A study on low-energy light absorption of SWNTs

H Li1,2, S Y Wu1, M Y Zhou1 and X R Liang1

1School of Basic Sciences for Aviation, Naval Aviation University, Yantai Shandong 264001, China

E-mail: 346521161@qq.com

Abstract. By using semi-empirical method, an approximately one-dimensional model on the basis of tight-binding theory is set up to calculate state density of different sorts of single-walled carbon nanotubes so as to explain the reason for three absorption peaks in the low energy level of light absorption spectrum.

1. Introduction

Since the synthesis of single-walled carbon nanotubes (SWNTs) by Iijima and Ichihashie [1,2], carbon nanotubes have received extensive attention as a photoelectric functional material with wide application prospects [3-13]. In 1998, Pichler [14] measured the photoconductivity of graphite and SWNTs, and three obvious absorption peaks were found out in the graphite, which were located at 4.5±0.05 eV, 13±0.05 eV and 15±0.05 eV, respectively. There were also three similar and slightly lower absorption peaks in SWNTs, which were located at 4.3±0.1 eV, 11.7±0.2 eV and 14.60±1 eV, respectively. At the same time, it was also found that SWNTs had absorption peaks in the lower energy region, which were located at 0.6±0.1 eV, 1.2±0.1 eV and 1.8±0.1 eV. After that, Kataura, Jost, Jeroen and others [15-17] also found the three characteristic absorption peaks in the low energy region of the SWNTs' light absorption spectrum.

SWNTs can be seen as a graphite plane curled in a certain direction. Graphite is a layered six angle structure and each layer expands in a two-dimensional plane, but its edge is unstable, which is just like a thin piece of paper and its edge is tilted up so as to form a more stable reel structure, that is carbon tube. The ratio of the length and the diameter of the carbon nanotube can reach 104-105 orders of magnitude. Therefore, we can conclude that the carbon nanotubes are one-dimensional or quasi one-dimensional system physically.

According to different ways of winding the graphite surface forming carbon nanotubes, the layers of carbon nanotubes can fall into two categories: non helix type and helix type [18]. The helix type is divided into the "armchair" structure and the "zigzag" structure. The spiral vector of carbon nanotubes is usually expressed as \( \mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \), in which \( n, m \) are integers, \( \mathbf{a}_1, \mathbf{a}_2 \) are the basis of the graphite lattice as shown in the figure 1. The angle \( \theta \) between \( \mathbf{C}_h \) and \( \mathbf{H}_1 \) is called the chiral angle. When \( n=m, \theta = 30^\circ \), this kind of carbon nanotube is called the chair type carbon nanotube, which is the armchair tube; when \( m = 0, \theta = 0^\circ \), this structure is called the sawtooth carbon nanotube, which is the zigzag tube; when \( 0^\circ < \theta < 30^\circ \), this structure is called the chiral carbon nanotubes. Carbon nanotubes are commonly characterized by \((m, n)\).
2. Model and formula

At present, there are wide and diverse methods to study carbon nanotubes in theory, including the tight binding method [19], the first principle or the AB initio method, the Green function method [20] and so on. We have established a simplified model that is to study non-spiral carbon nanotubes (armchair type SWNTs and zigzag type SWNTs). The armchair type carbon nanotubes are treated as a number of identical trans-polyacetylene chains which are arranged in the axial direction and the zigzag type carbon nanotubes are treated as a number of identical cis-polyacetylene chains which are arranged in the axial direction. In the circumferential direction, the same chains are combined by chemical bonds. Given the quasi one-dimensional nature of carbon nanotubes, the two non-helical carbon nanotubes are considered as one-dimensional systems formed by the combination of multiple conjugated polymer chains through interchain coupling in the simplified model. This model is called one-dimensional carbon nanotube model.

