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The rehybridization of electronic orbitals in carbon nanotubes*

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Rehybridization of electronic orbitals in carbon nanotubes contains tilting angles of π orbital, electrons wavefunctions of π orbital and σ orbital, degrees of hybridization, etc. In this paper, we have obtained analytical formulas of tilting angle of π orbital relative to tube surface, electrons wavefunctions of π orbital and σ orbital, degrees of hybridization, separately, as well as the numerical results.

Keywords: carbon nanotube, curvature effect, rehybridization of orbitals, degree of hybridization
PACC: 8140, 8120V, 8116T

1. Introduction

The electronic orbital hybridization in carbon nanotubes surface has been a topic of intense investigation ever since its discovery in 1991.[1,2] In graphite, a 2s electron hybridizes with two 2p electrons, forming three sp^2 orbitals at 120° relative to each other in an orbital plane, and one other orbital having $2p_z$ configuration at 90° relative to this plane. The sp^2 orbitals form the strong σ bonds between carbon atoms in the graphite planes, while the p_z or π orbitals provide the weak van der Waals bonds between the carbon atoms in these planes. For graphite the overlap of π orbitals on adjacent atoms in a given plane provides an electron bond network which gives a higher conductivity. The bonding in carbon nanoparticles and nanotubes is primarily of sp^2, although it may have some sp^3 characters in regions of high curvatures,[3] The π orbitals are no longer orthogonal to the surface when the graphite sheet rolls into carbon nanotubes, leading to significant rehybridization between π orbitals and σ bonds. It is difficult to predict the effect of curvature on the electronic properties because it determines the exact electronic wavefunctions expressed analytically in the curved graphite sheet. So far the π orbitals have been assumed to be orthogonal to the tubes surface,[4,5] which, of course, is overly simplified. The early studies have assumed that this kind of rehybridization can be neglected for most nanotubes. However, recently, one has found that this rehybridized plays an important role even at intermediate radii. Reich *et al*[6] have studied the electronic dispersion in chiral and achiral isolated nanotubes and bundles.The curvature of nanotube wall not only reduces the band gap of the tubes due to hybridization, but also changes the energies of the electronic states which are responsible for transitions in the visible energy range. Even for nanotubes with larger diameters (1–1.5 nm), a shift of the energy levels of ≈100 meV is obtained from their *ab initio* calculations.When tubes are bundled into ropes, the energy gap further decrease. Using first-principles total-energy pseudopotential calculations, Rubio *et al*[7] have studied the properties of chains of potassium and found the hybridization (for multivalent metal atoms) can result in its smaller cohesive energy. A series of researches of curvature effects of carbon nanotubes (CNTs) have been published recently.[8−13]

The degree of hybridization of carbon atoms can be expressed as $sp^{2+\eta}$ and $s^{\tau}p$, where 'η' and 'τ' are fractional numbers ($0 < \eta, \tau < 1$) for fullerenes and CNTs respectively.[14] The hybridization of electronic orbitals of carbon results from the curvature of the carbon skeleton due to strain in CNTs.[15] The rehybridization of electronic orbitals in CNTs contains tilting angles of the π orbital, the electrons wavefunctions

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of π orbital and σ orbital, degrees of hybridization, etc. In this paper, we obtain analytical formulas of tilting angle of π orbital relative to tube surface, electrons wavefunctions of π orbital and σ orbital, degrees of hybridization, separately, as well as numerical results.

2. Analytical formulas of tilting angle, wavefunctions and degree of hybridization

2.1. Tilting angle

It is convenient to discuss the curvature effects and the orbital rehybridization by using a chirality dependent coordinate system. The axis of the chirality dependent coordinate system consists of the line connecting the $(0,0)$ and the (n,m) carbon atoms $(\widehat{c})$, and its perpendicular line $(\widehat{t})$ (see Fig.1).[16]

The fixed and chirality dependent coordinate system are related by

$$\widehat{c} = \cos\theta\widehat{x} - \sin\theta\widehat{y}, \tag{1a}$$

$$\widehat{t} = \sin\theta\widehat{x} + \cos\theta\widehat{y}. \tag{1b}$$

where $\sin\theta = (n-m)/2c'_{\rm h}$, and $\cos\theta = \sqrt{3}(n+m)/2c'_{\rm h}$, with $c'_{\rm h} = \sqrt{n^2+m^2+mn}$ being the circumference of the tube in units of the equilibrium lattice vector length, and $|\boldsymbol{a}_1| = |\boldsymbol{a}_2| = a$ being the length of the lattice unit vector ($a = 0.246\,\text{nm}$).

