Symmetries and fuzzy symmetries of Carbon nanotubes

**Xuezhuang Zhao · Jianxia Cui · Zucheng Li ·
Zhenfeng Shang · Xiufang Xu · Shengkai Xing ·
Guichang Wang · Ruifang Li**

Abstract Carbon nanotubes (CNTs) possess the fuzzy cylinder group characteristic. Comparing with the linear and planer molecules, there are included the fuzzy symmetry of the cylinder screw rotation (CSR) in relation to some higher (>2) fold rotation axis. The CSR may be noted as the product of translation (T) and rotation (C). The CSR symmetry will be imperfect owing to the introduction of T. As the extent of whole translation is more than 10-fold than every time, the membership function of CNT in relation to CSR will be more than about 0.9, and such CNT may be seems as provided with the perfect CSR symmetry. For analyse the CNT we may using the cylindrical orthogonal curvilinear coordinate system. The MO ought to be provided with a pure irreducible representation, but the component of symmetry adapted atomic orbital (SA-AO) set may be not sole, and it is difficult to get and analyse the 'pure' π-MO. There are some various AO (1S-, 2S-, 2Pz-, 2Pr-, 2Pt of carbon and 1S- for hydrogen)-set components in a certain MO. For the CNT with the same diameter and different length, the MO energy and the SA-AO component versus the relative serial number will be with the similar distribution. The MOs of CNT with higher fold C symmetry may be provided with two-dimensional irreducible representation. For the molecular skeleton and the MO which belong to one-dimensional irreduable representation, their membership functions in relation to the CSR with the product of the same T and different C would be equality. However, for the single MO which belong

X. Zhao (✉) · Z. Shang · X. Xu · S. Xing · G. Wang · R. Li
College of Chemistry, Nankai University, 300071 Tianjin, China
e-mail: zhaoxzh@nankai.edu.cn

J. Cui
Bio Circuits Institute, University of California at San Diego, La Jolla, CA 92093, USA

Z. Li
Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada

to two-dimensional irreducible representation that may be somewhat difference. The torus carbon nanotube (TCNT) may be provided the symmetry with the torus group and torus screw rotation (TSR), such symmetry would be or near be not rare in nature. Similar as the planer rectangle (called as the MH rectangle) may composed the Hückel- or Möbius-strip band, the more MH rectangles in the cylinder CNT may be composed the more Hückel- or Möbius-strip bands, such strip bands set may be called strip tube, meanwhile the fuzzy CSR symmetry will be transform to the perfect TSR symmetry. The intersecting line (Z-axis) of the MH rectangles will be transform to the common basic circle of these strip bands. When the CNT to form a TCNT, as one of the MH rectangle form a Hückel-strip band or an $n(t)$-twisted Möbius-strip band itself, the other MH rectangle will be form the strip band with the same topological structure synchronously, and the set of these strip bands may be called the strip tube. The boundary closed curves of the strip band may reflect the torus group symmetrical characteristic of the relative strip bands. The closed curve may correspond to a cyclical group or subgroup. The number of carbon atomic pairs on the closed curve denoted the order of such group or subgroup. As the CNT to form the TCNT, it is different as the single MH rectangle, they may be to form the fractal-twisted Möbius-strip tube synchronously, in which the single Möbius-strip band may be formed from more one MH rectangle, however, single MH rectangle may enter into only one Möbius-strip band. As the hetero-CNT with the helical-structure distribution, such hetero-CNT may form the relative torus hetero-CNT, but according to the continuity of CNT tube side, a certain twisted to form Möbius-strip tube may often be required. There is some interaction between the distributional helical-structure and twisting way, such interaction may touch to the degree of tightness of the helical-structure distribution in torus hetero-CNT.

1 Introduction

Carbon nanotubes (CNT) is discovered by the Japanese physicist Iijima of NEC lab, Tsukuba in 1991, by using the higher resolution transmission electron microscope [1]. CNT is formed by folding the multilayer homocentric graphite, may be called multi-walled carbon nanotube. And then, in 1993, Iijima et al. discover the single-walled carbon nanotube (SWCNT) [2]. Owing to the novel structure and the special physical and chemical property of CNT, there is very interesting for extended researchers. About the structure, the CNT is a tubular molecule of carbon, connected each other through the hybrid σ bonding to form the cellular skeleton, and the conjugate π-electron cloud through the whole carbon nanotube. In nature, the CNT possess the fine electrical conductivity and higher mechanical strength [3]. In the fields of materials chemistry, store hydrogen and theoretical chemistry, there are a lot of theses and review being

reported [4–25]. However, we are more interesting in the characteristic of geometric structure, symmetry and fuzzy symmetry.

As regards the relationship between the structure and the symmetry of carbon nanotube (CNT), there are some research reports on CNT by means of the symmetry group theory. For the cylinder carbon nanotube there are some more studies. It is indicated that there is intimate relationship between symmetry of CNT and both their Raman and IR spectrum [26–29]. The point group which the finitude achiral zigzag and armchair single-walled CNT belong to ought to be the point group D_{Nh} or D_{Nd}, where N denoted the highest fold of the relative rotation axis [30,31]. Considering with the fuzzy symmetry, such molecules will be provided with the fuzzy cylinder group (or set) symmetry. These molecules may be provided with the fuzzy space symmetry transformation: one-dimensional period translation and relative screw rotation and glide reflection. We had probe some fuzzy cylindrical group and layer group symmetry molecules [32–36], but they usual are linear or plane, the relative screw rotation will be not higher than twofold. However, the higher fold screw rotation symmetry may be important for some molecular system (e.g. DNA), we ought to analyse them. As for the torus carbon nanotube (TCNT), after entering the new millennium, there are some more attention of men [37–44]. Although these papers refer to molecular design and some other theoretical side, considering the relationship between the special symmetrical characteristic (refer to the torus group symmetry [45,46]) and some important molecular characteristic (e.g. The DNA topology), in this paper we will make some analyse on such symmetry of TCNT provide for future further research.

2 Cylinder carbon nanotuble

Now we discuss the ordinary straight cylinder single-walled carbon nanotube (SWCNT), such SWCNT may be seen as the graphene can be curled to form a cylinder and the hydrogen atoms are omitted as condensation and bonding the adjacent carbon atoms. The Fig. 1a denote the graphene molecule, for concise the hydrogen atoms are omitted, where the carbon atoms may get the serial numbers according to the m- and n-directions and a certain carbon atom may be denoted as $C(m, n)$, in which the value ranges of m and n are [1, M] and [1, N], respectively. In this figure, the M and N are respective 17 and 8. As the carbon atoms $C(1, n)$ and $C(M, n)$ in left- and right-side with the same serial number n are overlap and cohere to form the zigzag single-walled carbon nanotube (ZSWCNT) it is shown in Fig. 1b, and the carbon atoms $C(m, 1)$ and $C(m, N)$ in up- and down-side with the same serial number m bonding to form the armchair single-walled carbon nanotube (ASWCNT) it is shown in Fig. 1c. As above-mentioned carbon atoms are some mismatched (the serial number m or n may be differ with a certain value) it will be formed the chiral SWCNT. But we will not analyse such SWCNT in this paper.

As shown in Fig. 1, the carbon atoms in same row with the identical n are linked together with the oblique bonds, and the carbons in same column with the identical m are linked together with the non-oblique bonds, ZSWCNT with the vertical bonds and ASWCNT with horizontal bonds. It will be affect some fuzzy symmetric characteristics of such two kinds of SWCNT.
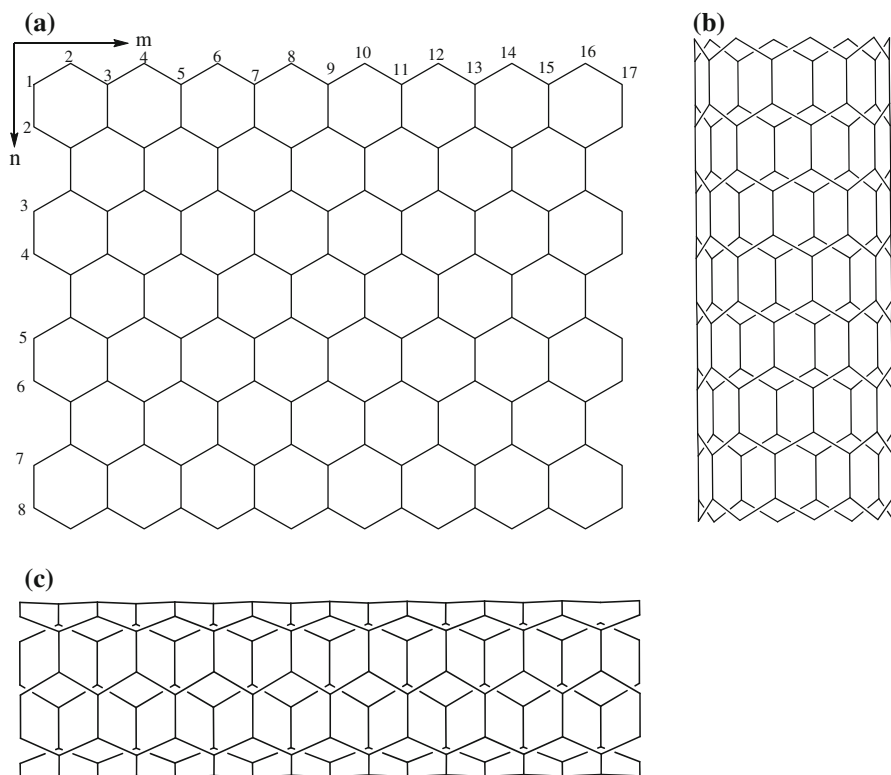
Fig. 1 The graphene molecule (**a**) curl to form the Zigzag carbon nanotube (ZSWCNT) (**b**) and Armchair carbon nanotube (ASWCNT) (**c**)

2.1 Symmetry and fuzzy symmetry of SWCNT molecular skeleton

Along to the central axis of SWCNT, there often is an r-fold rotation axis C_r, there is usual set as the Z-direction, and by using the cylinder curvilinear coordinate system to analyse. The ZSWCNT shown in Fig. 1b, its $r = 8 = (M - 1)/2$, there is an eightfold rotation axis C_8. The molecule shown in Fig. 1b will be provided with the symmetry of point group D_{rh}, where N must be the even number. Otherwise as N is odd number it will be provided with the symmetry of point group D_{rd}. The D_r is the intersection set and common subgroup of D_{rh} and D_{rd}, meanwhile both D_{rd} and D_{rh} are the subgroup of their union set D_{2rh}. That is to say:

$$D_r \subset D_{rd}, \quad D_r \subset D_{rh}, \quad D_r = D_{rd} \cap D_{rh}. \tag{1a}$$

$$D_{rd} \subset D_{2rh}, \quad D_{rh} \subset D_{2rh}, \quad D_{2rh} = D_{rd} \cup D_{rh}. \tag{1b}$$

Similar as the way in which we analyse the inner rotation process [47], the element (symmetry transformation) in the D_{2rh} may be classified to four subset: G_0, G_1, G_2 and G_3. Where the G_0 are the elements included in both D_{rh} and D_{rd}, simultaneously,

that is the intersection set subgroup D_r. In relation to G_0 for the ZSWCNT with the D_{rh} or D_{rd} symmetry the relative membership function usually equals one. As for G_1 there are the elements included only in D_{rh}, but not in D_{rd}, for the ZSWCNT with the D_{rh} symmetry (even number N) the relative membership function equals one but less one with the D_{rd} (odd number N) and may analyse their fuzzy symmetry only. As for G_2 there are the elements included only in D_{rd}, but not in D_{rh}, for the ZSWCNT with the D_{rd} symmetry (odd number N) the relative membership function equals one but less one with the D_{rh} (even number N) and may analyse their fuzzy symmetry only. However, for G_3 there are the elements not included in neither D_{rd} nor D_{rh}, for the ZSWCNT with the D_{rh} or D_{rd} symmetry (whether the odevity of N) the relative membership function less one and may analyse their fuzzy symmetry only.

As regards the fuzzy space symmetry, the SWCNT may be considered as the fuzzy cylinder group system. The relative symmetry transformation, it will be considered the cylinder screw rotation (CSR) mainly, in especial the higher (>2)-fold CSR. The CSR may be called screw rotation, in brief. The CSR may be considered as the combination of translation and rotation. As the space separation distance of translation will be null, the CSR will be the simple rotation, on the other hand, as the rotation angle equals zero, the CSR will be the simple translation. As shown in Fig. 1b the ZSWCNT (molecular length sufficient), the translation along the CNT centre axis, the period length ought to be the three times of the CC bond length ($3l_{cc}$). there are $2(M-1)$ carbon atoms [$C(m, n)$, where n may be defined as two sequential number and $m = 1, 2, \ldots\ldots, M-1$; note: the $C(1, n)$ and $C(M, n)$ are denoted the identical carbon atom], which are constituted by the $2(M-1)$ carbon atoms in two border row of Fig. 1a. It is noteworthy that the translate length included in CSR may be the integral multiple $1.5l_{cc}$. On the other hand, the minimum variation angle of rotation may be $2\pi/r = 4\pi/(M-1)$, but the rotation angle include in CSR may be the integral multiple $2\pi/(M-1)$. Then the CSR ought to be the combination (product) of above translation $T_n(1.5jl_{cc})$ and rotation $C_n(2\pi i/[M-1])$, where both i and j will be the integral number. For the relative CSR symmetry transformation of the ZSWCNT as shown in Fig. 1b, the i and j ought to be the same odevity, otherwise the relative CSR transformation would not be symmetry one. The transformation (the subscript n for T and C are omitted):

$$\text{CSR}(j, i) = T(1.5jl_{cc}) C(2\pi i/[M-1]) = C(2\pi i/[M-1]) T(1.5jl_{cc}). \quad (2)$$

In which there must be the same odevity of i and j. As the ZSWCNT molecule is finite, for the CSR transformation (2) with the same odevity of the i and j, the fuzzy symmetry of such molecular skeleton may be analysed. The membership function in relation to a certain symmetry transformation G would be [48]:

$$\mu(G) = \left[\sum_{m,n} (Y(m, n) \wedge Y(gm, gn)) \right] \Big/ \left[\sum_{m,n} (Y(m, n)) \right], \quad (3)$$

where the atom with the serial number (m, n) will be transformed to with the (gm, gn) through G. The atomic criteria before and after the transformation G are $Y(m, n)$ and

Y (gm, gn), respectively. For the molecular skeleton, their value may be the relative atomic number. For the ZSWCNT as shown in Fig. 1b, there are $N_C = N(M − 1)$ carbon atoms and $N_H = (M − 1)$ hydrogen atoms included in, the molecular formula would be the $C_{N(M−1)}H_{(M−1)}$. The denominator in Eq. (3) will be the $N(M − 1)Z_C + (M − 1)Z_H = (M − 1)(NZ_C + Z_H)$, where the Z_C and Z_H are the atomic numbers (6 and 1) of carbon and hydrogen, respectively. Considering the membership function in relation to CSR transformation, to start with we examine the simple translation alone the CNT center axis (the Z-direction), that is the i in Eq. (2) ought to be zero, and then the j must be the even number for CSR symmetry transformation. It is easy to get the numerator in Eq. (3) ought to be $(M − 1)[(N − j)Z_C + Z_H]$ and the membership function in relation to the translation $T(1.5jl_{cc})$ with the even number j would be the $[(N − j)Z_C + Z_H]/[NZ_C + Z_H]$. For the rotation $C(2\pi i/[M − 1])$ there is a perfect symmetry transformation with the membership function equal to one. It is easy to prove that in relation to the CSR(i, j) symmetry transformation with the even number j, the membership function of ZSWCNT skeleton:

$$\mu_Z (CSR (j, i)) = [(N − j) Z_C + Z_H] / [NZ_C + Z_H], \tag{4}$$

where the subscript Z follow the μ denoted the ZSWCNT. It is independent on i, yet. As for the odd number j, the i must be also odd and the Eq. (4) will be still right. As we ignore deviation from the Z_H, above Eq. (4) may be come down to $1 − (j/N)$. As the translation range allowed (in connection with N) will be more 10 times of the length for each one translation (in connection with j), the relative membership function will be more than 0.9, the fuzzy space group symmetry may be considered as near perfect. That is agreed as our previous results [32–34].

The ASWCNT (e.g. as shown in Fig. 1c), there is only four $(r = N/2)$-fold rotation axis C_r. It is notable that where the Z-axis direction will be m-axis direction which orthotropic to that of ZSWCNT. Such molecule ought to be provided with the point group D_{rh} symmetry, where M is odd number, as M is even number it would be with the point group D_{rd} symmetry. Therefore we may analyse the relative symmetry and fuzzy symmetry for the ASWCNT similar as for the ZSWCNT. For the ASWCNT the fuzzy symmetry in relation to CSR transformation, there are some special features differ with that for ZSWCNT. For ASWCNT, alone the Z (m-axis)-direction translation one periodic distance is agreement $2\sin 60°l_{CC} = 3^{1/2}l_{CC}$, near for ZSWCNT, alone the Z (n-axis)-direction translation half periodic distance. Included in CSR, the translation length will be the integral multiple of $\sin 60°l_{CC}$, and the rotation angle will be the integral multiple of $2\pi/r = 4\pi/N$. The CSR transformation would be the product of translation $T_m(\sin 60° jl_{cc})$ and rotation $C_m(2\pi i/N)$. Where both i and j are integer and their odevity are the same. Therefore, the CSR transformation (the subscript m for T and C are omitted):

$$CSR (j, i) = T (\sin 60° jl_{cc}) C(2\pi i/N) = C(2\pi i/N)T (\sin 60° jl_{cc}). \tag{5}$$

It is noted that the omitted subscript for T and C are different as Eq. (2). For the ASWCNT with finite length and CSR (5) with same odevity of i and j, we may analyse the relative fuzzy symmetry and get the relative membership function by using the

Eq. (3). For the ASWCNT shown in Fig. 1c, there are $N_C = MN$ carbon atoms and $N_H = 2N$ hydrogen atoms included with the formula $C_{MN}H_{2N}$. The denominator and numerator in Eq. (3) are $MNZ_C + 2NZ_H = N(MZ_C + 2Z_H)$ and $N[(M-j)Z_C + 2Z_H]$, respectively. The relative membership function would be:

$$\mu_A\,(CSR\,(j, i)) = [(M - j)\,Z_C + Z_H]\,/\,[MZ_C + Z_H],\qquad(6)$$

where the subscript A follow the μ is denoted the ASWCNT. As we ignore deviation from the Z_H, above Eq. (6) may be come down to $1 - (j/M)$. As the translation range allowed (in connection with M) will be more 10 times of the length for each one translation (in connection with j), the relative membership function will be more than 0.9, the fuzzy space group symmetry may be considered as near perfect. That is similar as the ZSWCNT.

