Fuzzy space periodic symmetries for polyynes and their cyano-compounds

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In our previous papers on the molecular fuzzy symmetry, we analyzed the basic characterization in connection with the fuzzy point group symmetry. In this paper, polyynes and their cyano-derivatives are chosen as a prototype of linear molecules to probe the one-dimensional fuzzy space group of parallel translation. It is notable that the space group is an infinite group whereas the point group is a finite group. For the fuzzy point group, we focus on considering the fuzzy characterization introduced due to the difference of atomic types in the monomer through point symmetry transformation in the beginning; and then we consider the difference between the infinity of space group and the finite size of real molecules. The difference between the point group and the space group lies in the translation symmetry transformation. This is the theme of this work. Starting with a simple case, we will only analyze the one-dimensional translation transformation and space fuzzy inversion symmetry transformation in this paper. The theory of the space group is often used in solid state physics; and some of its conclusions will be referred to. More complicated fuzzy space groups will be discussed in our future papers.

KEY WORDS: fuzzy symmetry, space periodic symmetry, polyynes and polyyne derivatives

1. Introduction

In theoretical chemistry, the fuzzy symmetry is an interesting area where a few important results [1–4] have been obtained. In our previous work [5–9] based on the study of the fuzzy symmetry character of molecules and their orbitals, we have analyzed the fuzzy symmetry of the point group. In addition, we have inquired into the time-space periodic symmetry and corresponding conservation
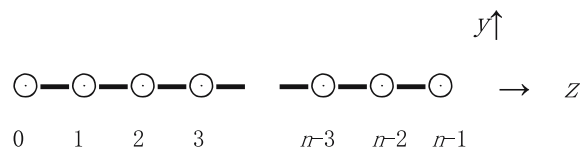
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Figure 1. The atomic serial numbers and Cartesian coordinates for the polyyne and their cyano-derivatives.

rules [10]. However, there is the ordinary symmetry but not the fuzzy symmetry in that paper. Now we are in a position to start examining the fuzzy symmetry related to the space group. Although we have analyzed the fuzzy symmetry related to the space group about $C_{16}H_2$ (polyyne with 16 C-atoms) [7] in brief, only the membership function for the individual molecule is introduced; more important area such as the representation components for the molecule orbitals (MO) has not been touched. This will be examined in this paper in some detail. The parallel translation fuzzy group symmetry of the one-dimensional lattice structure of the linear molecule will be dealt with in this work. More complex fuzzy space groups will be discussed in our future papers.

2.   The fuzzy symmetry of molecular skeletons

2.1.   Computational details

The atomic serial numbers and Cartesian coordinates for the molecules analyzed in this paper are shown in figure 1, where $\odot$ usually denotes the carbon atom, whereas it may also denote the nitrogen atom in the terminal (serial number: 0 and $n - 1$). As the terminal atom is a carbon atom, it may bind a hydrogen atom outside; when the terminal atom is a nitrogen atom, it may bind none. In figure 1, ▬ may be a single or triple bond. The z-axis and the molecular axis are taken to be the same; the x and y axes are orthogonal to each other but lie in the vertical plane of the z-axis. The MOs, the LCAO of valence shells, were calculated at a certain theoretical level using the Gaussian 98 program [11]. The π-MOs are combined using the p_x and p_y AOs. All the π-MOs are two-fold degenerate, *i.e.*, both their energies and membership functions are the same; and thus to analyze one of them should be adequate for our purpose. The σ-MOs are obtained by combination of the $sp(z)$-AOs, and these MOs are further from the frontier orbitals and their chemical activity will be less than that of the π-MOs. Like our previous paper [7, 8], and in this paper we will not analyze the σ-MOs.

The membership function of a molecular skeleton *related* to the symmetry transformation $\hat{G}$ [5–9] may be written as:

$$\mu_Y(\hat{G}/\mathbf{G}; M) = [\Sigma_J(Y_J \wedge Y_{GJ})]/[\Sigma_J(Y_J)] \tag{1}$$

where Y_J and Y_{GJ} are the criteria of atoms J and GJ, and GJ is produced from J atom though the symmetry transformation $\hat{G}$. Y may be the atomic number (Z_J) for the molecular skeleton. According to the LCAO-MO scheme, the ρth MO Ψ_ρ may be expressed as:

$$\Psi_\rho = \Sigma_J \Sigma_i a_\rho(J, i)\phi(J, i) \tag{2}$$

where $\phi(J, i)$ is the ith AO of the Jth atom; $a_\rho(J, i)$ is the corresponding coefficient, usually real number. The relative criterion Y_{Ji} for $\phi(J, i)$ can be taken as $a_\rho^2(J, i)$, and so equation (1) changes to:

$$\mu_Y(\hat{G}/G; M) = [\Sigma_J \Sigma_i(Y_{Ji} \wedge Y_{GJi})]/[\Sigma_J \Sigma_{Ji}(Y_{Ji})] \tag{3}$$