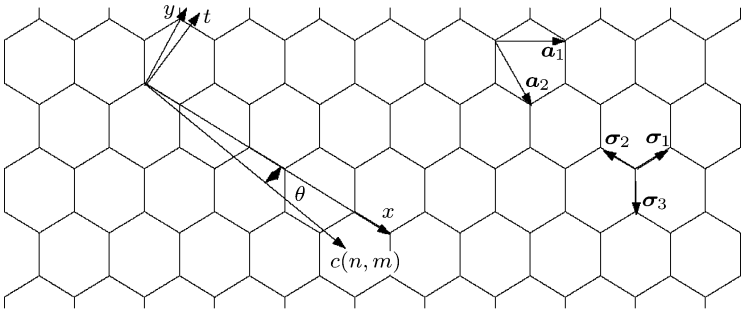


Fig.1. The fixed (x, y) and chirality dependent $(\widehat{c}, \widehat{t})$ coordinates, where $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$ and $\boldsymbol{\sigma}_3$ correspond to bonds 1, 2, and 3, respectively and $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the lattice vectors of the two-dimensional sheet.

Let $\boldsymbol{R}_1 = \boldsymbol{\sigma}_1$, $\boldsymbol{R}_2 = \boldsymbol{\sigma}_2$, $\boldsymbol{R}_3 = \boldsymbol{\sigma}_3$, the bond vectors will be given by

$$\boldsymbol{R}_1 = \frac{a}{2c'_{\rm h}}\left[(n+m)\hat{c} + \frac{1}{\sqrt{3}}(n-m)\hat{t}\right], \tag{2a}$$

$$\boldsymbol{R}_2 = \frac{a}{2c'_{\rm h}}\left[-m\hat{c} + \frac{1}{\sqrt{3}}(n+2m)\hat{t}\right], \tag{2b}$$

$$\boldsymbol{R}_3 = \frac{a}{2c'_{\rm h}}\left[-n\hat{c} - \frac{1}{\sqrt{3}}(2n+m)\hat{t}\right]. \tag{2c}$$

In graphite, the corresponding hybridized orbitals $|\sigma_i\rangle$ are listed as follows:[4]

$$\begin{aligned}\left|\sigma_1^0\right\rangle =& \sqrt{1/3}\,|s\rangle + \sqrt{2/3}(\cos 0^\circ\,|p_x\rangle \\ &+ \sin 0^\circ\,|p_y\rangle\,,\end{aligned} \tag{3a}$$

$$\begin{aligned}\left|\sigma_2^0\right\rangle =& \sqrt{1/3}\,|s\rangle + \sqrt{2/3}(\cos 120^\circ\,|p_x\rangle \\ &+ \sin 120^\circ\,|p_y\rangle\,,\end{aligned} \tag{3b}$$

$$\begin{aligned}\left|\sigma_3^0\right\rangle =& \sqrt{1/3}\,|s\rangle + \sqrt{2/3}(\cos 240^\circ\,|p_x\rangle \\ &+ \sin 240^\circ\,|p_y\rangle\,,\end{aligned} \tag{3c}$$

and

$$\left|\pi^0\right\rangle = |\mathrm{p}_z\rangle\,. \tag{3d}$$

where $\beta(\beta = 0^\circ, 120^\circ, 240^\circ)$ are the angles of the σ bonds relative to the x-axis direction, and the z-direction is perpendicular to the graphite surface.

Let $|s\rangle$ represent the atomic s-orbital, and $|t\rangle$, $|c\rangle$ and $|z\rangle$ denote the p orbitals along the translational, circumferential and normal directions on a nanotube, respectively, then from expressions (3a)–(3d), the four atomic wavefunctions will be written as.[1]

$$\begin{aligned}\left|\sigma_i^0\right\rangle =& \sqrt{1/3}\,|s\rangle + \sqrt{2/3}(\cos\beta_i\,|t\rangle + \sin\beta_i\,|c\rangle\,, \\ & i = 1,2,3,\end{aligned} \tag{4a}$$

and

$$\left|\pi^0\right\rangle = |z\rangle\,, \tag{4b}$$

where β_i is the angle of the σ bonds relative to the circumferential direction.