Now we consider hetero-ZSWCNT, in which some certain carbon atoms of ZSW-CNT are substituted by hetero-atoms according to the helical-structure distribution. In Fig. 1a, the carbon atoms with the serial number $(2, 1), (3, 2), (4, 3), (5, 4)\ldots\ldots$ are replaced by X atoms meanwhile the carbon atoms with the serial number with $(3, 1), (4, 2), (5, 3), (6, 4)\ldots\ldots$ replaced by Y atoms, as shown in Fig. 2a. The heterographene in Fig. 2a curl to form the hetero-ZSWCNT, the substitutive hetero-atom are distributed in the CNT wall according to the helical-structure form. As the paper towards the back the hetero-atoms are the left-hand helical-structure distribution (Fig. 2b), however as the paper forward they are the right-handed helical-structure distribution (Fig. 2c). There is a pair of optical enantiomer.

The CSR transformation (2) include the translation $T_n(1.5\,jl_{cc})$ and the rotation $C_n(2\,\pi\,i\,/[M - 1])$ with the same odevity of i and j. The ZSWCNT in relation to the pure rotation $C_n(2\,\pi\,i\,/[M - 1])$ (with $j = 0$ and $i =$ even number) ought to be provided the perfect symmetry and the relative membership function would be one. The hetero-ZSWCNT shown in Fig. 2b, c which include $N_C = N(M - 1) - 2N$ carbon atoms and $N_H = M - 1$ hydrogen atoms, the numbers of both X and Y atoms are $N = N_X = N_Y$, the relative formula would be $C_{N(M-1)-2N}X_N Y_N H_{M-1}$. Their membership function in relation to pure rotation would be less one. As $j = 0$ and $i = 2$, the membership functions of these two enantiomers:

$$1 > \mu_{Z,l}\,(CSR\,(0, 2)) = \mu_{Z,d}\,(CSR\,(0, 2)) > 0.\qquad(7)$$

Both are less one and the values of $\mu_{Z,l}$ and $\mu_{Z,d}$ equality. However, as the CSR included the translation, they may be unequality. For example, as the $i = j = 1$, the relative membership function:

$$1 > \mu_{Z,l}\,(CSR\,(1, 1)) > \mu_{Z,d}\,(CSR\,(1, 1)) > 0.\qquad(8)$$

Owing to according to CSR(1, 1) transformation, some of hetero-atoms in the hetero-CNT with l-distribution will be transform to the positions of other same hetero-atoms, but without such condition for the hetero-CNT with d-distribution.

By the way, the relative fuzzy symmetry of such hetero-CNT may be used to analyse the biologic molecule, we will do it in near future.
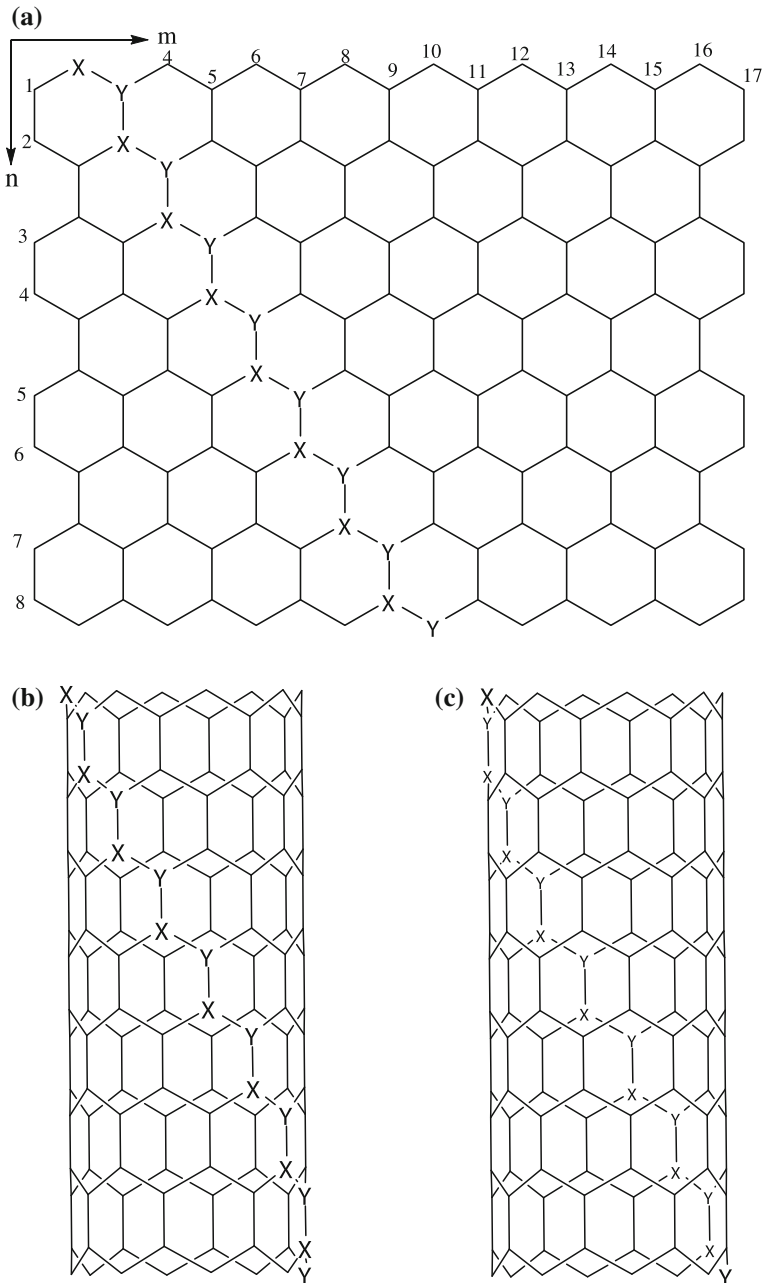
(a)

Fig. 2 The hetero-atom graphene (**a**) curl backward to form the hetero-ZSWCNT (**b**) with the left handed helical structure distribution and curl forward to form the hetero-ZSWCNT (**c**) with the right-handed helical-structure distribution

2.2 Symmetry and fuzzy symmetry of SWCNT molecular orbital

As a molecular skeleton is provided with a certain point group symmetry, the relative molecular orbital (MO) ought to belong a certain irreducible representation of such point group. In this paper we calculate the MOs of some SWCNT at STO-3G/HF level using the Gaussian [49]. Above SWCNT skeleton ought to be the cylinder group symmetry structure and using the cylinder orthogonal curvilinear coordinate system to analyse them more suitable as for the Hückel-cyclacene [45,46]. The Z-axis as same as the central axis of the SWCNT, the (r-, α-) or (X-,Y-) coordinate plane would be through the SWCNT center and orthogonal with the Z-axis. In fact, the Hückel-cyclacene may be consider as the ZSWCNT in Fig. 1b with $N = 2$.

2.2.1 Energy and symmetry characteristic of SWCNT molecular orbital

As the molecular skeleton is provided with the D_{rh} point group symmetry, the relative MO may belong to the irreducible representation:

$$A_{1g}, A_{2g}, B_{1g}, B_{2g}, A_{1u}, A_{2u}, B_{1u}, B_{2u}, E_{1g}, E_{2g}, \ldots \ldots \quad (\text{r:even})$$
$$E_{[(r/2)-1]g}, E_{1u}, E_{2u}, \ldots \ldots E_{[(r/2)-1]u},$$

or

$$A'_1, A'_2, A''_1, A''_2, E'_1, E'_2, \ldots \ldots E'_{[(r-1)/2]}, E''_1, E''_2, \ldots \ldots E''_{[(r-1)/2]}. \quad (\text{r:odd})$$

As the molecular skeleton is provided with the D_{rd} point group symmetry, the relative MO may belong to the irreducible representation:

$$A_1, A_2, B_1, B_2, E_1, E_2, \ldots \ldots E_{(r-1)}, \quad (\text{r:even})$$

or

$$A_{1g}, A_{2g}, A_{1u}, A_{2u}, E_{1g}, E_{2g}, \ldots \ldots E_{[(r-1)/2]g}, E_{1u}, E_{2u}, \ldots \ldots E_{[(r-1)/2]u}. \quad (\text{r:odd})$$

On the other hand, we may divide the atoms and AOs of SWCNT into some atom-set and AO-set. The atom-set may be hydrogen atom-set and carbon atom-set. As for the AO-set, there is only one 1s-AO-set for hydrogen atoms we consider, and five AO-sets for carbon atoms. For carbon atoms, the five AO-sets are the 1s-, 2s-, $2p_z$-, $2p_r$- and $2p_t$-AO-sets, where by means of the cylindrical orthogonal curvilinear coordinates (z, r, α) system, therefore for the 2p-AOs the $2p_Z$-, $2p_Y$- and $2p_X$- are replaced by $2p_z$-, $2p_r$- and $2p_t$ [45,46]. Various AO-sets may compose the SALC-AO-sets with the same irreducible representation, and they may form together the MO further more. Therefore though the MO is provided with a certain pure irreducible representation, but it may be included various SA-AO set component. Consequently, we may get the s-, p_z-, p_r- and p_t-AO set component included in each MO in SWCNT, by means the handling way as for Hückel-cyclacene [45,46].

For the graphene, the π-MO would be constituted by the p-AO set composed from the molecular plane perpendicular direction. Such p-AO set belong to the irreducible representation different diversed that from other AO-set of graphene, therefore irreducible representation which the π-MO of graphene belong to would be pure meanwhile the relative composed AO-set will be 'pure' too. However, the π-MO of SWCNT are formed by the p-AO set which vertical the cylinder surface and such p-AO may be provided with some irreducible representations which may exist in other AO-sets, therefore though the irreducible representation of a certain π-MO is pure, but the component of AO-set may be not only. Then there is difficult to isolate and get the 'pure' π-MO for analyse but we can analyse the virous AO-set components of a certain MO. As for the MO serial number J of the SWCNT, we usual set the $J = 0$ for non-bonding orbital (NBMO) energy level, $J < 0$ for bonding and $J > 0$ for anti-bonding ones. The absolute values of J from small to enlarge, are defined by the energy interval serial order between the MOs and NBMO. For comparing the characteristic of various sized SWCNT, the relative serial number J/Nc will be introduced sometimes, where Nc denoted the number of carbon and hetero-atoms of the CNT wall.

For the MO energy of SWCNT, to start with, we consider four ZSWCNT with the point group D_{6h} symmetry: Z-$C_{48}H_{12}$, Z-$C_{72}H_{12}$, Z-$C_{96}H_{12}$ and Z-$C_{144}H_{12}$, where the Z- denoted the zigzag, and which are follow with the relative formula. These CNTs are corresponding to the $M - 1 = 12$ and N = 4, 6, 8 and 12, respectively in Fig. 1. There are four ZSWCNT molecules with the same pipe diameter (degree of thickness) but virous of length. There are the figures of above four ZSWCNT in relation to the MO energy, E(MO), versus MO serial number J, as shown in Fig. 3a–d, respectively. According to the point group D_{6h}, there are eight irreducible representations may be belonged with these MO, and they will be denoted with various symbol in these figures. It is seems that the relationship of E(MO) versus J would be similar for these ZSWCNT in whole. As we combinate them to form Fig. 3e, such similarity will be more obviously. Using the J/Nc(relative serial number) to replace the J, the relative curves will overlap roughly, as shown in Fig. 3f. There is evident energy gap in J/Nc = 0.5, but it is not much clear in J/Nc = 0.

Now we examine three molecules in relation to ZSWCNT but with the symmetry other than point group D_{6h} : Z-$C_{84}H_{12}$, Z-$C_{144}H_{24}$ and Z-$C_{80}B_8N_8H_{12}$. Where the Z-$C_{84}H_{12}$ is provided the point group D_{6d} symmetry with $M - 1 = 12$ and $N = 7$, the Z-$C_{144}H_{24}$ is provided the point group D_{12h} symmetry with $M - 1 = 24$ and $N = 6$, as for the Z-$C_{80}B_8N_8H_{12}$, there are some carbon atoms of ZSWCNT are substituted by B- or N-atoms as shown the X- and Y- in Fig. 2 to form the hetero-ZSWCNT in which the $M - 1 = 12$ and $N = 8$ but without the point group D_{6h} symmetry. Owing to these molecules are provided with various point group symmetry, the irreducible representations which their MOs belong to would be differ to that of point group D_{6h}. the relative results of these molecule E(MO) are shown in Fig. 4. Comparing with the curve in relation to Z-$C_{84}H_{12}$ in Fig. 4a, it is between the curves in relation to Z-$C_{72}H_{12}$ and Z-$C_{96}H_{12}$ in Fig. 3e. As the horizontal ordinate J is replaced by J/Nc, the curve in relation to Z-$C_{84}H_{12}$ will be near the relative curve in Fig. 3f. As for the Z-$C_{144}H_{12}$ and Z-$C_{144}H_{24}$, these two ZSWCNTs with same number of carbon atoms but various thickness, their relative curves somewhat similar but with obvious different the energy gap in J/Nc = 0.5 is much less for Z-$C_{144}H_{24}$. As for the curves of
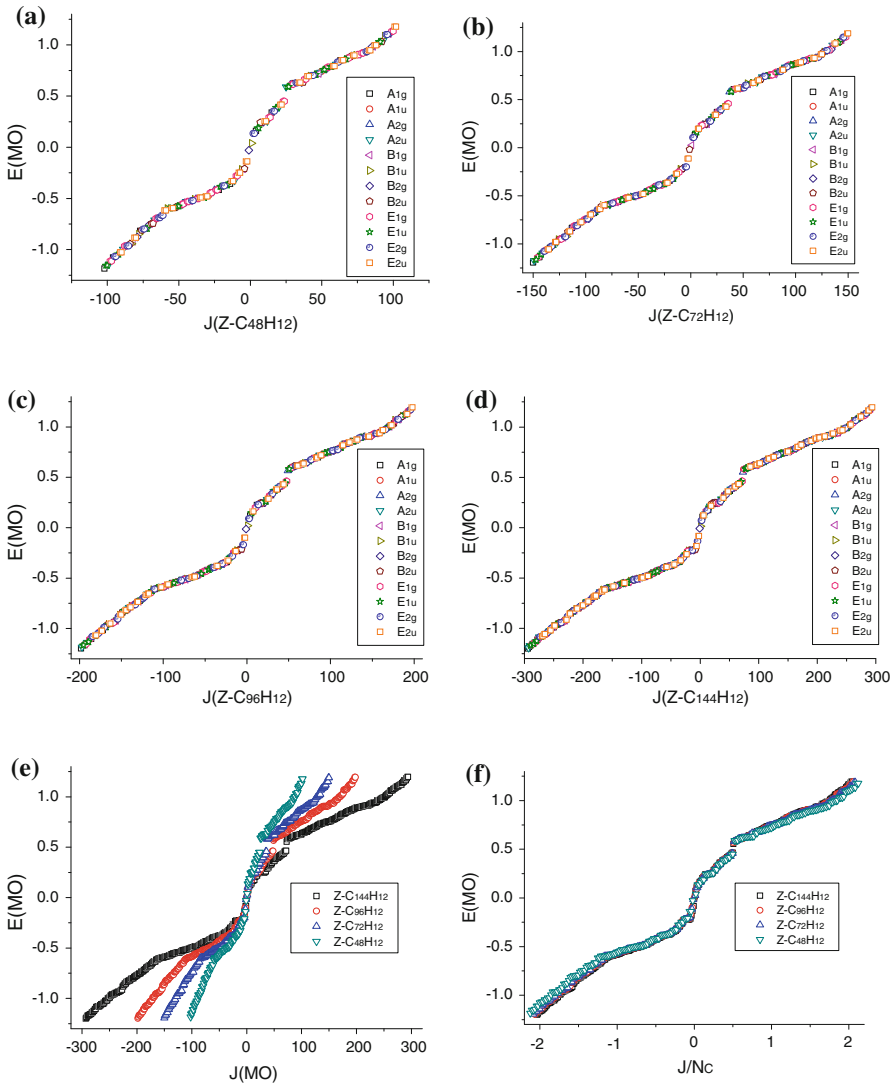
Fig. 3 The MO energy for four ZSWCNT with the same thickness. (**a**) Z-$C_{48}H_{12}$, (**b**) Z-$C_{72}H_{12}$, (**c**) Z-$C_{96}H_{12}$, (**d**) Z-$C_{144}H_{12}$, (**e**) E(MO) versus J, (**f**) E(MO) versus J/Nc

Z-$C_{80}B_8N_8H_{12}$ and relative un-substituted CNT, Z-$C_{96}H_{12}$ are closed, but for some more inner MOs (J < −198 and E(MO) < −5) will be some evident difference.