If there is only one AO in each atom to combine the MO, like the π-MO we analyzed in this paper, equation (3) will be reduced to equation (1).

2.2. The membership functions for molecular skeletons

Now we start to analyze the fuzzy symmetry of molecular skeletons. The MOs will be discussed in later sections.

If $\hat{G}$ is the parallel translation (towards the right or left) of m interatomic distance units, $\hat{T} - m$, the membership function of polyyne C_nH_2 molecular skeleton may be given as [7]:

$$\begin{aligned}\mu_{YT-m} &= [\Sigma_J(Y_J \wedge Y_{T-mJ})]/[\Sigma_J(Y_J)] \\ &= [\Sigma_J(Z_J \wedge Z_{T-mJ})]/[\Sigma_J(Z_J)] \\ &= [(n-m)Z_C + 2Z_H]/[nZ_C + 2Z_H] = (6n - 6m + 2)/(6n + 2) = \mu_{ZT-m}\end{aligned}$$
$$\tag{4a}$$
$$\tag{4b}$$

where Z_J is the atomic number. As shown in figure 2, the membership functions of some polyyne C_nH_2 molecular skeletons exist accompanying the transformation of translation of m interatomic distance units, $\hat{T} - m$. Figure 2(A) shows the relationship of membership function *vs.* n, and figure 2(B) membership function *vs.* m. As shown in figure 2(A), for translation transformation $\hat{T} - m$, when $n > 10m$, the membership function will be larger than 0.8. If we consider the polyyne as a one-dimensional crystal, the molecular crystal cell may has m atoms. As the crystal size is more than tenfold of the cell, the membership functions related to the space parallel translation group will be near or more than 0.9. It ought to be corrected in the ordinary crystal. As shown in figure 2, the membership function will be cut down as m increases or n decreases, and is the linearly dependent on m by the way. For the frontier orbitals [12] of $C_{16}H_2$, the dependence between the membership function and m is sawtooth-like [7]. This arises from the alternation of single- and tri- bonds. When we examine the MO fuzzy symmetry, the
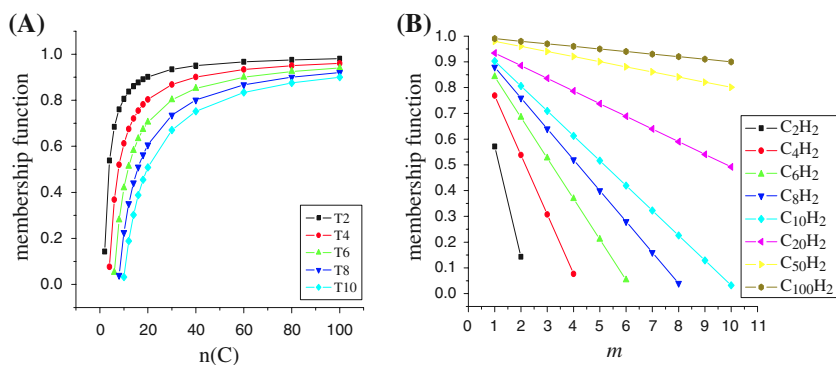
Figure 2. The membership functions for the some polyyne (C_nH_2) molecular skeletons related to m inter-atomic distance transformation ($\hat{T} - m$). (A) the membership functions *vs.* the numbers of C atoms, $n(C)$; (B) the membership functions *vs.* the numbers of translation inter-atomic distances, m.
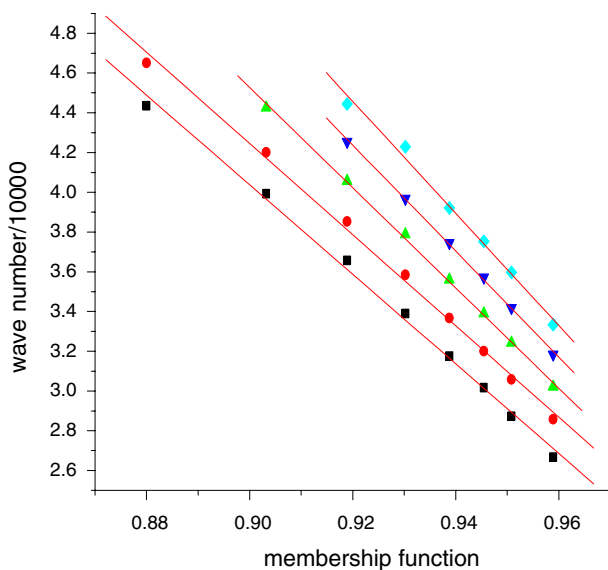