Let h_i represent the vertical distance of $\boldsymbol{R}_i$ projecting on the circumferential section, When the

graphite sheet rolls into a nanotube and the central angle of $\boldsymbol{R}_i$ projection on the circumferential section is denoted by ω_i in arc, we can obtain

$$h_1 = |\boldsymbol{R}_1| \sin\theta = \pi d \sin\theta / \sqrt{3} c'_{\mathrm{h}}, \tag{5a}$$

$$h_2 = |\boldsymbol{R}_2| \sin\left(\frac{\pi}{3} - \theta\right) = \pi d \sin\left(\frac{\pi}{3} - \theta\right) / \sqrt{3} c'_{\mathrm{h}}, \tag{5b}$$

and

$$h_3 = |\boldsymbol{R}_3| \sin\left(\frac{\pi}{3} + \theta\right) = \pi d \sin\left(\frac{\pi}{3} + \theta\right) / \sqrt{3} c'_{\mathrm{h}}, \tag{5c}$$

where d is the diameter of the CNTs, and

$$\omega_1 = 2\pi |\boldsymbol{R}_1| \cos\theta / c_{\mathrm{h}} = 2\pi \cos\theta / \sqrt{3} c'_{\mathrm{h}}, \tag{6a}$$

$$\omega_2 = 2\pi |\boldsymbol{R}_2| \cos\left(\frac{\pi}{3} - \theta\right) / c_{\mathrm{h}} = 2\pi \cos\left(\frac{\pi}{3} - \theta\right) / \sqrt{3} c'_{\mathrm{h}}, \tag{6b}$$

and

$$\omega_3 = 2\pi |\boldsymbol{R}_3| \cos\left(\frac{\pi}{3} + \theta\right) / c_{\mathrm{h}} = 2\pi \cos\left(\frac{\pi}{3} + \theta\right) / \sqrt{3} c'_{\mathrm{h}}. \tag{6c}$$

Let μ denote the angle included between two vectors, the $\cos\mu$ will be given by

$$\cos\mu = \cos\gamma_{11} \cdot \cos\rho_{21} + \cos\gamma_{12} \cdot \cos\rho_{22} + \cos\gamma_{13} \cdot \cos\rho_{23}, \tag{7}$$

where the γ_{11} represents the angle included between the vector $\boldsymbol{A}$ and the x-axis and the others have similar meanings. Let δ denote the tilting angle of π orbital relative to the tube surface, and suppose that the angles between the π orbital and each of the σ bonds are equal due to symmetry, then from expressions (2), (5), (6) and (7), we will obtain

$$\tan\delta = \sin^2\frac{\pi}{2n} \Big/ \left(\frac{\sqrt{3}\pi}{6n} + \sqrt{\frac{\pi^2}{12n^2} + \sin^2\frac{\pi}{2n}}\right), \quad \text{(zigzag)} \tag{8a}$$

$$\tan\delta = \frac{\tan\dfrac{\pi}{3n}\left(2D - \tan\dfrac{\pi}{6n}\right)}{2D + \tan\dfrac{\pi}{3n}}, \quad \text{(armchair)} \tag{8b}$$

and

$$\tan\delta = \frac{N\sin\omega - \sin^2\dfrac{\omega}{2}}{N\cos\omega + \dfrac{1}{2}\sin\omega}, \quad \text{(chiral)} \tag{8c}$$

where

$$D = \sqrt{\frac{\pi^2}{12n^2} + \sin^2\frac{\pi}{6n}},$$

$$N = \sqrt{\frac{\pi^2(n+2m)^2}{12(n^2+m^2+mn)^2} + \sin^2\frac{\pi n}{2(n^2+m^2+mn)}},$$

and

$$\omega = \frac{\pi n}{c'^2_{\mathrm{h}}}.$$

2.2. Wavefunctions

When the graphite sheet rolls into a nanotube, the three σ-bonds do not lie in the same plane any more, the hybridization of the σ-bonds is therefore changed as follows:

$$|\sigma_i\rangle = s_i |s\rangle + \sqrt{1 - s_i^2}\left(\sin\beta_i |t\rangle + \cos\frac{\omega_i}{2}\cos\beta_i |c\rangle - \sin\frac{\omega_i}{2}\cos\beta_i |z\rangle\right), \quad i = 1, 2, 3, \tag{9}$$

