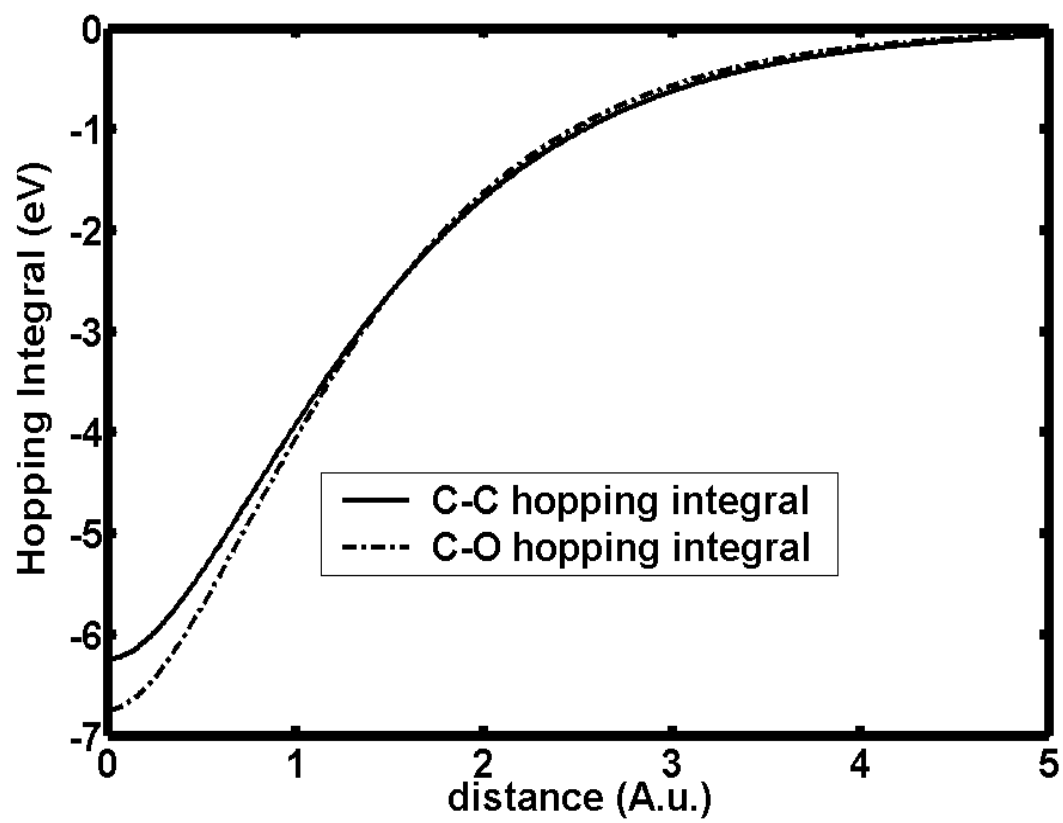


Figure 4.1: hopping tntegral with two atoms

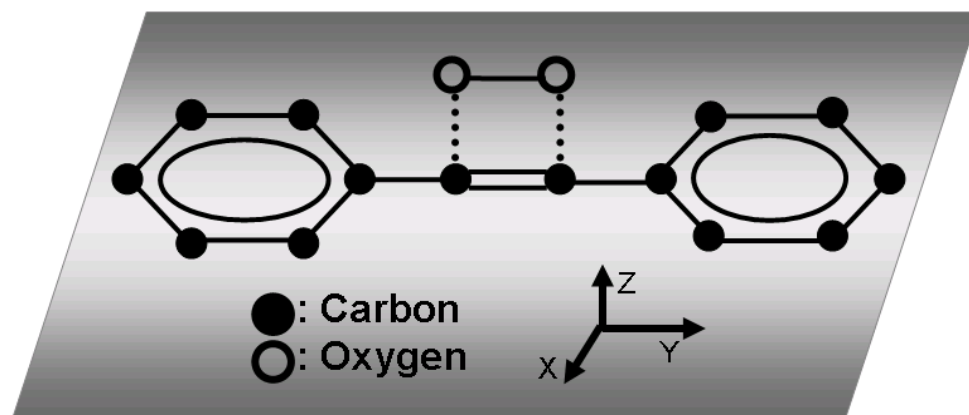


Figure 4.2: geometry of adsorption

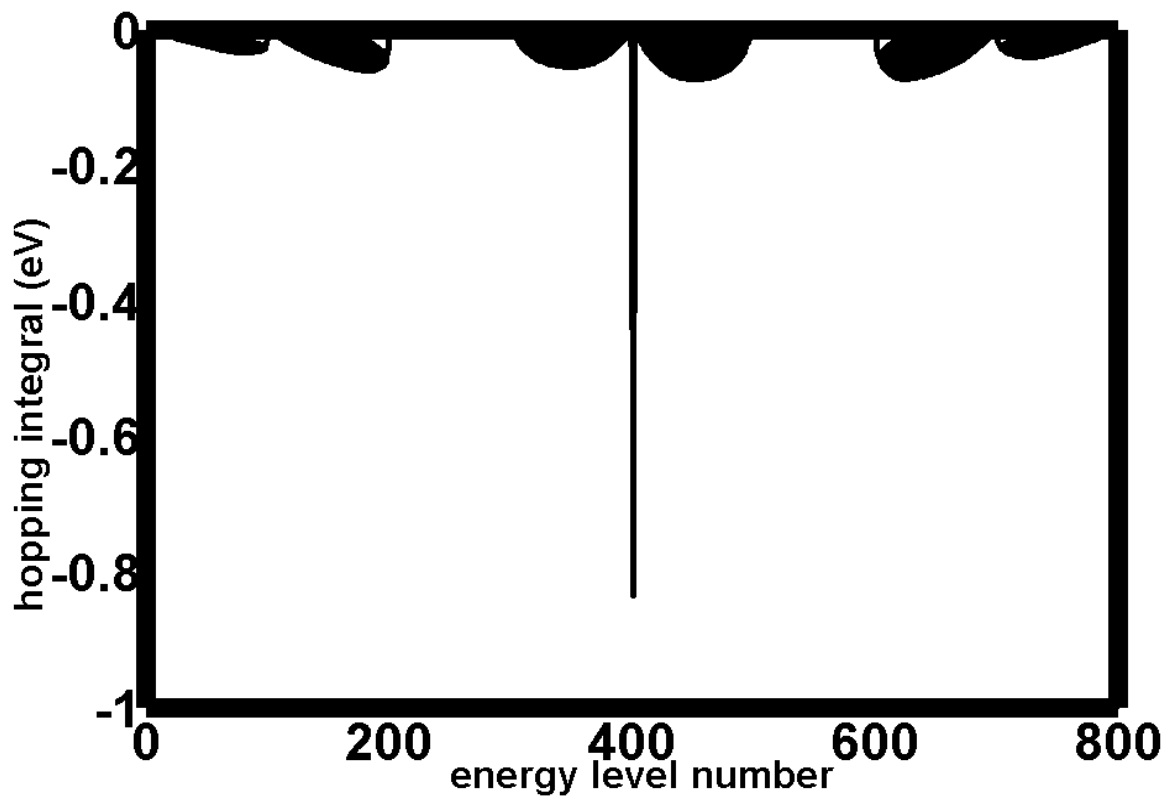


Figure 4.3: hopping integral between oxygen HOMO and PPV level

5. Electron-Hole Imbalance

5.1 Binding Energy

From the previous chapters, we know that when oxygen molecule is close to the defect sites, there will be a perturbation acting on polymer system. In order to quantify the degree of imbalance, we define an energy called the "binding energy".