Now we examine six ASWCNT molecules: A-$C_{48}H_{12}$, A-$C_{66}H_{12}$, A-$C_{72}H_{12}$, A-$C_{78}H_{12}$, A-$C_{96}H_{12}$ and A-$C_{144}H_{12}$, where the A- denoted the armchair, and which are follow with the relative formula. For above ASWCNT the A-$C_{66}H_{12}$ and A-$C_{78}H_{12}$ are possess the point group D_{3h} symmetry, and other are possess the point group D_{3d} symmetry. Corresponding to Fig. 1, these ASWCNT would be the N = 6, M = 8, 11, 12, 13, 16 and 24. These ASWCNT are provided with the same pipe diameter but
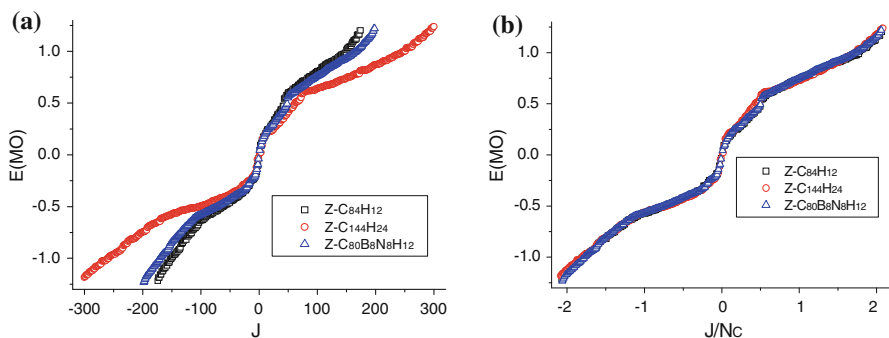
(a)

(b)

Fig. 4 The MO energy of three ZSWCNT molecules. (**a**) E(MO) versus serial number (J), (**b**) E(MO) versus relative serial number (J/Nc)

(a)

(b)

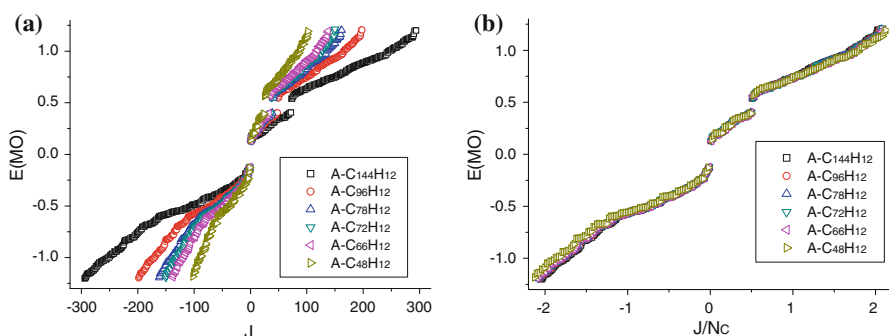**Fig. 5** The MO energy of six ASWCNT. (**a**) E(MO) versus serial number (J), (**b**) E(MO) versus relative serial number (J/Nc)

different length. The MO energy of these six ASWCNT versus serial number (J) and relative serial number (J/Nc) are shown in Fig. 5a, b, respectively. They are similar as of the ZSWCNT. The different for these two kinds of CNT there is the energy gap of ASWCNT is more obvious. It means that maybe there are more resistance and hardness for ASWCNT.

2.2.2 Various AO-set component of SWCNT MO

For AO-sets in relative SWCNT MO by using the cylindrical coordinate system [45,46] and at the HF/STO-3G level, we may divided as the 1S-, 2S-, 2Pz-, 2Pr- and 2Pt-AO set of carbon atoms and 1S-AO set of hydrogen atoms. Meanwhile we may get the various AO-set components of a certain MO and denoted as: $X(C_{1S})$, $X(C_{2S})$, $X(C_{2Pz})$, $X(C_{2Pr})$. $X(C_{2Pt})$ and $X(H_{1S})$, respectively. Roughly, the $X(C_{1S})$ will compose the un-bonding the inner AO. The $X(C_{2S})$, $X(C_{2Pz})$ and $X(C_{2Pt})$ will be process the sp^2-hybrid, then to form the σ-MO but the $X(C_{2Pr})$ to form the π-MO. However, it is differ from the graphene [36], for the SWCNT, the AO set in relation to $X(C_{2Pr})$, i.e. the C_{2Pr}-AO set may be belong to some irreducible representation which can also belong other AO sets, too. Therefore the MO may include but not
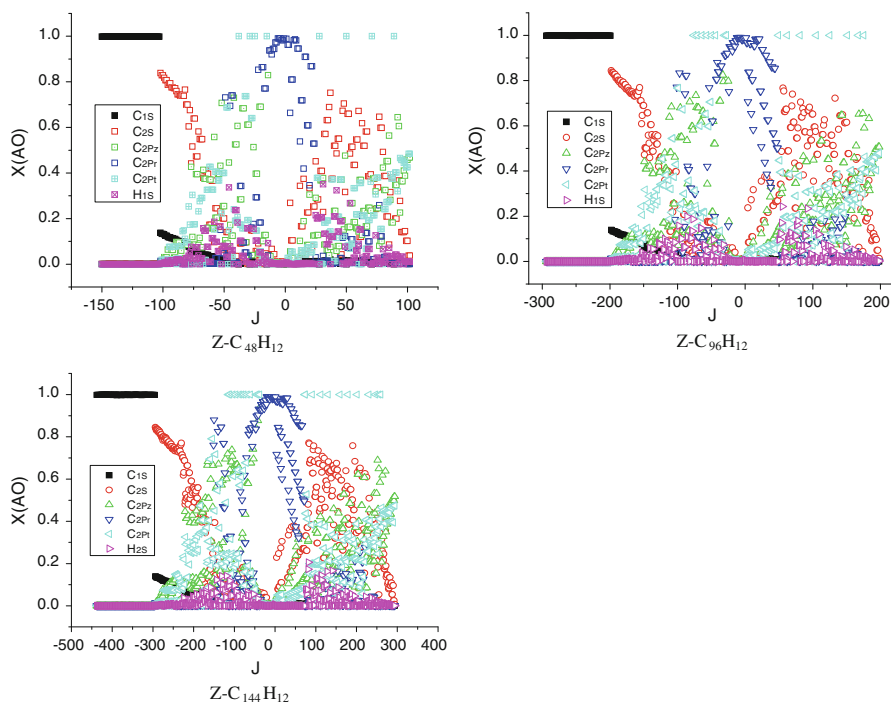
Fig. 6 The AO-set components versus J polt for three various ZSWCNT

only include the C_{2Pr}-AO set component $X(C_{2Pr})$ to form the MO with π-component as the principle but not pure π-one. Meanwhile some other MO may with σ-component as the principle but not pure σ-one may include some $X(C_{2Pr})$ component. By means of the way as Hückel-cyclacene [45,46] we may get the various AO-set components of SWCNT all MOs in relation to cylindrical coordinate.

To start with, we consider three kinds of ZSWCNT molecules: $Z-C_{48}H_{12}$, $Z-C_{96}H_{12}$ and $Z-C_{144}H_{12}$. All of them are provided with the symmetry of D_{6h}, in Fig. 1, the relative values M will be 13, but the values N will be the 4, 8 and 12, respectively. For above ZSWCNT, the AO-set components $X(AO)$ of all MO versus the MO serial number (J) are shown in Fig. 6. It is clear that there is a certain similarity for various ZSWCNT. The abscissa region extend over all MO, the number of MOs ought to be near direct ratio to the number (Nc) of atoms in CNT wall. Therefore it may be expected that using the J/Nc to replace the J for abscissa will be more suitable to reflect the MO substitutive characteristics.

For understanding the relative rule among various ZSWCNT, by means of the cylindrical coordinate system we may plot the figure for each carbon p-AO set component as shown in Fig. 7, where the abscissa being the (J/Nc). In Fig. 7, there are additional three ZSWCNT ($Z-C_{72}H_{12}$, $Z-C_{84}H_{12}$ and $Z-C_{144}H_{24}$ with the D_{6h}, D_{6d} and D_{12h} point group symmetry) and one hetero-CNT $Z-C_{80}B_8N_8H_{12}$ also to be considered.

As shown in Fig. 7, a certain AO-set component distributions for various ZSWCNT MO are some similarity. For example, the AO-set components the near frontal orbital
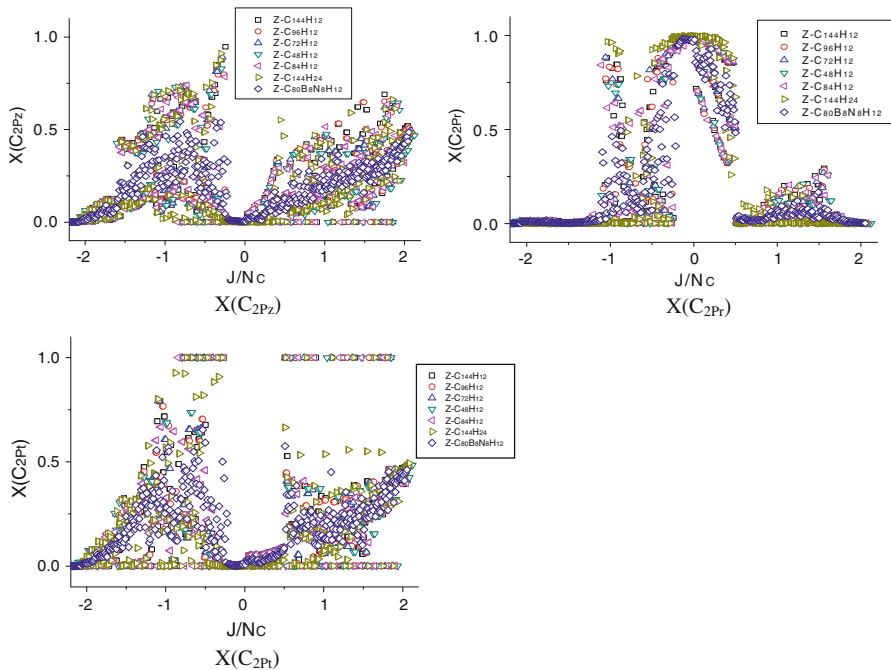
Fig. 7 The carbon p-AO set components versus J/Nc polt for some various ZSWCNT
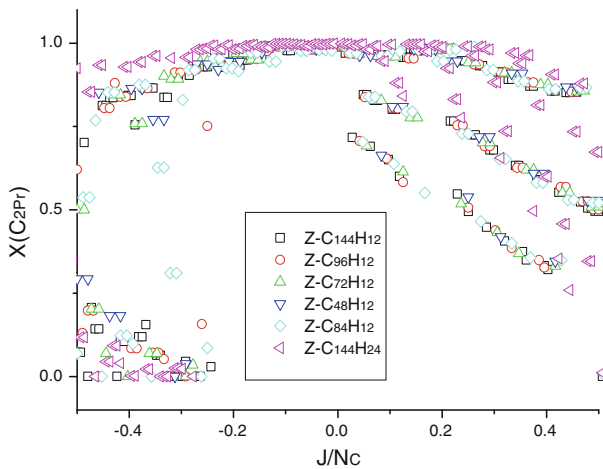

Fig. 8 The $X(C_{2Pr})$ distribution in relation to the near frontal orbital of six ZSWCNTs

(J/Nc near but not equal to null) will be less except for $X(C_{2Pr})$, certainly there are also somewhat discrepant. As shown in Fig. 8, there are the $X(C_{2Pr})$ distribution for the near frontal orbital of some ZSWCNT. Except the Z-$C_{144}H_{24}$, for the other five ZSWCNT with the roughly same diameter the $X(C_{2pr})$ distribution are similar. As for
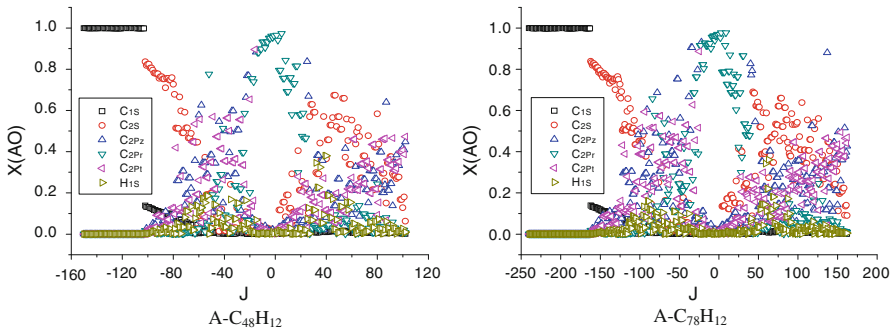
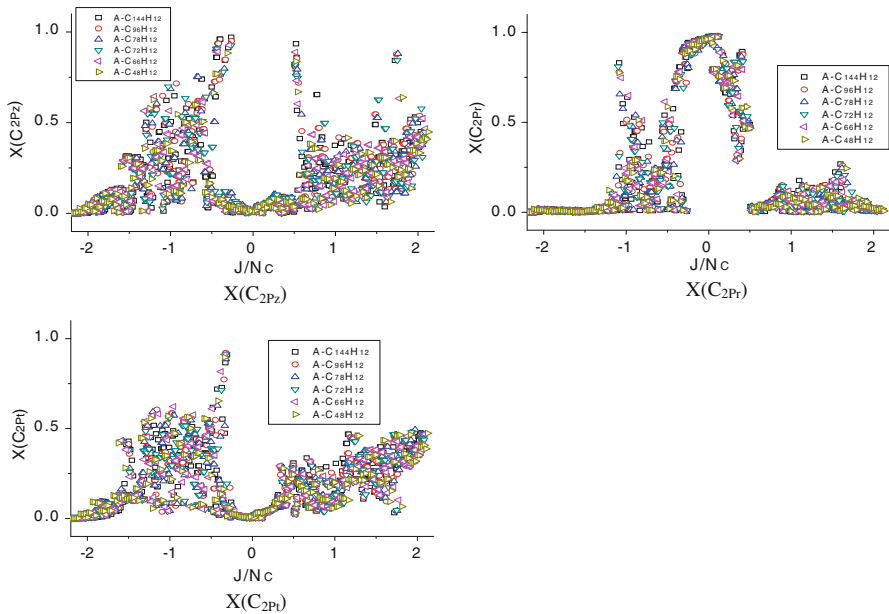**Fig. 9** The AO-set components versus J polt for two various ASWCNT

Fig. 10 The AO-set components versus J/Nc polt for various ASWCNT

the Z-$C_{144}H_{24}$, the relative X(C_{2Pr}) will be larger (near one). It means the Z-$C_{144}H_{24}$ with more pipe diameter, their wall more near the graphene.

Now, we consider two ASWCNT molecules, A-$C_{48}H_{12}$ and A-$C_{78}H_{12}$. Both of them are provided with relative value N in Fig. 1 will be 6. But the values M will be the 8 and 13, respectively. On the other hand the A-$C_{78}H_{12}$ will be provided with the D_{3h} point group symmetry but A-$C_{48}H_{12}$ with D_{3d} symmetry. Similar as the Fig. 6 for ZSWCNT, we may get Fig. 9.

Similar as Fig. 6, it may be expected as using the J/Nc to replace the abscissa J, the plot may reflect the MO intrinsic characteristics more clear. Similar as Fig. 7, we can obtain the Fig. 10. It is notable that the A-$C_{66}H_{12}$ and A-$C_{78}H_{12}$ ought to be provided with D_{3h} symmetry, and other ASWCNT with the D_{3d} symmetry.
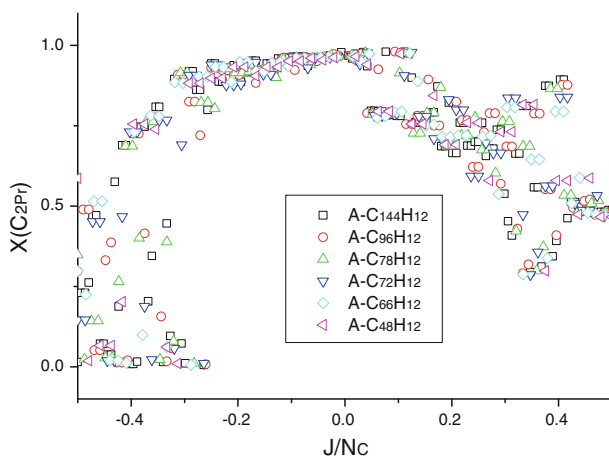
Fig. 11 The $X(C_{2Pr})$ distribution in relation to the near frontal orbital of six ASWCNTs

Comparing with the Figs. 6 and 7 of ZSWCNT and the Figs. 9 and 10 of ASWCNT, in relation to the AO-set component distribution are similar, roughly. But there are somewhat different characteristic, similarly, we can get the Fig. 11 for ASWCNT as the Fig. 8 for ZSWCNT, it is apparent that there are more dispersion for ASWCNT in the VMO region.

2.2.3 Fuzzy CSR symmetry of SWCNT MO

It is somewhat dissimilar from our previous work in relation to the fuzzy cylindrical group symmetry molecule [32,33,35], where the SWCNT may involve the higher (>2)-fold cylindrical screw rotation (CSR), and would probe the fuzzy symmetry in relation to CSR. Where we only analyse some ZSWCNT MO as the example (the ASWCNT will be omitted to save space). For the CSR(j, i) transformation of ZSWCNT may be denoted as the product of single rotation $C_n(2\pi i/[M-1])$ and translation $T_n(1.5jl_{cc})$. When and only when i and j are provided with the same odevity, such CSR may be symmetry or fuzzy symmetry transformation.