The Hamiltonian of the polymer chain described by the extended one-dimensional tight binding model is as follows:

\[
H_p = -\sum_{n,\sigma} [t_0 - \alpha_p (u_{n+1} - u_n) - t_1 \cos(n\pi)] (a_{n,\sigma}^+ a_{n+1,\sigma} + a_{n+1,\sigma}^+ a_{n,\sigma}) + \frac{1}{2} K_p \sum_n (u_{n+1} - u_n)^2
\]

in which \( a_{n,\sigma}^+ \) (\( a_{n,\sigma} \)) is the generation (disappearance) operator of an electron whose spin cis \( \sigma \) at a lattice point \( n \), \( t_{n,n+1} = t_0 - \alpha_p (u_{n+1} - u_n) - t_1 \cos(n\pi) \) is the transition integral of \( \pi \) electrons in adjacent grid points \( n \) and \( n + 1 \), \( t_0 \) is the transition integral of electrons in adjacent grid points when lattice points arrange equidistantly, \( \alpha_p \) is electroacoustic coupling constant, \( u_n \) is the position deviation of the \( n \) lattice point (CH group), \( t_1 \) is degenerate parameter, and \( K_p \) is the elastic coefficient of lattice.

In the axial direction, the Hamiltonian is the sum of Hamiltonian of all single organically conjugated polymer chains, which is expressed as follows:

\[
H_a = -\sum_{j,n,\sigma} [t_{0,j,n,\sigma} - \alpha_p (u_{j,n+1} - u_{j,n}) - t_1 \cos(n\pi)] (a_{j,n,\sigma}^+ a_{j,n+1,\sigma} + a_{j,n+1,\sigma}^+ a_{j,n,\sigma}) + \frac{1}{2} K_p \sum_{j,n} (u_{j,n+1} - u_{j,n})^2
\]

in which \( t_{j,n,n+1} = t_0 - \alpha_p (u_{j,n+1} - u_{j,n}) - t_1 \cos(n\pi) \). \( j \) represents the organically conjugated polymer chain of class \( j \), we assume that \( t_0, \alpha_p, t_1, K_p \) are the same in each chain.
In the circumferential direction, the Hamiltonian of the coupling term between chains is described as:

\[ H_i = - \sum_{j,(n,n')} t_\perp \left( a^+_j n_\sigma a^+_j (n+1)_{\sigma} + a^+_j (n+1)_{\sigma} a^+_j n_\sigma \right) \]  

(3)

in which \((n_j, n_{j+1})\) represents the nearest neighbor lattice point of two adjacent chains, and \(t_\perp\) represents the electron transition integral between the nearest two lattice points in the circumferential direction, which shows the intensity of interchain coupling.

By solving the Schrodinger equation

\[ \left( \sum_j H_j + H_i \right) \psi_\mu = \epsilon_\mu \psi_\mu, \quad \psi_\mu = \sum_{j,n} \psi_{\mu,j,n} |j,n\rangle \]  

(4)

we can get the eigenvalue \(\epsilon_\mu\) and the eigenfunction \(\psi_\mu\).

Total energy

\[ E = \sum_{\mu \in \text{OCC}} \epsilon_\mu + \frac{1}{2} K_p \sum_{j,n} \left( u_{j,n,I} - u_{j,n} \right)^2 \]  

(5)

The equilibrium equation of the lattice shape is

\[ \phi_{j,n} + \phi_{j,n+1} = (-1)^j \pi \lambda \left[ \sum_{\mu,\sigma} Z_{j,n,\mu,\sigma} Z_{j,n+1,\mu,\sigma} - \frac{1}{N} \sum_{m=1}^{N} \sum_{\mu,\sigma} Z_{j,n,\mu,\sigma} Z_{j,n+1,\mu,\sigma} \right] \]  

(6)

in which \(\phi_{j,n} = (-1)^j (\alpha_p / t_0) u_{j,n}\), references \([21]\), \(t_0 = 2.5\ eV\), \(\alpha_p = 4.1\ eV/\AA\), \(t_1 = 0.05\ eV\), \(K_p = 21\ eV/\AA\), \(\lambda = 2\alpha_p^2 / \pi K_p t_0\). \(\sum_{\mu \in \text{OCC}}\) represents the sum of the occupied energy levels of all electrons. The periodic boundary condition applies in the model.