where the mixing parameter s_i (approximately, $s_i = \sqrt{1/3}$) can be determined by the three orthonormality conditions $\langle\sigma_i|\sigma_j\rangle = \delta_{ij}$. The hybridized π orbital can now be calculated in terms of the local basis of atomic orbitals by using the orthonormality conditions,

$$\langle\pi|\sigma_i\rangle = 0. \tag{10}$$

From expressions (5), (6) and (9), we obtain

$$|\sigma_i\rangle = s_i |s\rangle + \sqrt{1 - s_i^2}\left[\left(h_i / E_i d\,|t\rangle \pm (\sin\omega_i / 2E_i)\,|c\rangle - \left(\sin^2\frac{\omega_i}{2} / E_i\right)|z\rangle\right], \quad i = 1, 2, 3, \tag{11}$$

where $E_i = \sqrt{(h_i/d)^2 + \sin^2(\omega_i/2)}$, in expressions (11), (12d), (13d) and (14d), the "$\pm$" signs refer to σ bonds $\boldsymbol{R}_1$ and $\boldsymbol{R}_2(\boldsymbol{R}_3)$, since their projections on the circumferential along the c axis point to the opposite directions. From expression (11), for different types of CNTs, the corresponding solutions are different from each other. For zigzag CNTs, it can be written as follows:

$$|\sigma_1\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[\left(\frac{\sqrt{3}\pi}{6n} / M\right)|t\rangle + \left(\sin\frac{\pi}{n} / 2M\right)|c\rangle - \left(\sin^2\frac{\pi}{2n} / M\right)|z\rangle\right], \tag{12a}$$

$$|\sigma_2\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[\left(\frac{\sqrt{3}\pi}{6n}/M\right)|t\rangle - \left(\sin\frac{\pi}{n}/2M\right)|c\rangle - \left(\sin^2\frac{\pi}{2n}/M\right)|z\rangle\right], \tag{12b}$$

and

$$|\sigma_3\rangle = \sqrt{1/3}\,|s\rangle - \sqrt{2/3}\,|t\rangle, \tag{12c}$$

where $M = \sqrt{\pi^2/12n^2 + \sin^2(\pi/2n)}$. Owing to symmetry, the π orbitals must tilt with respect to the t axis in the $t-z$ plane and the angle included between π orbital and $z$axis is δ. Taking the orthonormality conditions of $|\pi\rangle$, expression (10), into account, we obtain,

$$|\pi\rangle = (\sqrt{2}\sin\delta/\sqrt{1+2\sin^2\delta})\,|s\rangle + 1/\sqrt{1+2\sin^2\delta}(\cos\delta\,|z\rangle \pm \sin\delta\,|t\rangle). \tag{12d}$$

For armchair CNTs, we have

$$|\sigma_1\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[\cos\frac{\pi}{3n}\,|c\rangle - \sin\frac{\pi}{3n}\,|z\rangle\right], \tag{13a}$$

$$|\sigma_2\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[\left(\frac{\pi}{2\sqrt{3}n}/D\right)|t\rangle - \left(\sin\frac{\pi}{3n}/2D\right)|c\rangle - \left(\sin^2\frac{\pi}{6n}/D\right)|z\rangle\right], \tag{13b}$$

and

$$|\sigma_3\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[-\left(\frac{\pi}{2\sqrt{3}n}/D\right)|t\rangle - \left(\sin\frac{\pi}{3n}/2D\right)|c\rangle - \left(\sin^2\frac{\pi}{6n}/D\right)|z\rangle\right], \tag{13c}$$

where $D = \sqrt{\pi^2/12n^2 + \sin^2(\pi/6n)}$. Owing to symmetry, the π orbital must tilt with respect to the c axis in the $c-z$ plane and the angular included between π orbital and z axis is δ. Take the orthonormality conditions of $|\pi\rangle$, expression (10), into account, then the $|\pi\rangle$ will be given by

$$|\pi\rangle = \frac{\sqrt{2}\sin|\delta-\pi/3n|}{\sqrt{1+2\sin^2(\delta-\pi/3n)}}\,|s\rangle - \frac{1}{\sqrt{1+2\sin^2(\delta-\pi/3n)}}(\cos\delta\,|z\rangle \pm \sin\delta\,|c\rangle). \tag{13d}$$