Figure 3. For the polyynes, the dependent relationship between the wave numbers [14] of the molecular electronic spectral bands and the membership functions in relation to the translation fuzzy symmetry for the polyyne molecules. In this figure, the various points relate to various spectral bands, and the corresponding regression lines are denoted.

atomic criteria include such alternation, but the atomic criteria for the molecular skeleton do not. Therefore, we choose m as an even number.

Using the total energies (*TE*) calculated at RB3LYP/cc-pVDZ level [13] and divided by the number ($l = n/2$) of $C \equiv C$ units in the polyyne, we had obtained the relationship for TE/l vs membership function in linearly dependent [7]. As shown in figure 3, such a dependent relationship occurs between the wave
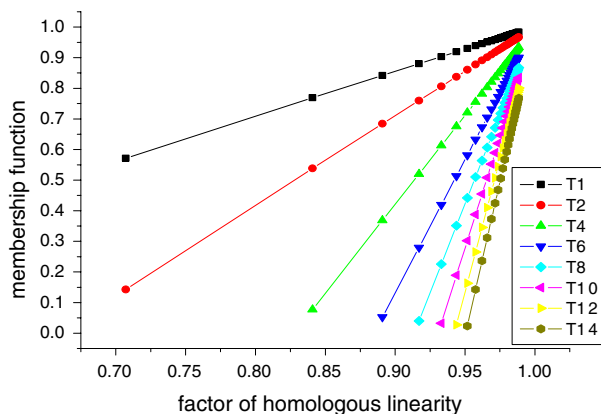
Figure 4. The rule of homologous linearity for polyyne membership function (μ_{ZT}). The number following T denotes the number of translation interatomic distance units (m).

numbers [14] of the molecular electronic spectral bands vs the membership functions related to the translation fuzzy symmetry for the polyyne molecules. Jiang has put forward a so-called 'the rule of homologous linearity' [14] to rationalize such relationships. He pointed out that there are homologous factors for homologous compounds, and there is a linear dependency between the properties of these compounds and their homologous factors. In fact, for the polyyne, there is also a linearly dependency between the membership functions of their translation fuzzy symmetry and their homologous factor. As shown in figure 4, all of the membership functions linearly depend on m. It may be useful to examine the homologous linearity further.

Equation (4a) can be applied to other molecules including other types of atoms with different corresponding criteria Y. For the polyyne, J is summed from serial number of the atom, -1 to n. We focus on the π-MO in this paper, and so the AO of the hydrogen atom is not needed. As one or both end carbon atoms are substituted by nitrogen atoms, the membership functions for the molecular skeleton related to the transformations $\hat{T} - m$ are given respectively as follows,

$$
\begin{aligned}
\mu_{YT-m} &= [\Sigma_J(Z_J \wedge Z_{T-mJ})]/[\Sigma_J(Z_J)] \\
&= [(n-m)Z_C + Z_H]/[(n-1)Z_C + Z_N + Z_H] = (6n - 6m + 1)/(6n + 2) \\
&= \mu^1_{ZT-m}
\end{aligned}
\tag{5a}
$$