3. Discussion and examples

The energy level distribution and density of states of two non-spiral carbon nanotubes (armchair type SWNTs and zigzag type SWNTs) are calculated by one-dimensional carbon nanotube model, so as to explain the formation of three absorption peaks in the low energy phase of the carbon nanotube experiment \([3]\).

The intrinsic states of electrons in the atom form a series of discrete energy levels, and we can explain their specific distribution by identifying each energy level. However, the distribution of electrons is very dense in the solid, it is meaningless to indicate each energy level by forming the energy level of quasi continuous distribution. Thus, we introduce the concept of "energy state density" in order to generalize the distribution of energy levels in this case.

The "energy state density" is defined as \(N(E) = \lim_{\Delta N \to 0} \Delta N / \Delta E\), in which \(\Delta N\) is the number of energy state, and \(\Delta E\) is the energy bite. We calculate the energy state density through Gauss expansion in order to analyse the electronic states near the Fermi level.

\[ N(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(E - E_\mu)^2}{2\sigma^2} \right] \]  

(7)

in which \(E_\mu\) is the eigen energy level, \(n_\mu\) is the energy level degeneracy, and \(\sigma\) is Broadening parameter.
We can get all the energy eigenvalues by diagonalizing Hamilton of equation (4). Density of states (DOS) will obtain through Lorentz broadening:

$$\rho(\varepsilon) = \frac{n_\mu}{(2\pi\sigma)^2} \exp\left[\frac{-(\varepsilon - \varepsilon_\mu)^2}{2\sigma^2}\right]$$

which shows the number of states in unit energy intervals. $N(\varepsilon)$ shows the sum of the all DOS.

Singular points of DOS mean the existence of quantized energy levels. By studying the DOS near the Fermi level, we can find the electron transition between the energy levels corresponding to the singular points, then figure out the light absorption of the carbon nanotube. First, we calculate the DOS of several zigzag-type SWNTs $(n, 0)$ near the Fermi level.

The diameter of zigzag-type SWNTs $(14, 0)$ is 1.10 nm. Figure 2 is the change diagram of the DOS of zigzag-type SWNTs $(14, 0)$. The diameter of zigzag type SWNTs $(16, 0)$ is 1.25 nm. Figure 3 is the change diagram of the DOS of zigzag-type SWNTs $(16, 0)$.

![Figure 2](image1.png)  
**Figure 2.** The change diagram of the DOS with the energy of zigzag type SWNTs$(14, 0)$.  

![Figure 3](image2.png)  
**Figure 3.** The change diagram of the DOS with the energy of zigzag type SWNTs$(16, 0)$.  

In the above two diagrams, the plane that energy equals zero is the Fermi plane, and each peak of energy is called singular point. We can draw the conclusion that zigzag-type SWNTs $(14, 0)$, $(16, 0)$ are semiconducting carbon nanotubes, because around Fermi level, their DOS are almost zero. This means that the Fermi level is formed around the band gap, which is characteristic of the semiconductor. Energy level transition between the first pair of the singular points of two carbon nanotubes is within the range of the first absorption peak in the low energy region of Pichler experimental optical absorption spectrum [17]. Table 1 shows the energy difference between the first pairs of the singular points of more semiconducting carbon nanotubes.

| zigzag    | (13,0) | (14,0) | (16,0) | (17,0) | (19,0) | (20,0) | (22,0) |
|-----------|--------|--------|--------|--------|--------|--------|--------|
| Diameter(nm) | 1.02   | 1.10   | 1.25   | 1.33   | 1.49   | 1.57   | 1.72   |
| $\Delta E$(eV) | 0.66   | 0.56   | 0.58   | 0.49   | 0.52   | 0.38   | 0.40   |