For simple rotation, there is without the translation and then the $j = 0$, therefore i must also be even. The $C_n(2\pi i/[M-1])$ with even number i, the membership function of ZSWCNT molecular skeleton for relative transformation usually equals one, however for the ZSWCNT MO it will be more complex. The membership function in relative transformation for the MO which belongs to one dimensional irreducible representation will be also one. However, for the MO which belongs to two-dimensional irreducible representation the relative membership function may be less one [50]. For example, the benzene MO belongs to two-dimensional irreducible representation the membership function in relation to C_6^0 and C_6^3 would be equal to one, but that in relation to C_6^1 and C_6^2 may be to 0.5. Such results are the same for the calculation at various levels. Above results are also right for the SWCNT with the C_6 symmetry, such as the SWCNT Z-$C_{48}H_{12}$, Z-$C_{72}H_{12}$, Z-$C_{96}H_{12}$ and Z-$C_{144}H_{12}$ that we analysed above. As
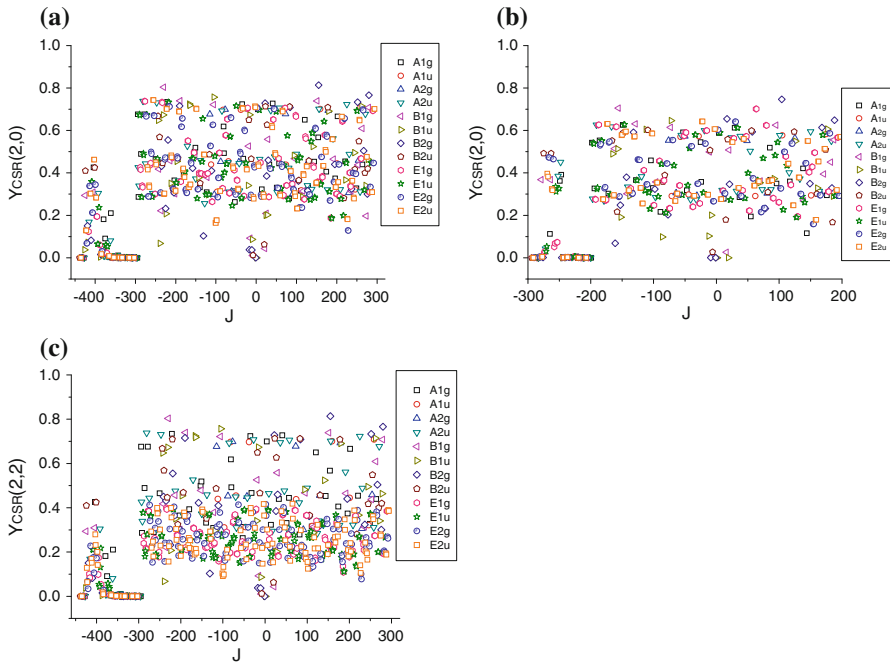
Fig. 12 The membership function of some ZSWCNTs in relation to the CSR transformation versus J(MO) serial number. (**a**) Z-$C_{144}H_{12}$ in relation to CSR(2, 0), (**b**) Z-$C_{96}H_{12}$ in relation to CSR(2, 0), (**c**) Z-$C_{96}H_{12}$ in relation to CSR(2, 2)

for the other fold rotation symmetry, the relative SWCNT, we may get the results as the full carbon ring molecules [34]. For the MO which belongs to one dimensional irreducible representation the relative membership function ought to be one. However, for the single MO which belongs to two-dimensional irreducible representation, the relative membership function may be less that one (not sure be 0.5).

As for the simple translation there is without the rotation and $i = 0$, therefore as j is even the $T_n(1.5jl_{cc})$, there may be the relative symmetry or fuzzy symmetry, the membership function will be more (near one). Although owing to the ZSWCNT is finitude, the relative membership function less one but may be considerable value. As j is odd number, the membership function in relation to $T_n(1.5jl_{cc})$ will be very small approach null. For ZSWCNT MO in relation to the simple translation ($i = 0$, j is even), by means of the fuzzy cylindrical group [32–35], we may get the relative membership function. As shown in Fig. 12a, b, there are the membership functions $Y_{CSR}(2, 0)$ in relation to the simple translation CSR(2, 0) for the MO of Z-$C_{144}H_{12}$ and Z-$C_{96}H_{12}$ versus the serial number J, respectively. Although the numbers of MO of Z-$C_{96}H_{12}$ and Z-$C_{144}H_{12}$ are different, the point-distribution for Fig. 12a, b will be the similar, roughly. The points with less J, ought to belong the MO composed by the inner 1s-AO of the carbon in CNT wall. Owing to the translation region (N) in Z-$C_{96}H_{12}$ would be less than that of Z-$C_{144}H_{12}$, the distribution region for vertical coordinates would be narrower. In additional, for the MO with one-dimensional irreducible representation
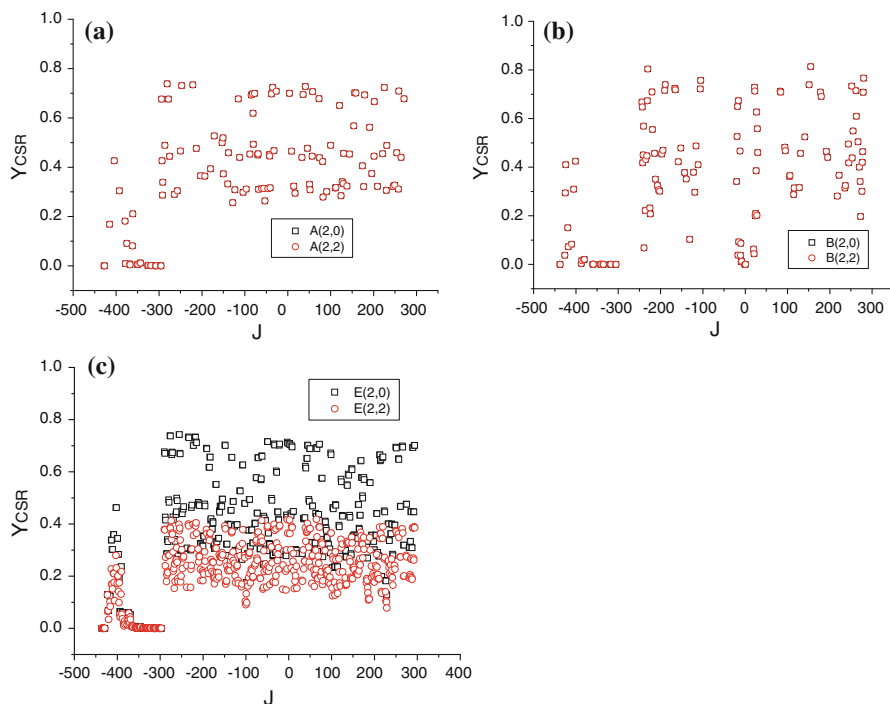
Fig. 13 The membership function Y_{CSR} of Z-$C_{144}H_{12}$ MO in relation to the CSR(2, 0) and CSR(2, 2) symmetry transformation versus the MO serial number (J). (**a**) MO with the A_{1g}, A_{1u}, A_{2g} and A_{2u} irreducible representation. (**b**) MO with the B_{1g}, B_{1u}, B_{2g} and B_{2u} irreducible representation. (**c**) MO with the E_{1g}, E_{1u}, E_{2g} and E_{2u} irreducible representation

the relative membership function will be the defined, for the MO with two-dimensional irreducible representation will be defined for MO complete set but not for single MO, it will depend on the complete set designate way. For the MO with the complete set in various designate way, the membership functions in relative point group transformation of single MO may be different [34,50]. In this paper we will analyse the MO which belongs to the one dimensional irreducible representation, mainly.

Now we consider the CSR(j, i) where both i and j are nonzero, the plot of membership function $Y_{CSR}(j, i)$ of Z-$C_{144}H_{12}$ in relation to the CSR(2, 2) transformation versus J would be shown in Fig. 12c. Comparing with the pure translation CSR(2, 0) as shown in Fig. 12a, it seems that there are some dots going down. As we divide the MO into three sets according to the irreducible representation (A, B and E), we may make the plot of the membership function in relation to the CSR(2, 0) and CSR(2, 2) transformation versus J as shown in Fig. 13.

For the MO belong to the one-dimensional irreducible representation, the membership function Y_{CSR} (2, 0) and Y_{CSR} (2, 2) versus J would coincide with each other, elementary, as shown in Fig. 13a, b. For the MO belong to the two-dimensional irreducible representation the relative $Y_{CSR}(2, 0)$ would be bigger than that of $Y_{CSR}(2, 2)$, as shown in Fig. 13c. It is notable that the CSR(2, 2) is the product of CSR(2, 0) and
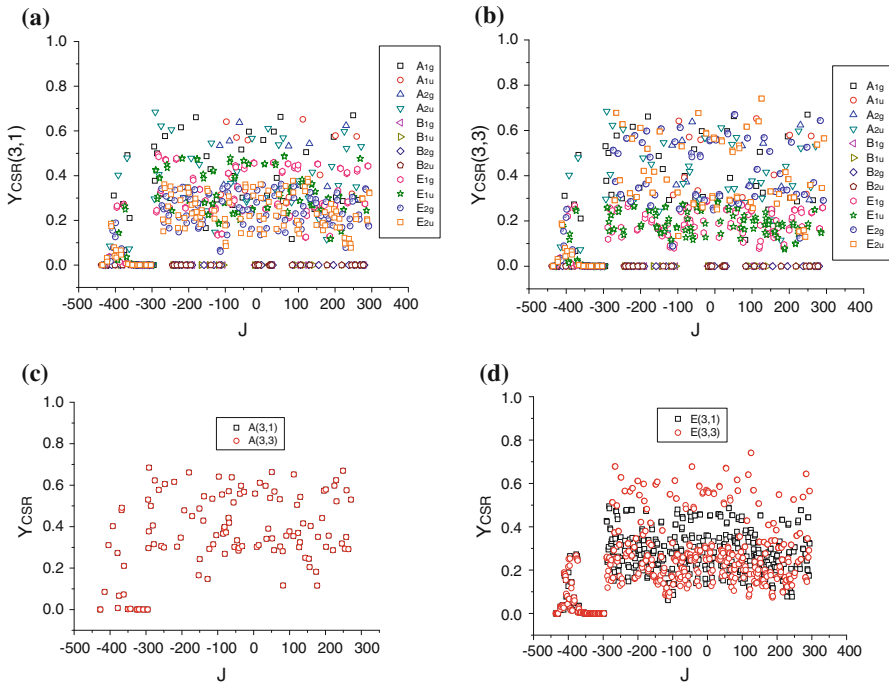
Fig. 14 The plot for the membership function of the Z-$C_{144}H_{12}$ MO in relation to CSR(3, 1) and CSR(3, 3) transformation versus J (serial number). (**a**) Z-$C_{144}H_{12}$ MO, $Y_{CSR}(3, 1)$ versus J. (**b**) Z-$C_{144}H_{12}$MO, $Y_{CSR}(3, 3)$ versus J. (**c**) Z-$C_{144}H_{12}$MO with A_{1g}, A_{1u}, A_{2g} and A_{2u}, $Y_{CSR}(3,1)$ and (3, 3) versus J. (**d**) Z-$C_{144}H_{12}$MO with E_{1g}, E_{1u}, E_{2g} and E_{2u}, $Y_{CSR}(3,1)$ and (3, 3) versus J

CSR(0, 2), there are difference in a pure rotation transformation CSR(0, 2) i.e. the factor C_6^1, although the relative membership function $Y_{CSR}(0, 2)$ is 0.5, but the ratio of $Y_{CSR}(2, 2)/Y_{CSR}(2, 0)$ may be between 0.5 and one.

For the cases of CSR(i, j) transformation with both i and j are odd, we examine the membership function of Z-$C_{144}H_{12}$MO in relation to the CSR(3, 1) and CSR(3, 3) transformation membership function versus J, as shown in Fig. 14. Figure 14a, b denote the membership function of Z-$C_{144}H_{12}$ MO in relation to $Y_{CSR}(3, 1)$ and $Y_{CSR}(3, 3)$ transformation distribution. For the MO with one-dimensional irreducible representation the plot of $Y_{CSR}(3, 1)$ and $Y_{CSR}(3, 3)$ versus J will be coincide each other, essentially, for various A-irreducible representation as shown in Fig. 14c. As for various B-irreducible representation, the relative membership function will be near null (figure is omitted). As for the MO with the two-dimensional irreducible representation, the relative $Y_{CSR}(3, 1)$ and $Y_{CSR}(3, 3)$ will be some difference as shown in Fig. 14d.

Now we consider the MO with A-irreducible representation as the instance in detail, using the relative serial number J/Nc to replace the J, to analyse four ZSWCNT, Z-$C_{144}H_{12}$, Z-$C_{96}H_{12}$, Z-$C_{72}H_{12}$ and Z-$C_{48}H_{12}$ with the same pipe diameter but different length, they are provided with the D_{6h} point group symmetry. For the MO with identical irreducible representation of above four ZSWCNT, the polt of $Y_{CSR}(1,1)$ versus J/Nc will be shown in one subgraph. As show in Fig. 15, the MO with the A_{1u}
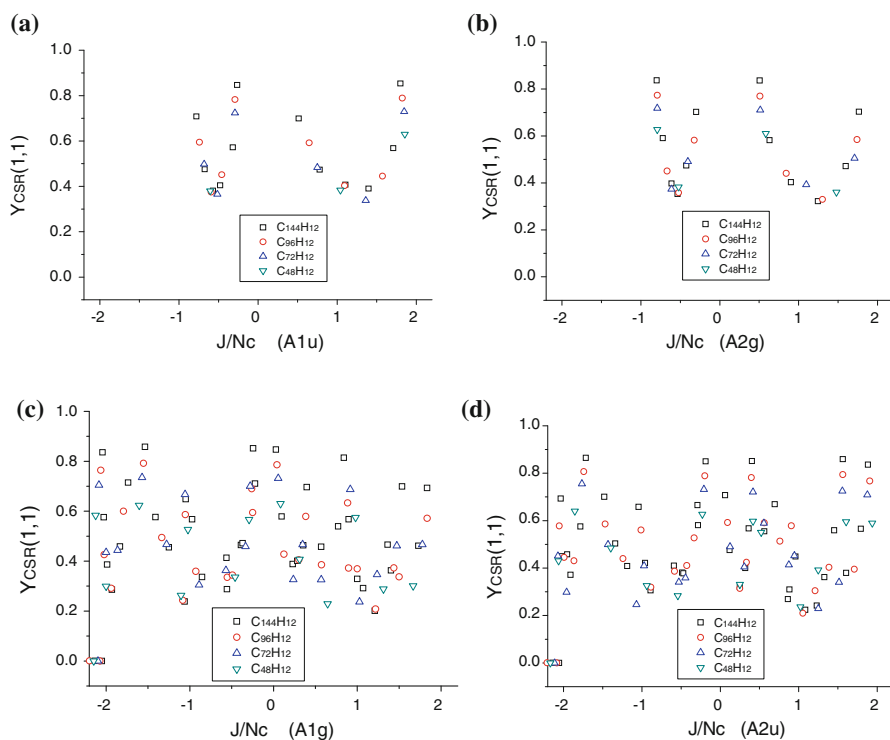
Fig. 15 The membership function of Z-SWCNT MO A-irreducible representation in relation to the CSR(1, 1) symmetry transformation versus the relative serial number (J/Nc). (**a**) MO with the A_{1u} irreducible representation, $Y_{CSR}(1, 1)$ versus J/Nc. (**b**) MO with the A_{2g} irreducible representation, $Y_{CSR}(1, 1)$ versus J/Nc. (**c**) MO with the A_{1g} irreducible representation, $Y_{CSR}(1, 1)$ versus J/Nc. (**d**) MO with the A_{2u} irreducible representation, $Y_{CSR}(1, 1)$ versus J/Nc

(Fig. 15a) and A_{2g} (Fig. 15b) are similar they may overlap to form the distribution rough near with two upward ringent curves, meanwhile the MO with A_{1g} (Fig. 15c) and with A_{2u} (Fig. 15d) are similar they may overlap to form the distribution rough near with more upward ringent curves. For the MO with B-irreducible representation, they may be analysed similarly, but the relative membership function will be very small. As for the MO with the two-dimensional E-irreducible representation, they would be analysed by means of the complete set not single MO.

3 Torus carbon nanotuble

After entering the new millennium, the torus carbon nanotuble (TCNT) are notable by more chemists [37–44]. It involves the molecular design and some other theoretical side. Owing the special symmetrical characteristic (involve to the molecular torus group symmetry [45,46]) and refer to some important molecular characteristic (e.g. the topological characteristic of DNA) in connected with TCNT, we will analyse TCNT in this paper. TCNT may be considered as the SWCNT curled along the Z-direction

and connected with the two mouths of tube side. In this paper, we only discuss the TCNT which will be formed from ZSWCNT and omitted from the ASWCNT. We may consider a plane molecule place in a certain rectangle, as the two sides of this rectangle may be overlying to form the Hückel or Möbius strip-like molecule [45,46]. Such rectangle may be called the MH-rectangle. The other two sides un-overlied of the MH-rectangle will form the boundary of Hückel- or Möbius-strip band. Molecular MH-rectangle boundary may be set in the position through more atoms in relative molecule, often. There is more than one MH-rectangle in one SWCNT molecule. Considering the ZSWCNT with the D_{rh} point group symmetry, where all of the mirrors (M_d and M_v) except one (M_h) perpendicular to Z-axis may be the noted as the MH-rectangle. The ZSWCNT with the $M - 1 = 12$ and the D_{6h} point group symmetry will be provided with 3 M_v and 3 M_d mirrors, therefore such ZSWCNT ought to include 6 MH-rectangles. The boundary of each MH-rectangle would be corresponding to the position with certain m and m+6 values. The MH-rectangle boundary from M_v and M_d include the carbon atoms with the similar distribution. However, as $M - 1 = 10$, the relative ZSWCNT with the D_{5h} point group symmetry will include 5 M_v mirrors and 5 MH-rectangle. The boundary of each MH-rectangle would be corresponding to the position with certain m and m+5 values. Two boundary of each MH-rectangle include the carbon atoms position would be the similar or some interlace.

