Quantum Chemistry Calculation on Oxygen and Nitrogen Adsorption in Carbon Nanotube

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Abstract: Oxygen and nitrogen adsorption in single-walled carbon nanotube (SWCNT) is studied by density function and discrete variational (DFT-DVM) method. The models of O\textsubscript{2} and N\textsubscript{2} adsorption in the SWCNT are optimized based on the energy minimization. The calculated results of density of state, populations and energy gaps of the molecular orbitals show that oxygen adsorption in SWCNT increases the carbon nanotube’s electrical conductivity more notably than nitrogen adsorption, which is consistent with the experiment.

Key words: single-walled carbon nanotube; quantum chemistry calculation; adsorption; electronic conductivity

1 Introduction

Carbon nanotube (CNT) has attracted much attention in recent years, because of its special structure and properties. One of its properties is that some kinds of gas can be adsorbed in the carbon nanotube. P G Collins \textit{et al}[1] found that the electrical resistance of nanotubes decreases dramatically when the nanotubes are exposed to air or oxygen, and an apparently semiconducting nanotube can be converted into an apparent metal. G U Sumanasekera \textit{et al}[2] found that besides oxygen, other kinds of gas, such as nitrogen and helium, also can be adsorbed by nanotube with different strengths of the adsorption. GU Chong \textit{et al}[3] studied the hydrogen adsorption in single-walled carbon nanotube (SWCNT) by Grand Canonical Monte Carlo simulation and discussed the influence on adsorption of different SWCNTs’ diameters and Van der Waals distances. The nature of the interaction between gas and carbon nanotube is not clearly realized so far. In this paper the effects of O\textsubscript{2} and N\textsubscript{2} gas adsorption in the SWCNT are studied by density function and discrete variational (DFT-DVM) method[4].

2 Calculation Method

DFT-DVM method[4] is to resolve the Kohn-Sham equation (in atomic unit):

\[
\begin{align*}
  & h_{ks} \varphi_i(r) = \\
  & \left[ -\frac{\nabla^2}{2} - \sum_q \frac{Z_q}{|r - R_q|} \right] \varphi_i(r) + \int \frac{\rho(r')}{r - r'} + d' + V_{xc} 
\end{align*}
\]

\[
\varphi_i(r) = \sum_q \varphi_q(r)  
\]

\[
\rho(r) = \sum_i n_i |\varphi_i(r)|^2
\]

Where, \(h_{ks}\) is Hamilton of single electron, \(\varepsilon_i\) is the energy value of single electron to be resolved, \(\rho(r)\) is the density function, \(\varphi_i(r)\) is the single electron wave function of molecule or cluster, \(n\) is the number of occupied electrons. The first term in the middle of equation (1) is kinetic energy. The second is Coulomb potential due to that the electrons are attracted by nuclei. The third is Coulomb potential due to that the electrons repel each other. \(V_{xc}\) is exchange potential. \(\varphi_i(r)\) is expanded to functions of atomic orbitals:

\[
\varphi_i(r) = \sum_{l=1} \chi_i(r) C_{il}
\]

The error function is found as:

\[
\Delta_{ij} = <\varphi_i|h_{ks} - \varepsilon_i|\varphi_j>
\]

A number of discrete sampling points in a three-dimensional grid are chosen. Variation is made to the parameter of \(C_{il}\) in the error function to obtain all the minima for the points. Using the multi-dimensional numerical integer method, self-consistent process is carried out to obtain \(\varepsilon_i\), \(\varphi_i(r)\) and others. DFT-DVM method can be used to calculate larger structure models of molecules, clusters and solids, so it has been widely used in chemistry, physics, material science and so on[4-6].

3 Calculation Models

Carbon nanotubes can be thought of as a graphitic
sheet that has been wrapped up into a cylinder, so it keeps the structural character of hexagonal ring. The calculated models are shown in Fig. 1. The model of SWCNT that not adsorb the gas is called model 0 and consists of 10 layers with 50 carbon atoms. These 50 atoms are divided into 10 types (shown in Fig. 1) with the operation of symmetry of $D_{5d}$ point group. Four adsorption systems, or 4 classes of models, are chosen as atom clusters by analogizing the results for $O_2$ and $N_2$ chemisorption on the graphite basal plane. The first adsorption system of model 1 is the gas molecule parallel to the tube axis closing to the middle point of two nearest carbon atoms (A site). Model 2 is the gas molecule parallel to the tube axis closing to the center of the hexagonal ring (B site). Model 3 is the gas molecule perpendicular to the tube axis closing to A site. Model 4 is the gas molecule perpendicular to the tube axis closing to A site. Oxygen atoms of model 3 or 4 can be divided into O (in) and O (out) according they are near to or far from the SWCNT.

![Calculated models. Model 0: isolated SWCNT; model 1-4: section of $O_2$ + SWCNT or $N_2$ + SWCNT](image)

**4 Results and Discussion**

The calculated results of model 0 show that an electric field with positive and negative charge centers is formed at the periphery of the isolated SWCNT from C(2) to C(5) layers (Table 1). Three nearest layers of C(1) and two C(2) are all with negative charge and there is a larger electronic density. The analyses of the charge density map show that electronic cloud concentrates on the adjacent carbon atoms in the hexagonal ring, so the adjacent atoms are connected by covalent bonds.

<table>
<thead>
<tr>
<th>Model</th>
<th>C(1)</th>
<th>C(2)</th>
<th>C(3)</th>
<th>C(4)</th>
<th>C(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>1.254</td>
<td>1.202</td>
<td>1.373</td>
<td>1.266</td>
<td>1.693</td>
</tr>
<tr>
<td>2p</td>
<td>2.797</td>
<td>2.874</td>
<td>2.542</td>
<td>2.809</td>
<td>2.190</td>
</tr>
<tr>
<td>Q</td>
<td>-0.051</td>
<td>-0.076</td>
<td>0.065</td>
<td>-0.075</td>
<td>0.117</td>
</tr>
</tbody>
</table>

The models of $O_2$ and $N_2$ adsorption in the SWCNT are optimized from the calculated total energies and the principle of the lowest energy. In Fig. 2, the horizontal axis is the distance between the gases ($O_2$ or $N_2$) and SWCNT, and the vertical axis is the calculated total energies. There is a lowest point of energy for each model, and the model on this point is the most stable. Comparing the different classes of models, the stable order is model 3 > model 1 and model 4 > model 2. Model 3 is in preference to exist when $O_2$ or $N_2$ is adsorbed in the SWCNT, then may be model 1 or 4, and model 2 is difficult to exist. The most stable models of $O_2$ and $N_2$ adsorption in the SWCNT are compared in the following.

Carbon nanotube is a semiconductor, so the electrical properties are affected by the concentration of carrier. The variations of electronic structure, such as the density of state (DOS) and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), directly lead to the change of the electrical conductivity. The total DOS is shown in Fig. 3. The Fermi level is set at the zero point on the horizontal axis in...