and

$$
\begin{aligned}
\mu_{YT-m} &= [\Sigma_J(Z_J \wedge Z_{T-mJ})]/[\Sigma_J(Z_J)] \\
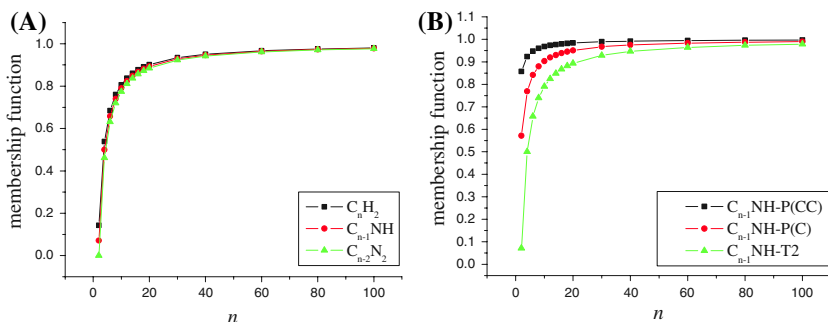&= [(n-m)Z_C]/[(n-2)Z_C + 2Z_N] = (6n - 6m)/(6n + 2) = \mu^2_{ZT-m}
\end{aligned}
\tag{5b}
$$

Figure 5. The membership functions for some polyynes (C_nH_2) and their cyano-derivatives ($C_{n-1}NH$ and $C_{n-2}N_2$) in relation to (A) translation transformation $\hat{T} - 2$ for C_nH_2, $C_{n-1}NH$ and $C_{n-2}N_2$; (B) the fuzzy space inversion transformation $\hat{P}$ about two various symmetrical centre, P(CC) and P(C), for $C_{n-1}NH$. For reference, the membership functions related to corresponding $\hat{T} - 2$ are also shown.

It is notable that here $m \neq 0$. Translation transformation towards right, $\hat{T} - m$, the criterion Y_J will be changed to Y_{J+m}, but that towards left, $\hat{T}-(-m)$, Y_J will be changed to Y_{J-m}. Though the $(Y_J \wedge Y_{J+m})$ and $(Y_J \wedge Y_{J-m})$ may be unequal, but $\Sigma_J(Y_J \wedge Y_{J+m})$ and $\Sigma_J(Y_J \wedge Y_{J-m})$ are equalization. This is because,

$$\begin{aligned} \Sigma_J(Y_J \wedge Y_{J+m}) &= (Y_0 \wedge Y_m) + (Y_1 \wedge Y_{m+1}) + (Y_2 \wedge Y_{m+2}) + \ldots + (Y_{n-m} \wedge Y_n) \\ &= (Y_m \wedge Y_0) + (Y_{m+1} \wedge Y_1) + (Y_{m+2} \wedge Y_2) + \ldots + (Y_n \wedge Y_{n-m}) \\ &= \Sigma_J(Y_J \wedge Y_{J-m}) \end{aligned} \tag{6a}$$

Figure 5(A) shows the membership functions for the polyyne (C_nH_2) and corresponding cyano-derivatives ($C_{n-1}NH$ and $C_{n-2}N$) related to the translation transformation $\hat{T} - 2$. It may be shown that the membership functions for these compounds are close.

According to equation (6a), it can be shown that the membership function of the inter-reversible symmetry transformation of m (integer) interatomic distance units towards right and left are the same. This satisfies the first condition for membership functions of fuzzy group [3, 15] and the condition of identity transformation ($m = 0$). However, another condition could not usually be satisfied,

$$\mu_{YT-(m+m')} \geqslant \mu_{YT-m} \wedge \mu_{YT-m'} \tag{6b}$$

and thus the fuzzy set of the space parallel translation transformation cannot form a fuzzy group.

For the above three molecular skeletons, the corresponding fuzzy parallel translation group may be denoted as follows by means of Zadeh's method [16, 17]:

$$\underset{\sim}{T}(C_nH_2) = \sum_m [(6n - 6m + 2)/(6n + 2)]/[\hat{T} - m] \tag{7a}$$

$$\underset{\sim}{T}(C_{n-1}NH) = \sum_m [(6n - 6m + 1)/(6n + 2)]/[\hat{T} - m] \tag{7b}$$

$$\underset{\sim}{T}(C_{n-2}N_2) = \sum_m [(6n - 6m)/(6n + 2)]/[\hat{T} - m] \tag{7c}$$

As all of the m related to the fuzzy parallel translation group are even, m in the summations of equation (7) will only run over the even number.

Another important fuzzy symmetry transformation for linear molecules is that of space inversion. Polyyne has a symmetric centre. The symmetric element of the conventional point group is definite, but the fuzzy symmetric element can be selected in various ways [7]. Membership functions corresponding to different ways differ, although all of them are between 0 and 1. They may be calculated using equation (1) with $\hat{G}$ taken as the space inversion transform ($\hat{P}$).