As the SWCNT curl and form the TCNT, the Z-axis of SWCNT will be form the basic circle of torus orthogonal curvilinear coordinates system [45,46]. The hydrogen atoms in two sides of SWCNT no longer exist. The fuzzy CSR symmetry in SWCNT will be transform to the prefect TSR symmetry.

Now we will analyse the various torus carbon nanotube include 360 carbon atoms and formed from the ZSWCNT with $M - 1 = 12$ and $N = 30$ as the prototypes and denoted as the TCNT360.

3.1 Symmetry and fuzzy symmetry of Hückel-TCNT360

Hückel-TCNT360 (denoted as the HTCNT360) means that such TCNT will be formed from the relative ZSWCNT(z-$C_{360}H_{12}$) by means of condensation all the CH bonds with the same even serial number in two side of TCNT, the relative molecular structure as shown in Fig. 16. Figure 16a, b are denoted the top view, but with the ball and stick graph and the space filling graph, respectively. Owing to the TCNT would be the pure carbon molecule. Although the all atoms that are included in TCNT are carbon ones, for convenient, the carbon atoms are being to the border of various MH-rectangle boundary will be distinguished by using the various colour in Fig. 16b.

For the TCNT molecules, the torus orthogonal curvilinear coordinate system (L, α, β) [45,46], may be used to analyse their geometrical characteristic suitably. According to the Fig. 16b, it seems that the carbon atoms in the boundary of identical MH-rectangle may be form the Hückel-strip band including the basic circle and all of these atoms would be provided with the same (or differ from π radian) β-coordinate value. Their L-coordinate value may be considered as the constant CNT radius but the α-coordinate value may be variation.
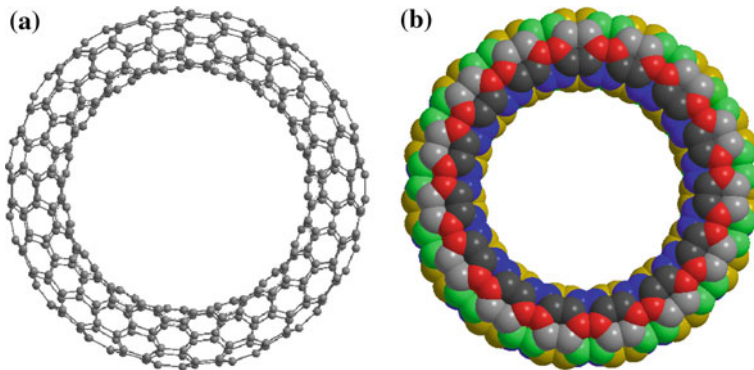
Fig. 16 The HTCNT360 molecular structure *(top view)*. (**a**) ball and stick graph and (**b**) space filling graph

According to Eq. (2), the fuzzy CSR symmetry transformation in relative z-$C_{360}H_{12}$ molecule would be $T(1.5 j l_{cc})C(2 \pi i/12)$, now in relative HTCNT360 it will be translated to the perfect TSR transformation:

$$TSR (L, \Delta \alpha, \Delta \beta) = TSR(L, 2 \pi j/30, 2 \pi i/12) = TSR \left(L, 12j^{o}, 30i^{o}\right)$$
$$= C_{\alpha}(2 \pi j/30)C_{\beta}(2 \pi i/12), \qquad (9)$$

where i and j would be the same odevity, C_{α} and C_{β} denote the rotation in relation to the α-and β-angle, respectively. That is the HTCNT360 would be provided with the symmetry of the transformation group as follows:

$$\mathbf{TSR_H} (j, i) = \{TSR(L, 2 \pi j/30, 2 \pi i/12); i \text{ and } j \text{ with the same odevity}\}. \quad (10)$$

HTCNT360 will be provided the common point group $\mathbf{D_{15h}}$ symmetry, i.e. the torus group which the HTCNT360 belong to would include the subgroups: $\mathbf{TSR_H}(j, i)$ as shown in Eq. (10) and point group $\mathbf{D_{15h}}$. It is notable that there are 30 carbon atoms respectively in the up and down boundaries of each Hückel-strip band, these atoms are paring to be provided the 15-fold rotation axis, $n(0) = 15$.

Now we discussed some important cyclical subgroups of $\mathbf{TSR_H}(j, i)$. By means of torus orthogonal curvilinear coordinate system, for the carbon atoms of HTCNT360, the L-coordinate values are elementary the same, the symmetry transformation in relation to the α- and β-coordinate would be considered, mainly. To start with we examine the transformation of the $\mathbf{TSR_H}(j, i)$ with unchanged the MH-rectangle which the atoms of TCNT belong to, these transformations are in relation to simple α-angle rotation. Corresponding to Eq. (10), the $i = 0$ and $j =$ even number, and replaced with $2j$. This subgroup:

$$\mathbf{TSR_H} (2j, 0) = \{TSR(L, 2 \pi *2j/30, 0); j = 0, 1, \ldots \ldots, 14\}$$
$$= \{[TSR(L, 2 \pi /15, 0)]^{j}; j = 0, 1, \ldots \ldots, 14\}. \qquad (10a)$$

As $j = 15$, the α-angle will rotate a circle, $\Delta \alpha = 2\pi$. The element of $\mathbf{TSR_H}(2j, 0)$ will be the TSR (L, 2π, 0) and equivalent to the identity element. Such rotation subgroup $\mathbf{TSR_H}(2j, 0)$ ought to be 15 order cyclical subgroup correspond to a usual rotation group. The $\mathbf{TSR_H}(j, i)$ would include the element inconnect with the pure β-angle transformation, such transformation will change the MH-rectangle of the carbon atoms being in TCNT. According to Eq. (10), $j = 0$ and $i = $ even number (replaced by $2i$). The relative rotation subgroup $\mathbf{TSR_H}(0, 2i)$ ought to be a 6-order cyclical subgroup:

$$\mathbf{TSR_H}(0, 2i) = \{TSR(L, 0, 2\pi * 2i/12); i = 0, 1, \ldots\ldots, 5\}$$
$$= \{[TSR(L, 0, \pi/3)]^j; j = 0, 1, \ldots\ldots, 5\}. \qquad (10b)$$

As $i = 6$, the relative element is TSR(L, 0, 2π) and equivalent to the identity element. Such subgroup would be different from the usual rotation group, where the rotation is not usual rotation in point group, it is not around the rotation axis but around the basic circle circumference, through such rotation the α-angle remain unchanged. As regards the cyclical subgroup of the $\mathbf{TSR_H}(j, i)$ refer both the α- and β-angle changed:

$$\mathbf{TSR_H}(j, j) = \{TSR(L, 2\pi j/30, 2\pi j/12); j = 0, 1, \ldots\ldots, 59\}$$
$$= \{[TSR(L, 2\pi/30, 2\pi/12)]^j; j = 0, 1, \ldots\ldots, 59\}. \qquad (10c)$$

It is noticed that this cyclical subgroup will be 60- not 30-order. As $j = 30$, the group element is TSR(L, 2π, π), where $\Delta \alpha = 2\pi$, α-angle rotate one circle, but $\Delta \beta = 5\pi$, β-angle rotate two and half circles, and such element will be not equivalence with the identity element. As $j = 60$, the group element is TSR(L, 4π, 2π), where $\Delta \alpha = 4\pi$, α-angle rotate two circles, $\Delta \beta = 10\pi$, β-angle rotate five circles, such group element and identity element ought to be equivalence. Therefore there is 60-order cyclical subgroup. It seems that there are somewhat similar with the Möbius-strip band, however the HTCNT is Hückel-TCNT indeed not the Möbius-TCNT. As a certain carbon atom in HTCNT is transformed successive according the TSR(L, $2\pi/30$, $2\pi/12$) transformation, this atom will be removed on HTCNT wall after 60 times then return to the original position, along the relative trajectory the α-angle rotates two circles and β-angle rotate five circles.

When the polyacene to form the Hückel-cyclacene, the MH-rectangle will be transform to a Hückel-strip band as a cylindric side [45,46]. As shown in Fig. 16b, accomplish the (z-$C_{360}H_{12}$) to constrict HTCNT360, the MH-rectangles will be transformed to the Hückel-strip bands as the circular truncated cone sides, mainly, but in some extreme cases as the cylindric side or concentric anchor ring plane. All these Hückel-strip band curved surfaces ought to be the topologic homeomorphous and with the corporate basic circle. As shown in Fig. 17a1–a3, there are the top view, side view and oblique view graphs of circular truncated cone side form Hückel-strip bands in HTCNT360, respectively, where two circles with different size are the boundary of Hückel-strip band. The globules in the boundary of Hückel-strip band denoted the carbon atom, and the red globules in middle-level may be linked to form the basic circle. All the basic circles of six Hückel-strip bands in HTCNT360 are identical. In the extreme case, the Hückel-strip band may be as the cylindric side ($\beta = 90°$) or
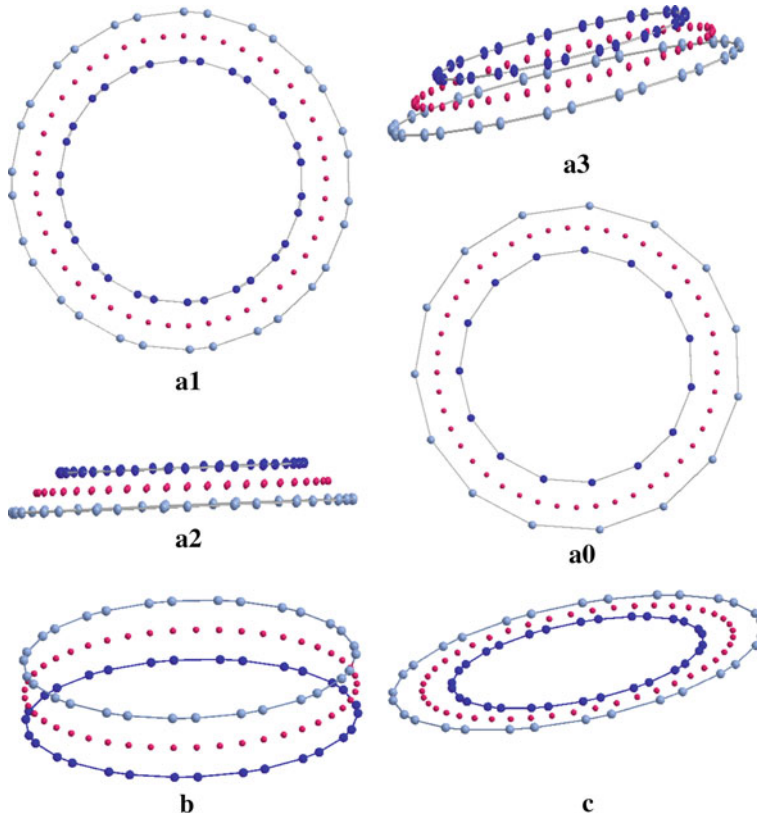
Fig. 17 The Hückel-strip band (annule) of HTCNT360. (**a0–a3**) circular truncated cone side form, (**b**) cylindric side form (**c**) concentric anchor ring plane form

concentric anchor ring plane (coplane with basic circle, $\beta = 0°$), the relative oblique view graphs are shown in Fig. 17b, c, respectively. All of these Hückel-strip bands will be provided with the boundary constituted by two closed curves which each run through 30 carbon atoms. These carbon atoms are pairing of every two atoms and to form the same structure unit, and there are 15 structure units included in every closed curve. Where 15 structure units reflect the order of the in relation to α-angle rotation symmetry transformation group, we may select one carbon atom from every structure unit in proper sequence and to compose one symmetry adapted linear combinations (SALC) atom set in relation to above rotation group. For each closed curve, there are such two similar (only differ one equivalent α phase angle) SALC atom-set. For a certain Hückel-strip band, above two closed curves will be differ with only one invariable β-phase angle (π). In additional, in Fig. 16b there are six Hückel-strip band, the up- and down-boundary of same Hückel-strip band are shown with the same color, however there are different color in Fig. 17. By the way, the globules in the boundary of strip band denoted the carbon atoms, as using the SALC-carbon atoms to replace the carbon atomic pairs in structural unit, the globules will be distributed more symmetry simply. As shown in Fig. 17a0, it is similar as Fig. 17a1 for SCAL-carbon atom.
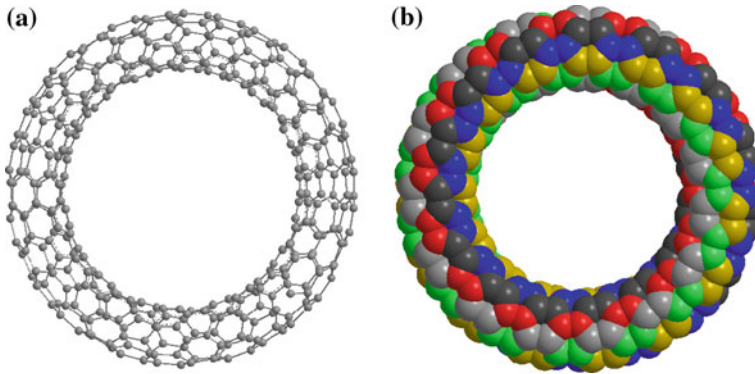
Fig. 18 The MTCNT360 molecular structure (*top view*). (**a**) ball and stick graph and (**b**) space filling graph

3.2 Symmetry and fuzzy symmetry of Möbius-TCNT360

Möbius-TCNT360 (denoted as the MTCNT360) means that such TCNT will be formed from the relative ZSWCNT(z-$C_{360}H_{12}$) by means of condensation all the CH bonds with the even serial number m and m $\pm$ (M − 1)/2 (i.e. the para-position) in two side of TCNT, the relative molecular structure as shown in Fig. 18. When the CNT is curled to form the TCNT, sametime the CNT would be around the tube core 180°(in accordance with the torus orthogonal coordinate system the β-angle rotate 180°). All of the MH-rectangles in z-$C_{360}H_{12}$ ought to be made one time Möbius-twisted and then butt joint. Similar as the Möbius-strip band molecule, such molecule may be called the Möbius-strip tube molecule. Figure 18a, b are denoted the top view, but with the ball and stick graph and the space filling graph, respectively. Owing to the MTCNT360 would be the pure carbon molecule, the all atoms included in MTCNT360 are carbon ones, for convenient, the carbon atoms are being to the border and various MH-rectangle boundary in primary ZSWCNT (z-$C_{360}H_{12}$) may be distinguished by using the various colour. By means of the torus orthogonal curvilinear coordinate system (L, α, β) [45,46], the MTCNT geometrical characteristic ought also to be described suitable. According to the Fig. 18b, it seems that the carbon atoms in the boundary of identical MH-rectangle may be form the Möbius-strip band including the basic circle and all of these Möbius-strip bands same topology would be provided with the same topologic structure as the usual Möbius-strip band [45,46]. The up- and down-boundary of any one certain MH-rectangle will be combined to form a continuous boundary closed curve, and the Möbius-strip band curved surface will be connected to an interconnected surface.

The relative fuzzy CSR transformation of Z-$C_{360}H_{12}$, T(1.5 jl_{cc})C($2\pi i/12$), would be changed to the perfect TSR transformation:

$$
\begin{aligned}
\text{TSR}(L, \triangle\alpha, \triangle\beta) &= \text{TSR}(L, 2\pi j/30, 2\pi[i/12 + j/60]) \\
&= \text{TSR}(L, 12j^{\text{o}}, 30i^{\text{o}} + 6j^{\text{o}}) \\
&= C_{\alpha}(2\pi j/30)\, C_{\beta}(2\pi[i/12 + j/60]), \quad (11)
\end{aligned}
$$

where the i and j ought to be the same odevity, too. The C_α and C_β will denote the rotation in relation to the α- and β-angle, respectively. Comparing with Eq. (9), for the C_β transformation there is additional term to reflect the effect of the Möbius-twisted. For the case of $i = 0$, as $j = 30$ i.e. the α-angle rotate one cycle (2π), the β-angle rotate only half-cycle (π). So that the MTCNT360 ought to be provided with the symmetry group using the Eq. (11) as the element:

$$\mathbf{TSR_M}\,(j, i) = \{\text{TSR}(L, 2\,\pi\,j/30, 2\,\pi[i/12 + j/60]);\ i\ \text{and}\ j\ \text{with the same odevity}\}. \tag{12}$$

In relation to the MTCNT360, now we analyse some important cyclical subgroups of the $\mathbf{TSR_M}(j, i)$. The cyclical subgroup of $\mathbf{TSR_M}(j, i)$ which includes the transformation only with the invariable MH-rectangle might be the $\mathbf{TSR_M}(2j, 0)$ as follows:

$$\mathbf{TSR_M}\,(2j, 0) = \{\text{TSR}(L, 4\,\pi\,j/30, 4\,\pi\,j/60);\ j = 0, 1, \ldots\ldots, 29\}$$
$$= \{[\text{TSR}(L, 2\,\pi/15, \pi/15)]^j;\ j = 0, 1, \ldots\ldots, 29\} \tag{12a}$$