When there is a hole injection into the polymer system, it will stay in the lower defect state. Similarly, when there is an electron injection into the polymer system, it will stay in the upper defect state. Our definition of binding energy is:

Binding energy Ω = the energy that move a carrier from ground state to continuous state.

In polymer device physics, the mobility is roughly proportional to $e^{-\frac{\Omega}{kT}}$. In room temperature, $kT \sim 25meV$. So, if the electron binding energy can be larger than hole binding energy 0.1 eV at least, there will be large mobility difference between them.

By this definition, we found that an electron injection or a hole injection will have the same binding energy whether there is a defect or not.

Can the perturbation induce any symmetry breaking of binding energy ?

5.2 Configuration

Before figure out the configurations, there are two things we need to know:

1. O_2^+ is found rarely but O_2^- is often found in many physical system. This means oxygen molecule can be an electron trap.
2. Because defect states are highly localized in space. Thus, defect energy levels doesn't like to be totally occupied by carriers because it might casuse strong coulomb replusive energy.[23]

Now, let's consider two different system.

1. **electron case:** there is an electron injection.
2. **hole case:** there is a hole injection.

Thus, we can figure out the most important condigurations:

(see fig 5.1 , **configuration, the upper is electron case and the lower is hole case**)

As a result , we can constructure the following matrix:

$$\begin{pmatrix} \langle g|H|g \rangle & \langle g|H|ex \rangle & \langle g|H|ct \rangle \\ \langle ex|H|g \rangle & \langle ex|H|ex \rangle & \langle ex|H|ct \rangle \\ \langle ct|H|g \rangle & \langle ct|H|ex \rangle & \langle ct|H|ct \rangle \end{pmatrix} , \text{ electron case}$$

$$\begin{pmatrix} \langle g|H|g \rangle & \langle g|H|ex \rangle \\ \langle ex|H|g \rangle & \langle ex|H|ex \rangle \end{pmatrix} , \text{ hole case}$$

5.3 Matrix Element

From the above analysis, we can find that the charge transfer state is only appare in electron injection case. The diagonal terms are certainly that sum all the occupied single particle state energy. For simplicity, we choose the ground state of netural system as zero point. Then , we have:

- *diagonal term*

electron case:

$$\begin{aligned}
\langle g|H|g \rangle &= \varepsilon_{d_+} \\
\langle ex|H|ex \rangle &= \varepsilon_{4N+2} \\
\langle ct|H|ct \rangle &= \varepsilon_{\pi^*} + U \\
&= (IP_o - IP_c) + [(EA_o - IP_c) - (IP_o - IP_c)] \\
&= EA_o - IP_c
\end{aligned}$$

hole case:

$$\begin{aligned}
\langle g|H|g \rangle &= -\varepsilon_{d_+} \\
\langle ex|H|ex \rangle &= -\varepsilon_{4N-1}
\end{aligned}$$

Here, we shift EA and IP of oxygen because we have taken the IP=-5eV of carbon in polymer (i.e. the Fermi level) be zero.

Next, we calculate off-diagonal terms. No matter what the bra and ket are, the main problem we need to solve is :

$$\langle \psi|H|\varphi \rangle = \langle \psi|H_{polymer}|\varphi \rangle + \langle \psi|H_{oxygen}|\varphi \rangle + \langle \psi|V_{int}|\varphi \rangle$$

In our calculation, we always take the energy basis of $H_{polymer} \otimes H_{oxygen}$, so the first two terms are just that sum all the electrons in polymer and oxygen single particle state. Thus, our main problem is how to solve the last term. As we know, the interaction term is written in site basis and the wavefunction is written in energy basis. So, to calculate the last term is not easy. In physical system, the most active charge is the one which is in the highest occupied level and this charge is also the most possible one to transfer from polymer to oxygen. To simplify our calculation, we can just take the single particle level's hopping integrals which belongs to the highest occupied level as those matrix elements if there is any charge transfers to oxygen from bra

state to the ket state. Otherwise, take the matrix element be zero. Thus, we have:

- *off-diagonal term*

electron case:

$$\langle g|H|ex \rangle = 0$$

$$\langle g|H|ct \rangle = t_{d_+-\pi^*}$$

$$\langle ex|H|ct \rangle \simeq 0$$

hole case:

$$\langle g|H|ex \rangle = 0$$

5.4 Imbalance

Now, we have already get all the informations of our problem. Similarly, we define "imbalance energy" :

imbalance energy Δ = the binding energy difference of electron case and hole case.