Similarly, for chiral CNTs, we obtain

$$|\sigma_1\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[(h_1/E_{1\mathrm{d}}\,|t\rangle + (\sin\omega_1/2E_1)\,|c\rangle - \left(\sin^2\frac{\omega_1}{2}/E_1\right)|z\rangle\right], \tag{14a}$$

$$|\sigma_2\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[(h_2/E_{2\mathrm{d}}\,|t\rangle - (\sin\omega_2/2E_2)\,|c\rangle - \left(\sin^2\frac{\omega_2}{2}/E_2\right)|z\rangle\right], \tag{14b}$$

$$|\sigma_3\rangle = \sqrt{1/3}\,|s\rangle + \sqrt{2/3}\left[(h_3/E_{3\mathrm{d}}\,|t\rangle - (\sin\omega_3/2E_3)\,|c\rangle - \left(\sin^2\frac{\omega_3}{2}/E_3\right)|z\rangle\right], \tag{14c}$$

and

$$|\pi\rangle \approx \sqrt{2}\lambda/\sqrt{1+2\lambda^2}\,|s\rangle + 1/\sqrt{1+2\lambda^2}(\cos\delta\,|z\rangle \pm \sin\delta\sin3\theta\,|t\rangle \pm \sin\delta\cos3\theta\,|c\rangle), \tag{14d}$$

where $\lambda = \sin\delta\left[\cos2\theta - (\pi/\sqrt{3}c_{\mathrm{h}}')\cos^2\theta c\tan\delta\right]$.

2.3. Degree of hybridization

Assume $\mathrm{sp}^{2+\eta}$ to represent the degree of hybridization of carbon atoms, and the η to denote the π orbital components which are contained in three σ bonds, then from the above discussion, the η will be written as

$$\eta = \frac{(2+c_1^2)}{3}\left[\left(\sin^2\frac{\omega_1}{2}/E_1\right)^2 + \left(\sin^2\frac{\omega_2}{2}/E_2\right)^2 + \left(\sin^2\frac{\omega_3}{2}/E_3\right)^2\right]. \tag{15}$$

From expression (15), the analytical formulas of η for zigzag, armchair and chiral CNTs, are respectively expressed as

$$\eta_1 = \frac{4(1+3\sin^2\delta)}{3(1+2\sin^2\delta)}\left[\sin^4\frac{\pi}{2n}\Big/\left(\frac{\pi^2}{12n^2} + \sin^2\frac{\pi}{2n}\right)\right], \tag{16a}$$

$$\eta_2 = \frac{2(1+3\sin^2(\delta-\pi/3n))}{3(1+2\sin^2(\delta-\pi/3n))}\left[\sin^2\frac{\pi}{3n} + 2\sin^4\frac{\pi}{6n}\Big/\left(\frac{\pi^2}{12n^2} + \sin^2\frac{\pi}{6n}\right)\right], \tag{16b}$$

and

$$\eta_3 = \frac{2(1+3\lambda^2)}{3(1+2\lambda^2)}\left[\sin^4\frac{\pi(n+m)}{f}\Big/\left(\frac{\pi^2(n-m)^2}{3f^2}+\sin^2\frac{\pi(n+m)}{f}\right)\right.$$
$$+\sin^4\frac{\pi n}{f}\Big/\left(\frac{\pi^2(n+2m)^2}{3f^2}+\sin^2\frac{\pi n}{f}\right)$$
$$\left.+\sin^4\frac{\pi m}{f}\Big/\left(\frac{\pi^2(2n+m)^2}{3f^2}+\sin^2\frac{\pi m}{f}\right)\right], \tag{16c}$$

where $f = 2(n^2+m^2+mn)$. Their corresponding numerical calculations are collected in Table 1.