In such group, owing to there are the Möbius-twisted in MTCNT360, in relative the α-angle rotation would be not pure but meanwhile in relation the β-angle rotation. It is not alike the subgroup $\mathbf{TSR_H}(2j, 0)$. The subgroup $\mathbf{TSR_M}(2j, 0)$ is a 30-order cyclical subgroup. As $j=15$, the group element ought to be TSR(L, $\Delta\alpha, \Delta\beta) = \text{TSR}(L, 2\,\pi, \pi)$, along the α-angle rotate one-cycle but along the β-angle rotate only half-cycle, such element would be not the identity one and (12a) is not the 15-order cyclical subgroup. As $j = 30$, the group element TSR(L, $\Delta\alpha, \Delta\beta) = \text{TSR}(L, 4\,\pi, 2\,\pi)$, along the α-angle rotate two cycles and along the β-angle rotate one-cycle, such element would be equivalence to the identity one TSR(L, 0, 0) so the (12a) is the 30-order cyclical subgroup. The $\mathbf{TSR_M}(2j, 0)$ is not the rotation group in usual point group. Based the transformation of $\mathbf{TSR_M}(2j, 0)$, in MTCNT360 the carbon atoms would not change the MH-rectangle they belong to. The $\mathbf{TSR_M}(j, i)$ could also include the rotation in relation to pure β-angle subgroup $\mathbf{TSR_M}(0, 2i)$, there is a six-order cyclical subgroup, with the formal as similar as the (10b), the transformation included in $\mathbf{TSR_M}(0, 2i)$ may lead to the atoms in MTCNT360 to transfer between various MH-rectangle. Such subgroup would be different from the usual rotation group, where the rotation is not usual rotation in point group, it is not around the rotation axis but around the basic circle circumference, through such rotation the α-angle remain unchanged. As regards the cyclical subgroup of the $\mathbf{TSR_M}(j, i)$ refer both the α- and β-angle changed, as follows:

$$\mathbf{TSR_M}\,(j, j) = \{\text{TSR}(L, 2\,\pi\,j/30, 2\,\pi[j/12 + j/60]);\ j = 0, 1, \ldots\ldots, 29\}$$
$$= \{[\text{TSR}(L, 2\,\pi/30, 2\,\pi[1/12 + 1/60])^j;\ j = 0, 1, \ldots\ldots, 29\} \tag{12b}$$

It is notable that, as $j = 30$, the element of $\mathbf{TSR_M}(j, j)$ will be the TSR(L,$2\pi, 6\,\pi$), where $\Delta\alpha = 2\,\pi$, α-angle rotate one circle, and $\Delta\beta = 6\,\pi$, β-angle rotate three circles, it is equivalence the identity element. It means that the subgroup (12b) would
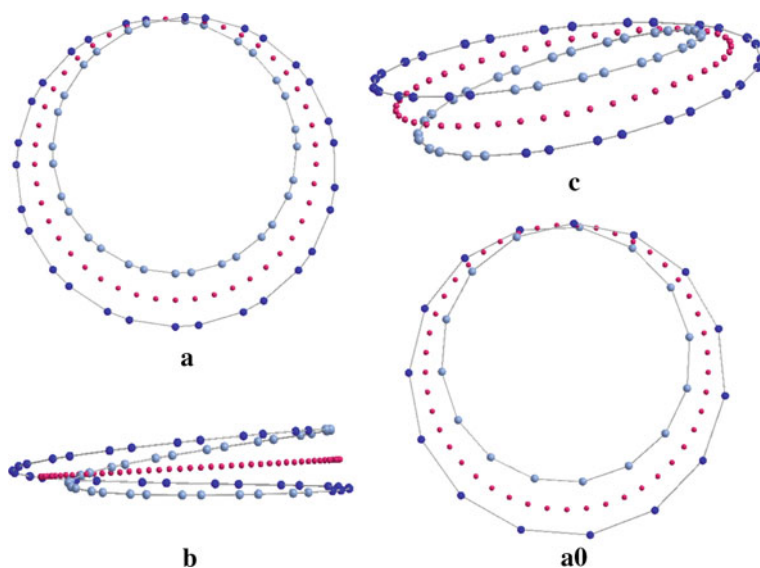
Fig. 19 The Möbius-strip bands in MTCNT360. (**a**) Top view, (**b**) side view, (**c**) oblique view

be the 30-order cyclical group. The MTCNT360 molecule also provided with usual point group C_2 symmetry. The molecular torus group of MTCNT360 would include the subgroup, the **TSR** group as shown in Eq. (11) and the point group C_2. The Fig. 18b shows that the various MH-rectangles in z-$C_{360}H_{12}$ would transform to the Möbius-strip band [45,46] in MTCNT360. As shown in Fig. 19, where the up- and down-boundary of the MH-rectangle will be linked to form one closed curve, the boundary of such Möbius-strip band boundary are the same (homeomorphism) as that of the cyclacenes [45,46]. There are six such Möbius-strip bands in MTCNT360, in each boundary there are 60 carbon atoms respectively. All of these may be correlated and transformed mutual by means of some certain symmetry operation. It is notable where a certain MH-rectangle could and only could form one Möbius-strip band, and a certain Möbius-strip band may be and only may be formed from a single MH-rectangle. There are independent each other. As for the Fig. 19a0, it is corresponding to the Fig. 19a but by using the SALC-carbon atoms to replace the carbon atomic pairs in structural unit.

3.3 Symmetry and fuzzy symmetry of multi-twisted Möbius-TCNT360

Multi-$n(t)$-twisted Möbius-TCNT360 (denoted as the $M^{n(t)}$ TCNT360) means that such TCNT will be formed from the relative ZSWCNT(z-$C_{360}H_{12}$) by means of condensation all the CH bonds follow the $n(t)$-Möbius-twisted in two side of TCNT, where $n(t)$ is an integer. As $n(t) = 0$ and 1, the $M^{n(t)}$ TCNT360 will be the HTCNT360 and MTCNT360, respectively. As $n(t)$ will be the opposite numbers with the same absolute value, the relative TCNT ought be the optical enantiomer each other. When the ZSWCNT(z-$C_{360}H_{12}$) is curled to from the $M^{n(t)}$TCNT, the β-angle will be twisted

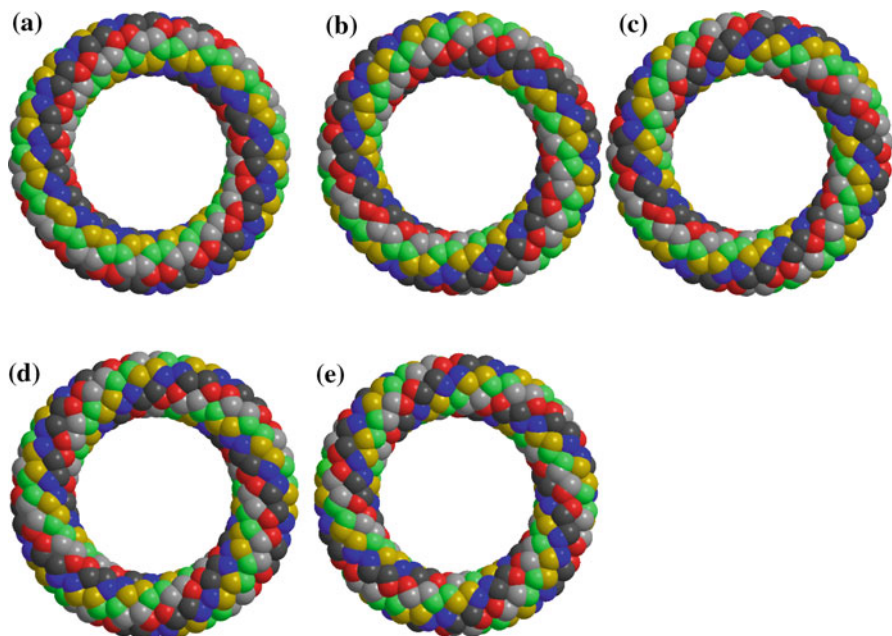**Fig. 20** The space filling graphs of the $M^{n(t)}$TCNT360 molecular structure. (**a**) $n(t) = 2$, (**b**) $n(t) = 3$, (**c**) $n(t) = 4$, (**d**) $n(t) = 5$, (**e**) $n(t) = 6$

the $n(t)$ π (in accordance with the torus orthogonal coordinate system the β-angle rotate $n(t)$ π). All of the MH-rectangles in z-$C_{360}H_{12}$ ought to be made $n(t)$ time Möbius-twisted and then butt joint. Similar as the Möbius-strip band molecule, such molecule may be called the Möbius-strip tube molecule. It is notable that the relative ZSWCNT will be not provided with the optical activity. It means that the optical activity structure is not owing to the mismatch of α-angle but to the mismatch of β-angle. In this paper we will analyse the case of $n(t) > 0$, mainly.

As shown in Fig. 20, there are the space filling graphs of $M^{n(t)}$ TCNT360 molecular structure with the $n(t) = 2$ to 6. The various color spherules denote the carbon atoms to make a distinction between various MH-rectangle boundaries of relative Möbius-strip band which these atoms belong to. As for the space filling graphs of the $M^{n(t)}$TCNT360 molecular structure with $n(t) = -2$ to -6, it is easy obtained from the mirror image of Fig. 20, and they are omitted here.

For the geometrical characteristic of $M^{n(t)}$TCNT, it is also suitable to analyse using the torus orthogonal curvilinear coordinate system (L, α, β) [45,46]. As shown in figure, every such molecule would include six Möbius-strip bands and each Möbius-strip band would be formed from identical MH-rectangle. All of the Möbius-strip bands in a certain molecule include an identical basic circle. As the $n(t)$ is odd number the up- and down-boundary will be connected to form a continuous boundary closed curve, but as $n(t)$ is even number the up- and down-boundary will be to form the boundary closed curves respectively (may be to form the catenane). Such boundary curves are provided to the boundary curve as the same topologic structure of usual Möbius-strip band boundary [45,46] with the same $n(t)$ value.

Corresponding to the fuzzy symmetry in relation to the CSR transformation of z-$C_{360}H_{12}$. according by means of the Eq. (2), would be $T(1.5jl_{cc})C(2\pi i/12)$, it ought to be change to the prefect TSR transformation:

$$\text{TSR}(L, \Delta\alpha, \Delta\beta) = \text{TSR}(L, 2\pi j/30, 2\pi[i/12 + n(t)j/60]), \qquad (13)$$

where the i and j will be the same odevity. It means that the $M^{n(t)}$TCNT360 will be provided to the group symmetry included the element as shown in Eq. (13):

$$\text{TSR}_{n(t)\mathbf{M}}(j, i) = \{\text{TSR}(L, 2\pi j/30, 2\pi[i/12 + n(t)j/60]);$$
$$i \text{ and } j \text{ with same odevity}\}. \qquad (14)$$

Now we analyse some important cyclical subgroups of the $\text{TSR}_{n(t)\mathbf{M}}(j, i)$ in relation to the $M^{n(t)}$TCNT360. For $\text{TSR}_{n(t)\mathbf{M}}(j, i)$, the transformation cyclical subgroup which do not refer to the MH-rectangle the carbon atoms being may be denoted as:

$$\text{TSR}_{n(t)\mathbf{M}}(2j, 0) = \{\text{TSR}(L, 4\pi j/30, 4n(t)\pi j/60); \ j = 0, 1, \ldots\ldots, J_M\}$$
$$= \{[\text{TSR}(L, 2\pi/15, n(t)\pi/15)]^j; \ j = 0, 1, \ldots\ldots, J_M\}, \quad (14a)$$

Such subgroup will include the rotation in relation to the α-angle. It is notable that it is not only pure in relation to α-angle but also to β-angle rotation. As $n(t)$ is even, $J_M = 15$ and $\text{TSR}_{n(t)\mathbf{M}}(2j, 0)$ ought to be 15 order subgroup. As $n(t)$ is odd, $J_M = 30$ and $\text{TSR}_{n(t)\mathbf{M}}(2j, 0)$ ought to be 30 order subgroup.

For $\text{TSR}_{n(t)\mathbf{M}}(j, i)$, the transformation rotation cyclical subgroup which only refer to the pure β-angle may be denoted as the $\text{TSR}_{n(t)\mathbf{M}}(0, 2i)$, that is a six-order subgroup. Such subgroup will be similar as Eq. (10b) in form, the group element will give rise to the atoms in $M^{n(t)}$TCNT would be transferred between the various MH-rectangle, and it is different from the usual rotation in point group, it is not the rotation along the fixed axis but along the basic circle circumference. Through such rotation the α-angle will remain unchanged. The J_M-order cyclical subgroup of $\text{TSR}_{n(t)\mathbf{M}}(j, i)$ which may be referred to the change of α- and β-angle, simultaneously, as follows:

$$\text{TSR}_{n(t)\mathbf{M}}(j, j) = \{\text{TSR}(L, 2\pi j/30, 2\pi[j/12 + jn(t)/60]); \ j = 0, 1, \ldots\ldots, J_M - 1\}$$
$$= \{[\text{TSR}(L, 2\pi/30, 2\pi[1/12 + n(t)/60])]^j; \ j = 0, 1, \ldots\ldots, J_M - 1\}. \quad (14b)$$

As $j = 30$, the element of $\text{TSR}_{n(t)\mathbf{M}}(j, j)$ will be the $\text{TSR}(L, 2\pi, 2\pi[5/2 + n(t)/2])$, then $\Delta\alpha = 2\pi$ the α-angle rotate one circle, and $\Delta\beta = [5 + n(t)]\pi$ the β-angle rotate $[5 + n(t)]/2$ circles. It means that as $n(t)$ is odd, the β-angle rotate integer circles, $\text{TSR}_{n(t)\mathbf{M}}(j, j)$ ought to be the 30-order cyclical subgroup ($J_M = 30$), however as $n(t)$ is even, the β-angle rotate semi-integer, $\text{TSR}_{n(t)\mathbf{M}}(j, j)$ would be the 60-order cyclical subgroup ($J_M = 60$). It is notable that where the dependence on the $n(t)$odevity will be different for the subgroups $\text{TSR}_{n(t)\mathbf{M}}(j, j)$ and $\text{TSR}_{n(t)\mathbf{M}}(2j, 0)$.

There are six topologic homeomorphous Möbius-strip bands in every $M^{n(t)}$ TCNT360 molecule and 60 carbon atoms included in each band. These bands may be
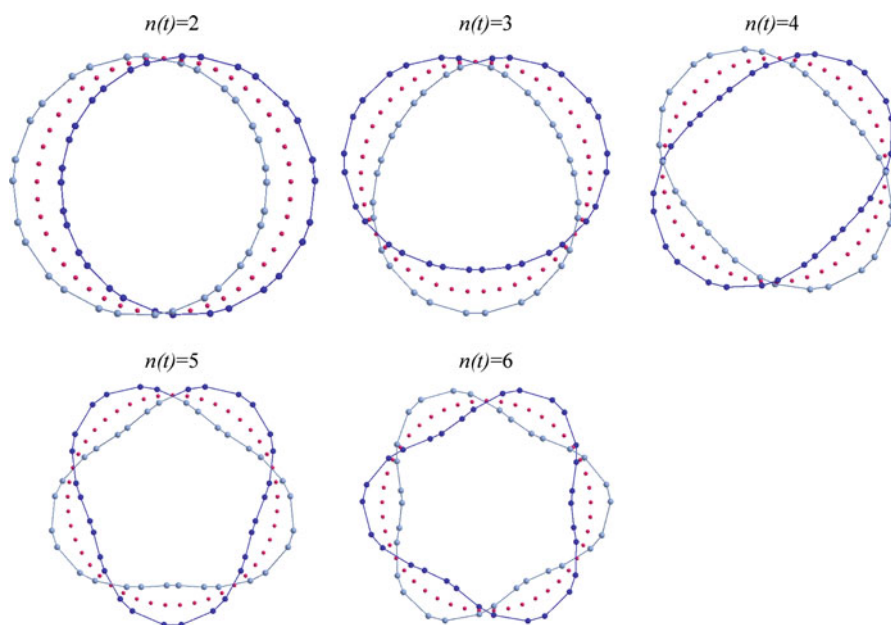
Fig. 21 The Möbius-strip bands of $M^{n(t)}$TCNT360

provided with the similar shape elementary and may be related to each other through a certain symmetry transformation. As shown in Fig. 20, it seems that these TCNT may provided with the symmetry of usual point group $D_{n(t)}$, but it may be not the perfect symmetry [45,46]. According to the usual point group theory, the $M^{n(t)}$TCNT360 molecule my be provided the perfect symmetry of the point group $D_{(n(0),n(t))}$. Owing to where the $n(0) = 15$, for $n(t) = 2, 3, 4, 5$ and 6, they will be provided only with the perfect symmetry of the point group C_2, D_3, C_2, D_5 and D_3, respectively. It is apparent that where every Möbius-strip band boundary will be formed from one and only one HM-rectangle boundary. As $n(t)$ is odd, the up- and down-boundary of the HM-rectangle will joint to form a continuous boundary curve, as $n(t)$ is even, the up-and down-boundary of the HM-rectangle will be maintained as two separated boundary curves. Each of six Möbius-strip bands for a certain $M^{n(t)}$TCNT360 molecules would be similar as the topologic uniformity. As shown in Fig. 21, there are the Möbius-strip bands in relation to the five kinds of $M^{n(t)}$TCNT360 shown in Fig. 20. Similarly, we may get the figures in connection with the SALC-carbon atoms to replace the carbon atomic pairs in structural unit, but there are omitted here.

By the way, the Möbius- and Hückel-strip bands of the TCNT as shown in Figs. 17, 19 and 21, may reflect the symmetry in relation to the α-angle rotation group **TSR**(j, j) of these strip bands which formed from relative MH-rectangles. As there is only one closed curve in boundary, the relative symmetry transformation group will be a **TSR** cyclical transformation group, the closed curve run through carbon atonic pair number may denoted the order of such **TSR** group. To make such graph, we may be using one point to replace the carbon atom-pair (the structure unit). One set of the carbon

atoms in a certain position of every structure unit may be constructed a SA-atom set in relation to such symmetry transformation. Where there are two such SA-atom sets. As there are two closed curves in boundary, the relative symmetry transformation group ought to be not a single **TSR** cyclical transformation, but include a **TSR** cyclical subgroup, where two closed curves may be corresponding to one cyclical subgroup and its coset, respectively.