In our system:

$$\Delta = \frac{1}{2} \left\{ [\varepsilon_{d_+} - (EA_o - IP_c)] + \sqrt{[\varepsilon_{d_+} - (EA_o - IP_c)]^2 - t_{d_+-\pi^*}^2} \right\}$$

Like those analyses in the previous chapters, we know we will get a adsorption distance, hopping ineegral and coupling energy between ground state and charge transfer state in the electron case when we get a defect order parameter . Thus, we can analysis the realation between defect order parameter and imbanalce energy.

(see fig 5.2 , imbalance energy and defect order parameter)

Beside, we can also let $t_{d_+-\pi^*}$ slightly change if our estimate on it is not accurate enough.

(see fig 5.3 , imbalance energy and $t_{d_+-\pi^*}$ in a fixed defect order parameter)

Finally, we will discuss some things about EA.

In gas phase , EA is -1eV. In most polymer system, the conduction band is around 1.5~2eV higher than Fermi-level (E_F is -5eV to vacuum). It seem strange if EA is lower than conduction band . Because, when defect exist and the upper defect state might be higher than EA (i.e. acceptor level), the charge transfer state will be ground state in electron case. And this fact is unreasonable because the oxygen molecule is just adsorptive not bonding.

Therefore, we believe the EA of oxygen in polymer is -1 ~ -3.5 eV.

5.5 Summary

In this chapter, we get many important things:

1. Deeper defect will induce stronger e-h imbalance.
2. In most case, the imbalance energy Δ can be from 0.1eV to 0.8eV easily. In otherwise, the electron-hole mobility difference can be form 10^2 to 10^{14} . This means that althouhg oxygen molecule adsorption is an slight perturbation to the system, it can induce an extreme symmetry breaking in polymer transport properties.