Table 1. Numerical calculations of Degree of hybridization.

zigzag			armchair		chiral			
n	d	η_1	d	η_2	n	m	d	η_3
1	0.07926	0.82200	0.13728	0.65695	2	1	0.2097	0.26845
2	0.15852	0.52114	0.27456	0.20034	4	3	0.48212	0.05447
3	0.23778	0.25978	0.41184	0.09052	6	5	0.75608	0.02225
5	0.39630	0.09741	0.68640	0.03280	8	7	1.03037	0.01199
7	0.55481	0.05008	0.96067	0.01676	10	9	1.30480	0.00748
8	0.63407	0.03840	1.09825	0.01284	20	19	2.67727	0.00178
10	0.79259	0.02462	1.37281	0.00822	30	29	4.05000	0.00077
20	1.58518	0.00617	2.74562	0.00206	40	39	5.42274	0.00043
30	2.37778	0.00274	4.11843	0.00091	50	49	6.79552	0.00028
40	3.17037	0.00154	5.49124	0.00051	60	59	8.16831	0.00019
50	3.96296	0.00099	6.86405	0.00033	70	69	9.54111	0.00014
60	4.75550	0.00069	8.23685	0.00023	90	89	12.28670	8.44E-05

Suppose that the mode of hybridization of π orbital can be expressed as $s^\tau p$, where τ denotes the s-orbital components which are contained in the π bond, then from expression (12d), (13d) and (14d) the values of τ corresponding to zigzag, armchair and chiral CNTs will be given respectively by

$$\tau_1 = 2\sin^2\delta/(1+2\sin^2\delta), \tag{17a}$$
$$\tau_2 = 2\sin^2(\delta-\pi/3n)/(1+2\sin^2(\delta-\pi/3n)), \tag{17b}$$
$$\tau_3 = 2\lambda^2/(1+2\lambda^2). \tag{17c}$$

Their results of numerical calculation are given in Table 2.

Table 2. Numerical calculations of $s^\tau p$ hybridization.

zigzag			armchair		chiral			
n	d	τ_1	d	τ_2	n	m	d	τ_3
1	0.07926	0.24711	0.13728	0.274353	2	1	0.20970	0.11197
3	0.23778	0.12840	0.41184	0.058261	4	3	0.48212	0.03705
5	0.39630	0.05724	0.68640	0.021578	6	5	0.75608	0.01643
7	0.55481	0.03120	0.96097	0.011097	8	7	1.03037	0.00914
9	0.71333	0.01942	1.23553	0.006735	10	9	1.30477	0.00579
10	0.79259	0.01586	1.37281	0.005461	20	19	2.67727	0.00141
20	1.58518	0.00408	2.74562	0.001369	30	29	4.0499	0.00062
30	2.37776	0.00182	4.11843	0.000609	40	40	5.49124	0.00034
40	3.17037	0.00103	5.49124	0.000343	50	49	6.7955	0.00022
50	3.96296	0.00066	6.86405	0.000219	60	59	8.16831	0.00015
60	4.75555	0.00046	8.23685	0.000152	70	69	9.54111	0.00011

3. Discussion

The relations between the tilting angles of the π orbitals and the chiral indices (n, m) of CNTs, and the analytical formulas of the tilting angles of π orbitals relative to the tubes surface of zigzag, armchair and chiral CNTs have been obtained, respectively. Numerical calculations of the tilting angles of the π orbitals for different chiral indices are collected in Table 3. From Table 3, it follows that the tilting angles of the π orbitals gradually become unanimous with the indices (n, m) increasing. For zigzag, armchair and chiral CNTs, when $n = 69$, $n = 40$ and $n = m = 40$, the corresponding tilting angles of the π orbitals are $0.7529°$, $0.7501°$, $0.7501°$, respectively, showing that the tilting angles of the π orbitals for different CNTs relative to the tubes surface are equal to each other in a high accuracy. In fact, when $n, m \gg 1$, than $\tan\delta \approx \delta$, $\sin(\pi/2n) \approx \pi/2n$, and $\cos(\pi/3n) \approx 1$. From expression (8), the δ can be written as follows:

$$\delta \approx \pi/2\sqrt{3}n, \quad \text{(zigzag)} \tag{18a}$$

$$\delta \approx \pi/6n, \quad \text{(armchair)} \tag{18b}$$

$$\delta \approx \pi/2\sqrt{3(n^2+m^2+mn)}, \quad \text{(chiral)}. \tag{18c}$$

Notice that $\pi d = na$ (zigzag), $\pi d = \sqrt{3}na$ (armchair), and $\pi d = a\sqrt{n^2+m^2+nm}$ (chiral), then for the different CNTs, the tilting angles of the π orbitals will be given as

$$\delta = a/2\sqrt{3}d. \tag{19}$$

The results of numerical calculation are listed in Table 3.