3.4 Symmetry and fuzzy symmetry of fractal-twisted Möbius-TCNT360

By means of torus orthogonal curvilinear coordinate, plane molecular follow the MH-rectangle curl to form the Hückel or various Möbius-strip band as the α-angle rotate half-cycle (180°; π radian) and adjoint with the β-angle change $n(t)180°$, the molecular skeleton may recover, such molecule may be provided the relative symmetry. Where the $n(t)$ would be the integer (include the null, positive and negative integer). On the other hand, the $n(t)$ may also be the fractional number, such molecule may be called the fractal-twisted Möbius-TCNT. For example, the TCNT360 formed from ZSWCNT(z-$C_{360}H_{12}$), as the CNT must only be twisted n_{ft} (integer) times 60°, then it may be formed the $M^{n(t)}TCNT360 = M^{n(ft)/3}TCNT360$. As the $n(ft)$ don't include the factor 3, the $n(t)$ will no longer be the integer, such TCNT may be called the fractal-twisted Möbius-TCNT. In principle, the in relation with the TSR symmetry transformation which the fractal-twisted Möbius-TCNT360 may be also denoted by Eq. (13), but where $n(t)$ ought to be not the integral but the fraction value. The relative **TSR** group would be the 90 order group. It may be but not always the 90 order cyclical group. It may be 90 order cyclical group but also may be a 90 order symmetry including a 45 order cyclical subgroup. For $M^{n(ft)/3}TCNT360$, the relative **TSR** group as:

$$\mathbf{TSR}_{n(t)\mathbf{M}}(j, i) = \{TSR(L, 2\pi j/30, 2\pi[i/12 + n(ft)j/180]);$$
$$i \text{ and } j \text{ with same odevity}\}. \tag{15}$$

As the $n(ft) = 1$ and 2, they will respectively be:

$$\mathbf{TSR}_{(1/3)\mathbf{M}}(j, i) = \{TSR(L, 2\pi j/30, 2\pi[i/12 + j/180]); i \text{ and } j \text{ with same odevity}\} \tag{16a}$$

$$\mathbf{TSR}_{(2/3)\mathbf{M}}(j, i) = \{TSR(L, 2\pi j/30, 2\pi[i/12 + j/90]); i \text{ and } j \text{ with same odevity}\}. \tag{16b}$$

The cyclical subgroup with $i = 0$ will be:

$$\mathbf{TSR}_{(1/3)\mathbf{M}}(2j, 0) = \{TSR(L, 4\pi j/30, 4\pi j/180); j = 0, 1, \ldots\ldots, 89\}$$
$$= \{[TSR(L, 2\pi/15, \pi/45)]^j; j = 0, 1, \ldots\ldots, 89\} \tag{17a}$$

$$\mathbf{TSR}_{(2/3)\mathbf{M}}(2j, 0) = \{TSR(L, 4\pi j/30, 8\pi j/180); j = 0, 1, \ldots\ldots, 44\}$$
$$= \{[TSR(L, 2\pi/15, 2\pi/45)]^j; j = 0, 1, \ldots\ldots, 44\} \tag{17b}$$

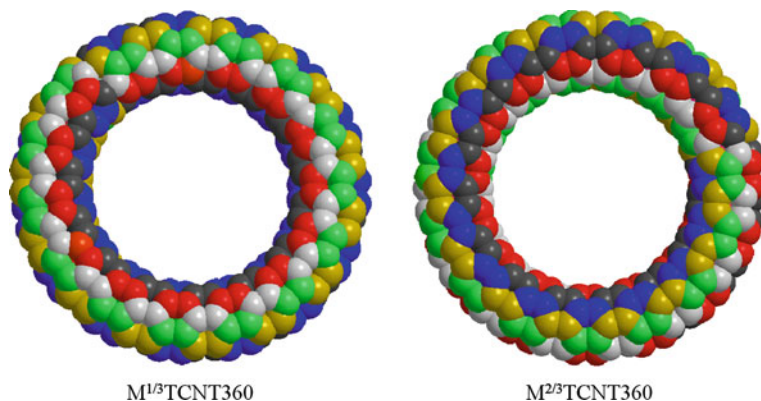M$^{1/3}$TCNT360   M$^{2/3}$TCNT360

Fig. 22 The space filling graph of the molecular skeleton structure in M$^{n(ft)/3}$TCNT360

As $j = 45$, the elements in Eqs. (17a) and (17b) ought to be the TSR(L, 6π, π) and TSR(L, 6π, 2π), respectively. The latter will be equivalence to the identity element, but the former will not be. It means that the **TSR**$_{(1/3)\mathbf{M}}(2j, 0)$ will be the 90-order cyclical group, but the **TSR**$_{(2/3)\mathbf{M}}(2j, 0)$ be the 45-order cyclical group. In relation to $i = j$, the:

$$\mathbf{TSR}_{(1/3)\mathbf{M}}(j, j) = \{\text{TSR}(L, 2\pi j/30, 2\pi[j/12 + j/180]); \ j = 0, 1, \ldots\ldots, 44\}$$
$$= \{[\text{TSR}(L, \pi/15, \pi j[8/45])^j; \ j = 0, 1, \ldots\ldots, 44\} \quad (18a)$$
$$\mathbf{TSR}_{(2/3)\mathbf{M}}(j, j) = \{\text{TSR}(L, 2\pi j/30, 2\pi[j/12 + j/90]); \ j = 0, 1, \ldots\ldots, 89\}$$
$$= \{[\text{TSR}(L, 2\pi/15, [17/90]\pi)]^j; \ j = 0, 1, \ldots\ldots, 89\}. \quad (18b)$$

It means that the **TSR**$_{(1/3)\mathbf{M}}(j, j)$ is the 45-order cyclical group, but the **TSR**$_{(2/3)\mathbf{M}}$ (j, j) is the 90-order cyclical group.

Above such **TSR**$_{(1/3)\mathbf{M}}$ and **TSR**$_{(2/3)\mathbf{M}}$ cyclical subgroups may be provided with various orders. It owing to that these two groups refer to three MH-rectangles of M$^{1/3}$TCNT360 and M$^{2/3}$TCNT360, respectively, and to form the relative Möbius-strip bands with various topologic characteristic. The Fig. 22 shows that the space filling graphs of the skeleton structure in M$^{1/3}$TCNT360 and M$^{2/3}$TCNT360. The various color balls may denote the carbon atoms in the boundary of various MH-rectangle. Where one Möbius-strip band may be composed with three MH-rectangles, every molecule may include two Möbius-strip bands. The Möbius-strip bands of such two molecules would be provided the various topological characteristic. Now we analyse their Möbius-strip band, respectively.

For the M$^{1/3}$TCNT360 molecule, there are two Möbius-strip band, every Möbius-strip band will be formed by means of three MH-rectangle, they include the carbon atoms with the serial number m in Fig. 1 being odd or even respectively, they are topology homeomorphous. Each Möbius-strip band may include 180 carbon atoms, every two carbon atoms compose a structure unit, corresponding to one 90 order **TSR** cyclical group. As shown in Fig. 23, there is the boundary of such Möbius-strip band. Where the Fig. 23a–c may show the relative top view, side view and oblique
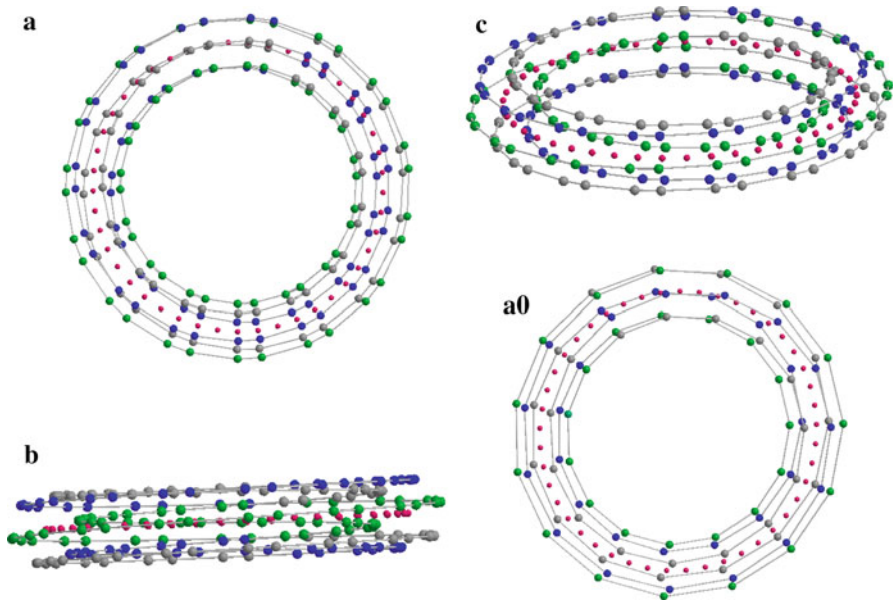
Fig. 23 The boundary of Möbius-strip band in $M^{1/3}$TCNT360. (**a**) top view, (**b**) side view, (**c**) oblique view, (**a0**) top view (with SALC-carbon atom)

view, respectively, meanwhile the Fig. 23a0 will show also the top view but using the SALC-atoms to replace the carbon atomic pair in structural unit.

It is notable that there are the continuous closed curves in three-dimensional space. Three different color curve section and the through globules are denoted that originated from different MH-rectangles boundary. Each two closer atoms compose one structure unit and there are 180 carbon atoms to compose 90 structure units. The mid red globules may joint to form the basic circle. As every structure unit along Möbius-strip band boundary move to next structure unit, that is corresponding to one time of TSR symmetry transformation and to compose the 90-order cyclical group. The Möbius-strip band boundary will be around the basic circle, the up- and down-boundary of a certain MH-rectangle may be through the plane of basic circle. The up- and down-boundary of a certain MH-rectangle they ought to not joint in the Möbius-strip band.

As for the $M^{2/3}$TCNT360 molecule, there are also two Möbius-strip band, every Möbius-strip bandwill be formed by means of three MH-rectangle, they include the carbon atoms with the serial number m in Fig. 1 being odd or even respectively, they are topology homeomorphous. Each Möbius-strip band may include 180 carbon atoms, every two carbon atoms compose a structure unit, corresponding to one 90 order **TSR** group, but it is not one 90 order cyclical group. Though such two Möbius-strip bands in $M^{2/3}$TCNT360 are topologic homeomorphous each other, but they are not topologic homeomorphous with the Möbius-strip bands in $M^{1/3}$TCNT360. As shown in Fig. 24, there is the boundary of such Möbius-strip band. Where the Fig. 24a–c may show the relative top view, side view and oblique view, respectively, meanwhile the Fig. 24a0 will show also the top view but using the SALC-atoms to replace the carbon atomic pair in structural unit.
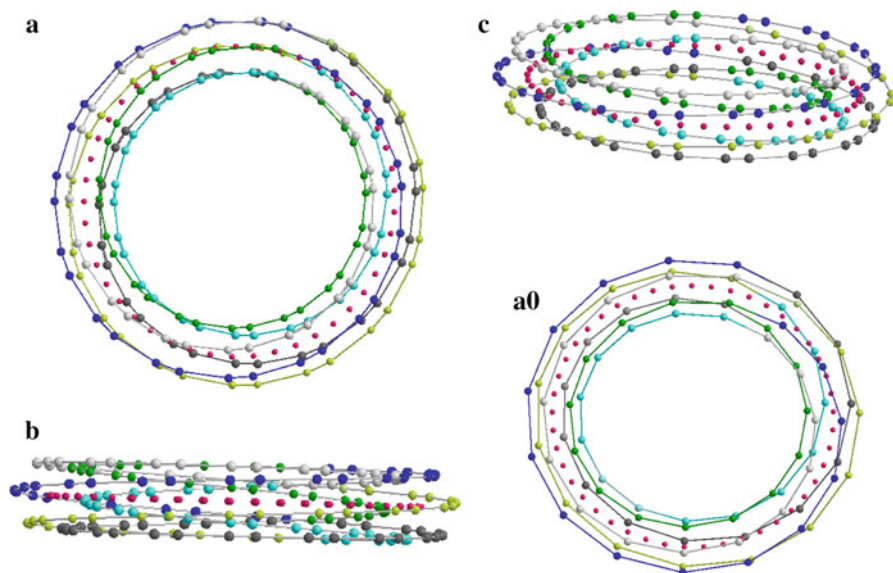
Fig. 24 The boundary of Möbius-strip band in $M^{2/3}$TCNT360 (**a**) *top view*, (**b**) side view, (**c**) oblique view, (**a0**) top view (with SALC-carbon atom)

It is notable that there is not a continuous closed curve in three-dimensional space, but there is a catenane composed by means of two complex closed curves. Above closed curves are formed by among the up- or down-boundary of three MH-rectangle. Three different color curve section and the through globules are denoted that originated from different MH-rectangles boundary. Each two closer atoms compose one structure unit and there are 90 carbon atoms to compose 45 structure units in one closed curve, and correspond to one 45-order cyclical subgroup and one relative coset. The mid red globules may joint to form the basic circle. Anyone closed curve of the Möbius-strip band boundary may be around the basic circle and through the plane of basic circle.

By the way, as shown in the figures A0 of above Figs. 17, 18, 23 and 24 the SALC-atoms linked by using Hückel- or Möbius-strip boundary, they seem as two or one rosary bunch, and may reflect the relative TSR group symmetry.

As for the difference between the Möbius-strip bands of these TCNT, there are two similar boundary closed curves for $M^{2/3}$TCNT360 and only one closed curve for $M^{1/3}$TCNT360. Owing to both two closed curves of $M^{2/3}$TCNT may pass through the basic circle plane, the Fig. 24 not clear. We make the top view graph with one of these two closed curves in the Fig. 24a, a0 (as shown in Fig. 25a and b, respectively).

For such different characteristic of the Möbius-strip band of the $M^{2/3}$TCNT360 and $M^{1/3}$TCNT360, it is easy to understand. The Möbius-strip bands of both these two molecules are formed from MH-rectangles, the dihedral angle for these rectangles will be 60°, by using the torus curvilinear coordinate system, the points with the same α-value in various MH-rectangles, their β-value would be differ 60°. For the points in Möbius-strip band boundary of $M^{1/3}$TCNT360, they forward lead the α-value change 360° and the relative structure units remove 15 times, meanwhile the β-value change 60°, and then arrive at another MH-rectangle boundary. When and only when through
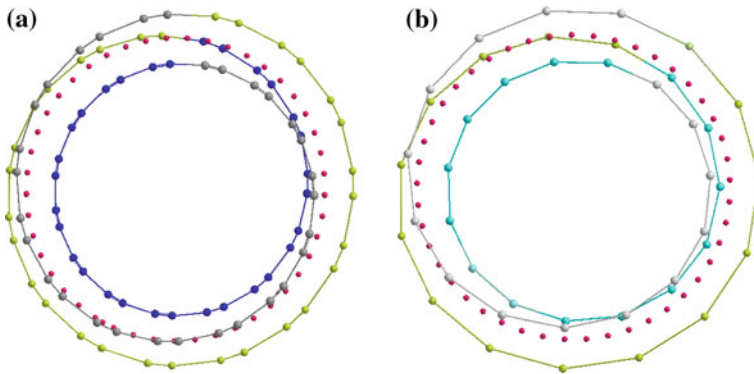
Fig. 25 One closed curve (*top view*) of Möbius-strip band boundary in $M^{2/3}$TCNT360. (**a**) the carbon atomic pair for each structural unit, (**b**) one SALC-carbon atom for each structural unit

six times such variation include α-value change with six times 360° and β-value change with one time 360°, the point in Möbius-strip band may through all of the boundary which ought to be formed from the all up- and down-boundary of three MH-rectangles and return to the original position. That is one 90-order cyclical group. On the other hand, for the points in Möbius-strip band boundary of $M^{2/3}$TCNT360, they forward lead the α-value change 360° and the relative structure units remove 15 times, meanwhile the β-value change 120°, and then arrive at another MH-rectangle boundary. When through three times such variation include α-value change with six times 360° and β-value change with one time 360°, the point in Möbius-strip band may through the boundary which ought to be formed from the up- or down-boundary of three MH-rectangles and return to the original position. That is one 45-order cyclical group.

Although here we only analyse the TCNT360, it is no difficult to other carbon nanotube, TCNT, by the similar way. Above TCNT360 are based on the ZSWCNT(z-$C_{360}H_{12}$) which would be provided with the D_{rh} symmetry. The ZSWCNT shown in Fig. 1, as the maximum value (N) of the serial number n is even number, the ZSWCNT will be connected the relative carbon atoms of the CNT tube sides with same odevity of the serial number m to compose the TCNT, but as the maximum value (N) of the serial number n is odd number, the ZSWCNT will be connected the relative carbon atoms of the CNT tube sides with different odevity of the serial number m to compose the TCNT. For the latter cases, the formed TCNT can not be the Hückel-type (HTCNT), it must be the fractal twisted $M^{n(ft)}$TCNT. Such ZSWCNT which would be provide with the point group D_{rd} symmetry, the relative Möbius-strip band may be formed from more MH-rectangle.