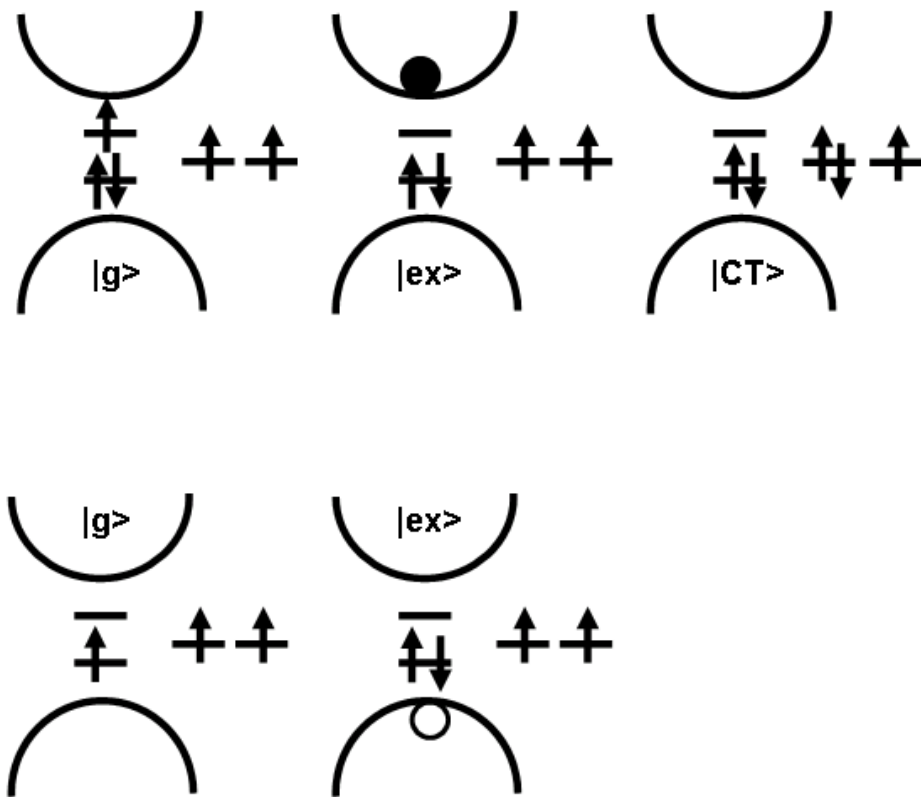


Figure 5.1: configurations

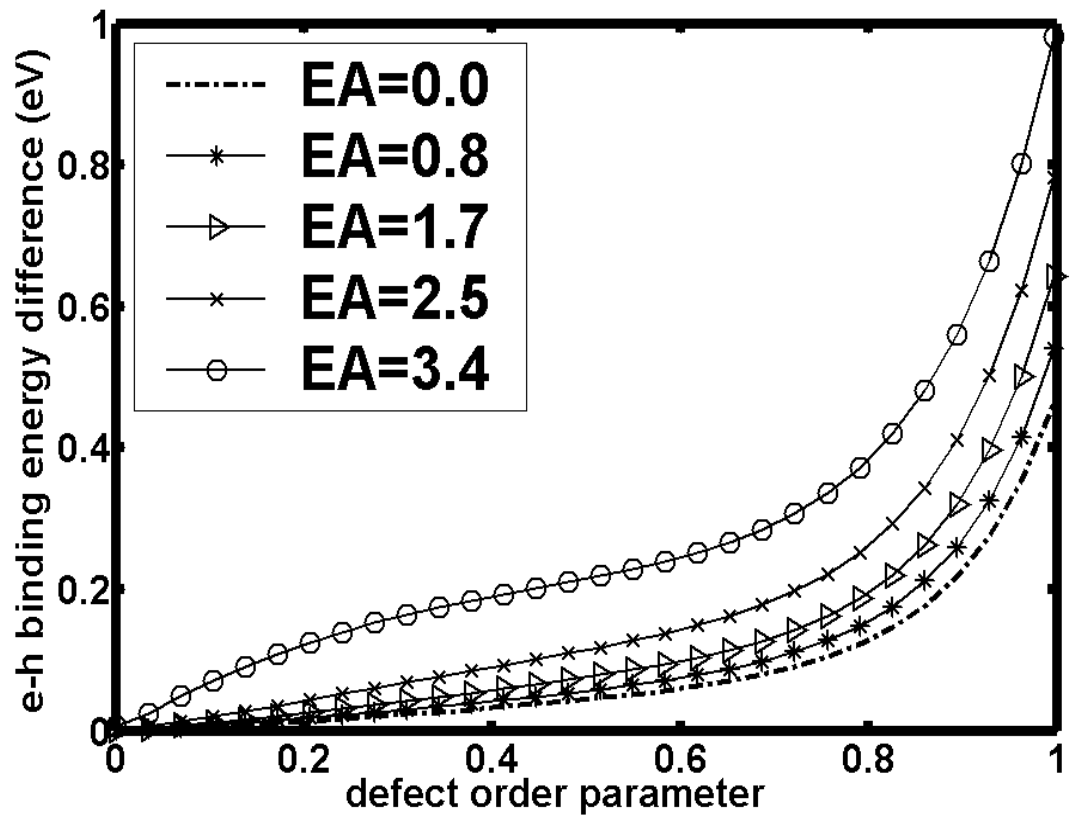


Figure 5.2: imbalance energy in different order parameter

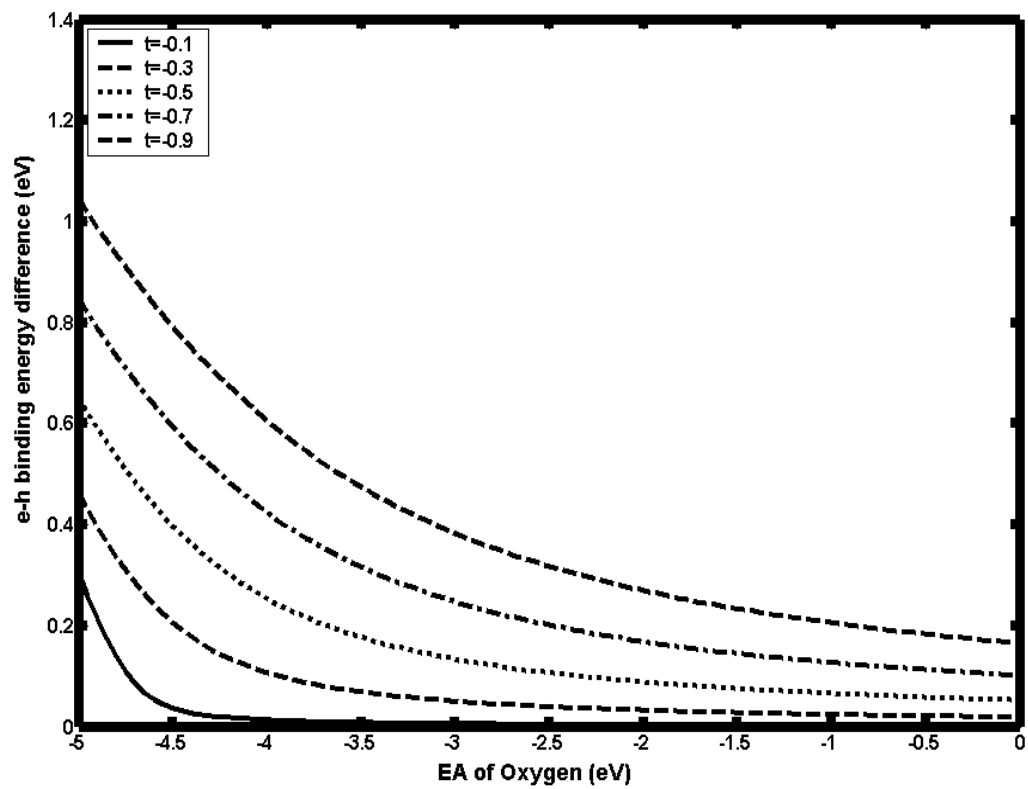


Figure 5.3: imbalance with different coupling energy

6. Conclusion and Outlook

6.1 Conclusion

In the previous chapter, we have gotten many important physical concepts. When defect exist, it will create some energy levels in the forbidden band and those electrons which locate at defect state will deeply affect the electronic properties. In polymer system, defects are more interesting because it will enhance oxygen adsorption. As we know, no matter how perfect vacuum you can make, there always exist a few oxygen molecules in the air. In our calculation, even though there are only one oxygen molecule and one defect, there are still significant symmetry breaking. So, we can assert that electron-hole transport imbalance is almost an unavoidable result and oxygen is the key.

Altogether, our central concepts is:

"Defect will enhance oxygen adsorption and it will cause charge transfer to oxygen. Thus, an electron trap is formed. Transport symmetry is breaking."

6.2 Outlook

In this thesis, we have discussed many things about polymer physics. But, there are still many problems we need to solve. For example, in the imbalance problem, there are many other reasons for this phenomenon[21] and oxygen adsorption may not be the only thing that can cause this result. So, we could expect there will be more experiments to tell us more about oxygen and polymer behavior.

Polymer physics is much different from inorganic semiconductor physics and it is also an interesting area in theoretic physics. We believe there will be more and more exciting discoveries in the future.

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