As you can see from the table above, the diameters of the five zigzag-type carbon SWNTs $(13,0)$, $(14,0)$, $(16,0)$, $(17,0)$ and $(19,0)$ are distributed between 1-2 nm, and the energy level transition between their first pair of the singular points is within the range of the first absorption peak obtained from the experiment. The singular points indicate the existence of the quantum energy level. By calculating the energy levels, We can get the energy corresponding to the first pair of singular points.
In the change diagram of the DOS, the first singular point on the left side of the Fermi plane corresponds to two energy levels, $N/2$ and $N/2-1$, the two energy levels are energy merger. Similarly the first singular point on the right side of the Fermi plane corresponds to two energy levels, $N/2$ and $N/2-1$, the two energy levels are energy merger. In which $N$ is the total number of lattice. By calculating the electron transition probabilities between these four levels we can arrive at such a conclusion that electronic transition may occur between the first pair of the singular points in the five carbon nanotubes above, but the energy levels of the electron transition are different. The electron transition of SWNTs $(13,0)$, $(16,0)$ mainly occur between $N/2 - N/2+2$, $N/2-1 - N/2+1$ energy levels; the electron transition of SWNTs $(14,0)$, $(19,0)$ mainly occur between $N/2 - N/2+1$, $N/2-1 - N/2+2$ energy levels; however, in the case of SWNTs $(17,0)$, all four situations are likely to occur, and $N$ is the total number of lattice points. Therefore, the first absorption peak obtained in the experiment is caused by the electron transition between the first pair of the singular points of semiconducting carbon nanotubes.

Next, we will study the DOS of several armchair-type SWNTs $(n, n)$. The diameter of armchair type SWNTs $(9, 9)$ is 1.22 nm. Figure 4 shows its DOS. The diameter of armchair-type SWNTs $(10, 10)$ is 1.36 nm. Its DOS is shown in figure 5.

![Figure 4. DOS of armchair-type SWNTs (9, 9).](image1)

![Figure 5. DOS of armchair-type SWNTs (10, 10).](image2)

From the above figure 5 we see that there is a minimum of DOS near the Fermi level of the armchair-type SWNTs. It shows that it is a type of metallic carbon nanotube. We take two very obvious singular points as an example, which are the two peaks pointed by the arrow in the figure 5. The two peaks indicate that there is a quantum energy level near the singular points, and the DOS around the quantum energy level is large, so the electron transition is easy to occur. The energy difference between the two singular points is about 1.81 eV, which indicates that if there is an electron transition between the two energy levels, the photon energy needed is about 1.81 eV, which requires the absorption of the photon energy. This value is within the range of the third absorption peak in the low energy region of the experiment.

| Table 2. Energy difference between the first pair of the singular points of armchair type carbon nanotubes with different diameters. |
|-----------------|-----|-----|-----|-----|-----|
| Armchair        | (7,7) | (8,8) | (9,9) | (10,10) | (11,11) |
| Diameter(nm)    | 0.95  | 1.08  | 1.22  | 1.36  | 1.49  |
| $\Delta E$(eV)  | 1.80  | 1.82  | 1.81  | 1.80  | 1.80  |
When calculating the DOS of several other armchair-type SWNTs, we found such pair of singular points always exists, and their energy difference is about 1.80 eV, which is shown in table 2.

By calculating the transition probability between the singular points in the armchair-type SWNTs, it is confirmed that there is electron transition between the singular points in the several kinds of armchair-type SWNTs above. The transition probability between the energy levels is different, which is the same case with zigzag-type SWNTs. Therefore, the third absorption peak is formed by the electron transition of metallic carbon nanotube in the experiment.

4. Conclusion

By calculating the DOS of several carbon nanotubes in the diameter range of the experiment we found that energy difference between the first pair of singular points near Fermi level of the semiconducting zigzag-type SWNTs is basically consistent with the size of the absorption peak of 0.6±0.1 eV obtained in the experiment. We also got the conclusion that the electron transition can occur between the energy levels of the singular points. Therefore, the first absorption peak in the low energy region of Pichler experimental optical absorption spectrum of SWNTs is caused by the electron transition between the first pair of the singular points of the semiconducting carbon nanotubes. From the DOS of two metallic armchair type SWNTs we can get the third absorption peak, 1.8±0.1 eV, which is caused by the electron transition between their two most obvious singular points, with the size basically the same. Several other armchair carbon nanotubes also exhibit this property. The reason for the second absorption peak is not clear. It may be caused by the optical absorption of spiral metallic carbon nanotubes, or caused by the electron transition between the second pair or the third pair of singular points of the semiconducting carbon nanotubes.

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