3.5 Symmetry and fuzzy symmetry of Hetero-TCNT

The torus carbon nanotube (TCNT) would be the pure carbon molecule. As some carbon atoms among the TCNT are substituted by non-carbon atoms, it may be called the hetero-torus carbon nanotube. Now we consider the hetero-TCNT360, as shown in Fig. 2, the hetero-atoms (X and Y) replace some carbon atoms of the ZSWCNT(z-$C_{360}H_{12}$), two sides of such hetero-CNT combined to form the hetero-
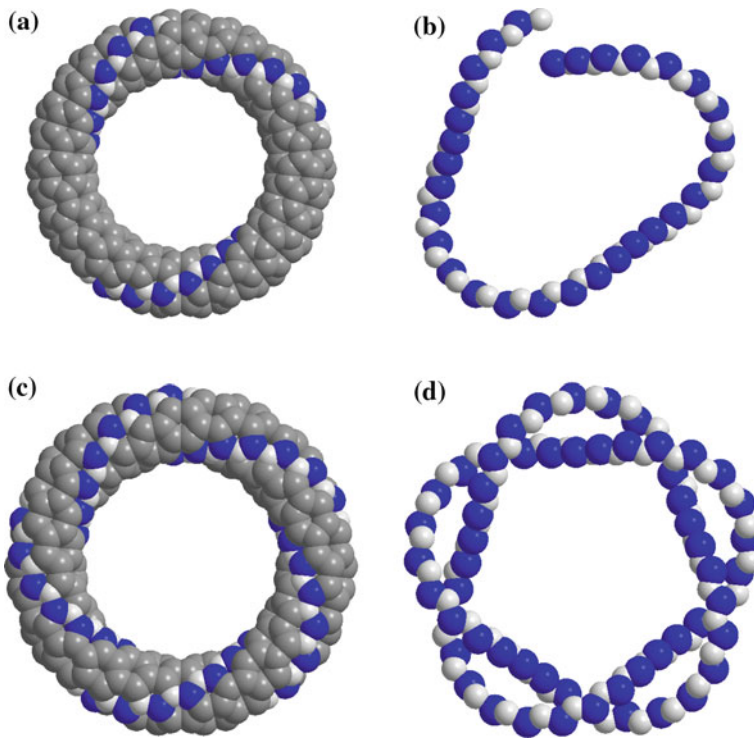
Fig. 26 The molecular skeletons of hetero-HTCNT360 and hetero-HTCNT360-2 and the hetero-atoms among them. (**a**) hetero-HTCNT360, (**b**) the hetero-atoms in hetero-HTCNT360, (**c**) hetero-HTCNT360-2, (**d**) the hetero-atoms in hetero-HTCNT360-2

TCNT360, with the formula as $C_{300}X_{30}Y_{30}$. by means of the Hückel model, we may get the hetero-HTCNT as shown in Fig. 26a. For example, the X and Y may be the B and N atoms, respectively. It is notable that the goubles with various denoted various element atoms not all the carbon atoms. Where the X and Y atoms distribute in the TCNT wall with the helix form, using the torus orthogonal curvilinear coordinate system to analyse the distribution curve as the α-angle changes one circle (2π radian or $360°$), the β-angle will be change two-and-half circles(5π), therefore the helix form distribution curve would be discontinuous, as shown in Fig. 26b. As above helix form distribution curve the α-angle changes two circles (the relative molecule denoted as hetero-HTCNT360-2), the β-angle will be change five circles, the relative curve may be all continuous. Such hetero-HTCNT360-2 molecule and the hetero-atoms among such molecule are shown in Fig. 26c, d, respectively. Owing to above dis-continuity destroy the symmetry of TCNT, as shown in Fig. 26a the hetero-HTCNT360 will be provided without the perfect symmetry in relation to the torus group or **TSR** group, but the hetero-HTCNT360-2 as shown in Fig. 26c will be with the symmetry of $\mathbf{TSR_H}(j, j)$ group, as Eq. (10c) denoted. As we want to eliminate such dis-continuity when α-angle change one circle, by means of Eq. (14b) the $\mathbf{TSR}_{n(t)\mathbf{M}}(j, j)$ requests that the $n(t)$ must odd number twisted HTCHT, the relative $M^{n(t)}$TCNT may be realized.
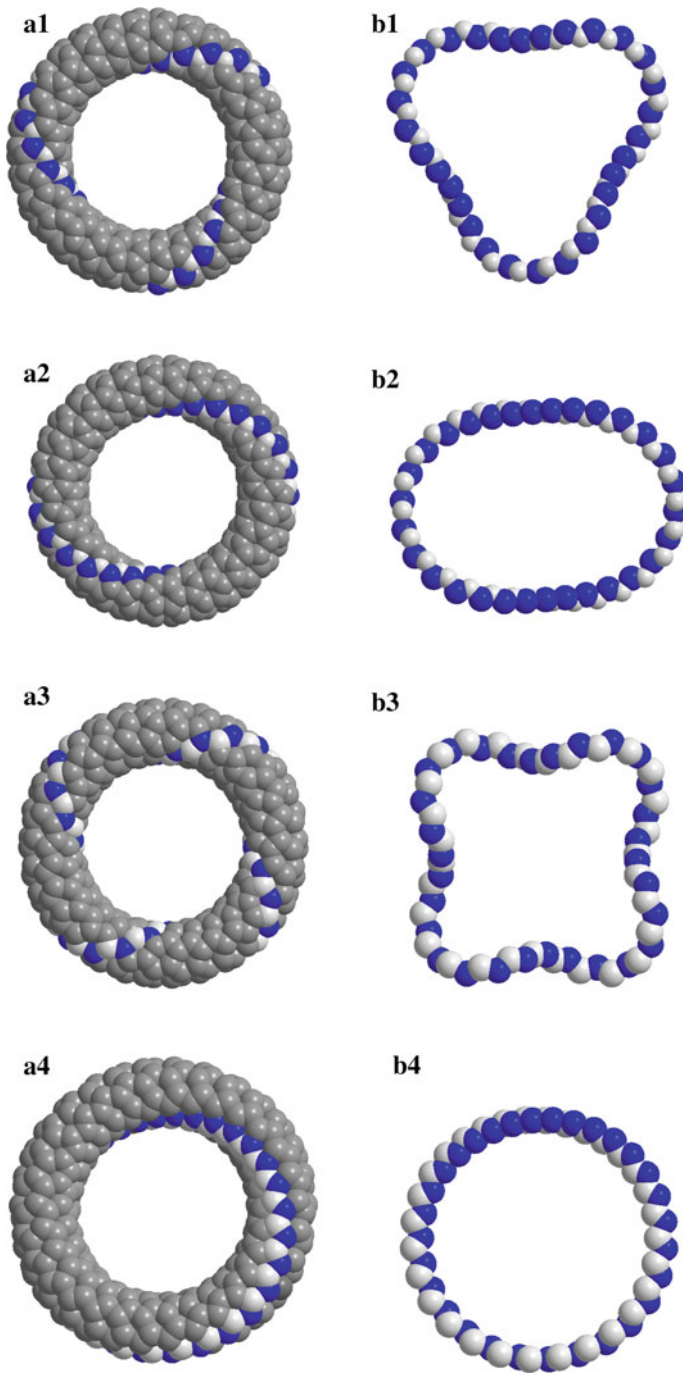
Fig. 27 Hetero-$M^{n(t)}$TCNT360 (**a**) and the hetero-atoms among them (**b**). (**a1**) hetero-MTCNT360, (**b1**) hetero-atoms in hetero-MTCNT360, (**a2**) hetero-M^{-1}TCNT360, (**b2**) hetero-atoms in hetero-M^{-1}TCNT360, (**a3**) hetero-M^3TCNT360, (**b3**) hetero-atoms in hetero-M^3TCNT360, (**a4**) hetero-M^{-3}TCNT360, (**b4**) hetero-atoms in M^{-3}TCNT360

As mentioned above, for eliminate such discontinuous it is odd number multi-twisted Möbius form to compose. Now we examine cases for along positive or negative direction with once or triple twisted. As the pure carbon TCNT the same multi-twisted with the opposite directions, they would be the optical enantiomer, however for the hetero-TCNT it will be more complex. For the once twisted MTCNT as the α-angle rotated one circle the β-angle will be twisted π radian and for hetero-HTCNT360 the hetero-atoms distribution as the α-angle revolve one circle the β-angle will be twisted 5π, therefore for the hetero-MTCNT as the α-angle revolve one circle the β-angle will be twisted 6π radian (three circles). Such hetero-MTCNT and the helix distribution of hetero-atom among may be shown in Fig. 27a1, b1, respectively. For hetero-M^{-1}TCNT with along negative direction once twisted as the α-angle revolve one circle the β-angle will be twisted 4 π radian (two circles). Such hetero-MTCNT and the helix distribution of hetero-atom among may be shown in Fig. 27a2, b2, respectively. Similarly, for the relative hetero-M^3TCNT and hetero-M^{-3} TCNT we may get the Fig. 27a3, b3, a4 and b4. According to Eq. (14b) as $n(t)$ equal to the odd number: 3, 1, −1 and −3, for α-angle change every circle the β-angle will follow twisted with the 4, 3, 2 and 1 circle, respectively, agree with the Fig. 27.

Such positive or negative directional twisted for the helical-structure of molecular skeleton may produce some important affect in molecular biology research. The relative title, e.g. the DNA topology, we will examine them in subsequent works.

Of course, for the various hetero-CNT to form the TCNT, as the α-angle change one circle the intersect value of β-angle may be not the integral multiples of π, and it may be in connection to the fractal twisted Möbius-model combination to eliminate discontinuity. The processing way will be the similar as above in principle. As mention above, as the CNT to form the TCNT, the primary fuzzy CSR symmetry may transform to a certain perfect TSR symmetry, for above hetero-TCNT it must be also satisfied the continuity condition of hetero-atom helix-distribution.

It is evident that though the TCNT composed by hexatomic ring mainly will be on the cards, but only by hexatomic ring would be difficulty. Owing to we examine the TCNT with the purpose of analyse the TSR symmetry that is suitable. Although the TCNT with such TSR symmetry may be not easy, but some torus non-carbon nano-tube [51] had been reported for which may be provided such symmetry. In especial, as more flexibility and weak bonds [52] included, such TSR symmetry and fuzzy symmetry may be appeared more possibility. In this paper using the TCNT as the example, we analyse the TSR symmetry and the relative multi- or fractal-twisted Möbius tubular molecular, such helix-structure molecules really exist in nature, but more complex than TCNT.

4 Conclusion

The carbon nanotube (CNT) carries a structure that is an approximate cylinder, and it may be analysed by fuzzy cylindrical group. For such fuzzy cylindrical group, the fuzzy higher-(>2)-fold screw rotation transformation and the related symmetry need to be examined, and this paper focuses on such symmetry analysis. Since the new millennium, the torus carbon nanotube (TCNT) became a hot topic. Such TCNT

with torus group symmetry possess some important application aspects in molecular science. On the symmetry and fuzzy symmetry of cylinder and torus CNT, we get some interesting results as the following:

1. For the single-walled carbon nanotube (SWCNT), there is an r-fold rotation axis, Cr, along central shaft, which is usually set as the Z-direction and analyzed by using the cylindrical coordinate system. According to general point group theory, the SWCNT molecules often possess D_{rh} or D_{rd} symmetry. We divide the elements of D_{2rh} point group into four subsets according to the intersection-union logic relationship among these point groups and analyse the related point symmetry and fuzzy point symmetry of SWCNT. As for the fuzzy space symmetry, SWCNT may be considered as the fuzzy cylindrical group, and for the corresponding symmetry transformation we mainly investigate the cylindrical screw rotation transformation (CSR), especially the higher (>2)-fold CSR, besides the point symmetry transformation, Generally speaking, CSR is the combination of the translation transformation and the rotation transformation. If the translation distance is null, the CSR will be the pure rotation transformation; and if the rotation angle is zero, the CSR will be the pure translation transformation.

   For the zigzag SWCNT (ZSWCNT), the period length of the relative translation transformation along the Z-direction is triple of CC bond length (l_{cc}). The translation length included in CSR is the integer multiples of $1.5l_{cc}$, and the rotation angle is integer multiples of $2\pi/(M-1)$, where $(M-1)$ represents the number of carbon atoms for each layer. The CSR transformation is the product of above transformation $T(1.5 jl_{cc})$ and rotation transformation $C(2\pi i/[M-1])$, where both i and j are integers with the same odevity. For the ZSWCNT with finite length, we could analyse the fuzzy symmetry of such molecular skeleton. For ZSWCNT with the formula of $C_{N(M-1)}H_{(M-1)}$ (shown in Fig. 1b), according to CSR(i, j) transformation, the membership function of such molecular skeleton would be independent of i and equal to $[(N-j)Z_C + Z_H]/[NZ_C + Z_H]$. If we ignore the small deviation of Z_H, it will be simplified as $1 - (j/N)$. When the range of all translation allowed (represented by N) is more than 10-fold of the distance of each translation (represented by j), the relative membership function would be more than 0.9, and the fuzzy space group symmetry could be seen as perfect. That is the same as our previous work [32,33]. For ASWCNT, we may get the similar result.

2. The SWCNT molecular skeleton carries the cylindrical group symmetry. To analyse such molecules, it is appropriate to use the cylindrical coordinate system. The corresponding MO belongs to a certain pure irreducible representation, but the SA-AO set component in a certain MO may be not unique and hence it is difficult to isolate the pure π-MO. Analysing the MO energy level will base on all MOs without dividing them into σ- and π-MO. Meanwhile the serial number of MO (denoted as J : MO and NBMO energy levels are separated by the order J) will be replaced by the relative serial number (denoted as J/Nc:Nc is the number of atoms in the SWCNT wall). For the ZSWCNTs with same pipe diameter (i.e. the same thickness) and different lengths, the distribution graph of MO energy versus relative serial number will roughly appear on an identical curve. Even when some of carbon atoms are replaced by heter-atoms the deviation will not deviate too

much. However, for the SWCNT with different pipe diameter, the deviation may be somewhat evident.

3. Although the MO in SWCNT would belong to the pure irreducible representation, the SA-AO set component in a certain MO may be not unique. By the cylindrical coordinate system to analyse zigzag- or armchair-SWCNT with same pipe diameter and different lengths, the distribution graphs of certain SA-AO (the 1S-, 2S-, 2Pz-, 2Pr-, 2Pt- of carbon atom and 1S-AO of hydrogen atom) set component versus the relative serial number will be similar, which is true especially to the MOs near the frontier MO which are usually considered as the π-MOs. Although it is not composed only by the Pr-AOs, the components of 2Pr will weigh more (may less 0.5). The distribution curves of the component of same kind SWCNT versus the relative serial number will be similar too.

4. For the fuzzy symmetry of the SWCNT, we mainly focus on analysing the relative cylindrical screw rotation (CSR) transformation symmetry. CSR may be denoted as the product of translation (T) and rotation (C). To SWCNT, the imperfect symmetry of CSR is usually caused by the imperfection of translation (T). The rotation (C) of the SWCNT skeleton may carry the perfect symmetry, but the SWCNT MO may belong to a two dimensional irreducible representation with higher-fold rotation (C). As for the single MOs that belong to two-dimensionality, the relative membership function may be less than one. It is not caused by the imperfect symmetry. On the other hand, owing to the molecular finiteness, the symmetry related to translation (T) would be imperfect. Both the skeleton and MO would be imperfect and the relative membership function would be less than one. The membership function related to CSR, which is the product of C and T, would be less than one in general. For the SWCNT molecular skeleton and the MOs that belong to the one-dimensional irreducible representation, the membership functions related to CSR with the same T but different C would be the same, however, for the single MO which belongs to the two-dimensional irreducible representation such membership functions may be somewhat different. For the MOs of ZSWCNTs with different lengths, the distributions of CSR membership function versus the relative serial number are interrelated.

5. Recently, the theory of torus carbon nanotube (TCNT) has attracted the interest of some chemists. Though it seems not easy to obtain TCNTs with ideal structures, the symmetry and fuzzy symmetry of the torus group and torus screw rotation, which is intrinsic to TCNT, indeed exist in nature. Thus we take TCNT as a typical example and provide foundation for further study of other relative systems. Similar to that the plane rectangle (denoted as MH rectangle) could curl to form the Hückel- or Möbius-strip band, the cylindrical SWCNT is composed of multi-MH rectangle. As SWCNT forms TCNT, the fuzzy CSR symmetry will transform into certain perfect TSR symmetry. The multi-MH rectangle in SWCNT will be combined to form multi-Hückel- or Möbius-strip band in a certain way. Meanwhile the intersecting line of the multi-rectangle, Z-axis, will transform to the common basic circle of those strip bands.

6. As SWCNT curls to form TCNT, one of the MH rectangles forms a Hückel-strip band, and all of the other MH rectangles will also form the Hückel-strip band. The set of all those MH rectangles forming the Hückel-strip band becomes the Hückel-

strip tube. As SWCNT curls form the TCNT, one of the MH rectangles forms an $n(t)$-fold twisted Möbius-strip band, and all of the other MH rectangles will also form $n(t)$-fold Möbius-strip bands. The set of all the MH rectangles forming the $n(t)$-Möbius-strip band set will be called $n(t)$-Möbius-strip tube. Such strip bands are topologically equivalent to the identity strip tube in the sense of structure. All of the Hückel-strip bands and even-fold twisted Möbius-strip bands include two closed curves (could be a catenane) as the boundaries. The odd-fold twisted Möbius-strip bands include only one closed curve (could be a knot) as the boundary. Such closed curve boundaries reflect the symmetrical characteristics of the torus group related to the strip bands, while the closed curves correspond to a cyclical group or a cyclical subgroup and its coset. The number of carbon atom pairs (the structure unit) is the order of the corresponding group, subgroup, or coset.

7. As SWCNT curls to form the TCNT, it also could form Möbius-strip tube by fractal twisting, among which a single Möbius-strip band might be formed by multi-MH rectangle while any single MH rectangle only forms into one Möbius-strip band. The corresponding order of the related TSR group may be multi-fold of that of the related MH-rectangle. Such Möbius-strip band may be bounded with one or two closed curves, and would not be drawn in Euclidean space easily.

8. As the hetero-SWCNT with a helical-structure distribution curls form the related torus hetero-CNT, a certain twisted way (in particular, the fractal twisted way) may often be necessary to maintain the continuity in tube side of the Möbius-strip tube. Such helical-structure substitute distribution and the twisted way will be interacted and make the helical-structure distribution more relax or less stiff. The related phenomena appear in some molecular biologic processes.

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