Table 3. Numerical calculations of tilting angles of π orbital.

zigzag			armchair		chiral			
n	$\tan\delta$	$\delta/(°)$	$\tan\delta$	$\delta/(°)$	n	m	$\tan\delta$	$\delta/(°)$
3	0.2820	15.7475	0.1787	10.1297	4	3	0.1579	8.9724
4	0.2181	12.3024	0.1326	7.5542	6	5	0.0983	5.6152
5	0.1769	10.0338	0.1056	6.0276	10	9	0.0561	3.2120
10	0.0901	5.1502	0.0525	3.0034	16	15	0.0342	1.9559
25	0.0362	2.0755	0.0210	1.2002	30	29	0.0179	1.0226
35	0.0259	1.4835	0.0150	0.8572	38	37	0.0140	0.8035
40	0.0227	1.2983	0.0131	0.7501	40	40	0.0131	0.7501
50	0.0181	1.03886	0.0105	0.6001	50	49	0.0106	0.6081
60	0.0151	0.86581	0.0087	0.5001	70	69	0.0076	0.4327
69	0.0131	0.7529	0.0076	0.4348	98	97	0.0054	0.3082

The degree of hybridization of orbitals is described by the π orbital components which are contained in three σ bonds and the s-orbital components which are contained in the π bond. Owing to the approximation, the values of η_i and τ_i in expressions (16) and (17) slightly deviate from their real values. Originally, the deviations are mainly due to the granted $s_i = \sqrt{1/3}$ in expressions (9) and (11). We analyse the deviations of zigzag CNTs in the following. For zigzag CNTs, the π orbitals must tilt with respect to the t axis in the $t - z$ plane and the angle included between the π orbital and the z axis is δ. Suppose that the $|\pi\rangle$ can be expressed as

$$|\pi\rangle = c_1|s\rangle + c_2(\cos\delta|z\rangle + \sin\delta|t\rangle), \tag{20}$$

then from Eq.(13), $|\sigma_3\rangle$ will be expressed as

$$|\sigma_3\rangle = \sqrt{\frac{1-c_1^2}{3}}|s\rangle - \sqrt{\frac{2+c_1^2}{3}}|t\rangle. \tag{21}$$

From $\langle\pi|\sigma_3\rangle = 0$, we can obtain

$$c_1\sqrt{\frac{1-c_1^2}{3}} - c_2\sqrt{\frac{2+c_1^2}{3}}\sin\delta = 0,$$

and

$$c_1 = c_2\sqrt{(2+c_1^2)/(1-c_1^2)}\sin\delta. \tag{22}$$

In order to obtain expression (12d), we have assumed that $c_1^2 \ll 1$, thereby obtained $c_1 = \sqrt{2}c_2\sin\delta$, i.e. $c_1 = \sqrt{2}\sin\delta/\sqrt{1+2\sin^2\delta}$, where $c_2 = 1/\sqrt{1+2\sin^2\delta}$, if we did not assume that $c_1^2 \ll 1$, thereby the value of c_2 does not change as a function, $c_2 = 1/\sqrt{1+2\sin^2\delta}$. And then from expression (22), we have

$$c_1' = \sin\delta\sqrt{(2+c_1^2)/(1-c_1^2)}/\sqrt{1+2\sin^2\delta},$$

and

$$c'^2_1/c^2_1 = (1 + c^2_1/2)/(1 - c^2_1) \geq 1. \qquad (23)$$

The results are listed in Table 4. It can be discussed similarly for armchair and chiral CNTs.

Table 4. Numerical calculations of deviation for degree of hybridization.

n	1	3	4	5	7	10	50
c'^2_1/c^2_1	1.49233	1.22097	1.13619	1.09107	1.04831	1.02418	1.00099

4. Conclusion

(1) The δ is descending with the chiral indices and the diameters of CNTs increasing, along with the chiral indices, and the reverse is equally true. The tilting angle of the π orbital gradually reduces, when $n, m \gg 1$, for various CNTs, their values of δ can become unanimous, that is, $\delta = a/2\sqrt{3}d$.

(2) The rehybridization of orbitals depends on the chiral indices and diameters of CNTs. From expressions (12d), (13d) and (14d), the wavefunction of the π orbital contains not only components of σ bonds,but also components of s orbitals, which is the primary feature in rehybridization of orbitals of CNTs.

(3) The degree of hybridization of orbitals is described by components contained in three σ bonds and the s-orbital components contained in the π orbitals, and it varies with the chiral indices and diameters of CNTs.

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