For the polyyne molecule (figure 1), the symmetric centre would be the position between $n/2 = q$-th and the $(q + 1)$-th C atoms. If q is odd the centre will be on a triple $C \equiv C$ bond, and if q is even the center is on a single C–C bond. As the polyyne molecule is composed of infinite $C \equiv C$ units, it can be thought as a one-dimensional infinite crystal formed by such $C \equiv C$ cells. The symmetric centre may be between any two consecutive C-atoms, and so there are infinite symmetric centre. Since the polyyne molecule is composed of finite $C \equiv C$ units, the common symmetric centre is unique, but the fuzzy symmetric centre can be selected in various ways. For such fuzzy symmetric centre, the relative membership functions will be between the 0 and 1. Meanwhile, the membership function will become smaller as the distance between fuzzy centre and common symmetric centre increases. For the polyyne molecule composed of n C-atoms, when the fuzzy symmetric centre lies l C-atoms away from the common symmetric centre, the membership function related to the fuzzy symmetric centre can be obtained as follows:

$$\mu_{YP(l)} = [\Sigma_J(Y_J \wedge Y_{P(l)J})]/[\Sigma_J(Y_J)] \tag{8a}$$

As the criteria are the atomic numbers, we get:

$$\mu_{YP} = [\Sigma_J(Z_J \wedge Z_{P(l)J})]/[\Sigma_J(Z_J)] = [2\{(n/2) - l\}Z_C + 2Z_H]/[nZ_C + 2Z_H]$$
$$= [6n - 12l + 2]/[6n + 2] = \mu_{ZP} \tag{8b}$$

As $l=0$, it will be the common symmetric centre, and the membership function is one. On the other hand, the membership function for the identity transformation is also one. Interestingly, equations (8a, b) and (4a, b)

are similar. If the distance between fuzzy symmetric centre and common symmetric centre is l C-atoms, the membership function of such fuzzy space inversion transformation ought to be equal that related to the translation of a polyyne with m C $\equiv$ C units (*i.e.*, $m = 2l$ atoms). It is clear that this conclusion can only be established when the common symmetric centre exists; otherwise the distance from the common symmetric centre cannot be determined. As an example of dicyano-polyyne molecular skeletons, if the fuzzy symmetric centre is j C-atoms from the common symmetric centre, the membership function related to the space inversion transformation will be $(6n - 12j)/(6n + 2)$, and if $m = 2j$, it will be the same as that in equation (5b). However, for corresponding monocyano-polyyne molecular skeleton, there is no common symmetric centre, we can only analyze its fuzzy symmetric centre. As shown in figure 1, if the nitrogen atom is assigned serial number $J = 0$, and the carbon atom that links an outside hydrogen atom $J = n - 1$, the fuzzy symmetric centre, P(CC), is between two carbon atoms with serial numbers $J = q - 1 = (n/2) - 1$ and $J = q = (n/2)$, and its corresponding membership function is $6n/(6n + 2)$. However, if the fuzzy symmetric centre, P(C), of the same molecule is set on the carbon atom with $J = q = (n/2)$, the relative membership function is $(6n - 4)/(6n + 2)$. Both membership functions will be between the 0 and 1, as shown in figure 5(B) for those related to the fuzzy space inversion transformation $\hat{P}$ about these two fuzzy symmetric centers of monocyano-polyyne molecules. For reference, the membership function corresponding to translation transformation $\hat{T} - 2$ was shown in this figure.

3.   The membership functions for molecular orbitals

3.1.   Primary analyze

The MOs of the polyyne derivatives may be analyzed similarly as in section 2.2, but atomic number Z (as the atomic criteria Y of the molecular skeleton) must be changed to the atomic criteria of the MO as in section 2.1. Since the criteria of the same atoms can be different, therefore the calculation of membership functions for MOs will be more complicated than that for the molecular skeleton. The square of the LC-p_x or p_y AO coefficient was used as the atomic criterion of the π-MO, whereas the summation of the square of LC-s AO coefficients and the square of LC-p_z AO coefficients for the σ-MO was used as the atomic criterion [5–6] of the σ-MO.

As shown in the previous paper [7], for the HOMO and LUMO of hexadec-polyyne, $C_{16}H_2$, the membership functions related to transformation $\hat{T} - m$ decrease saw-toothedly as m increases. This arises from the alternation of single- and triple-bonds. The alternation effect is naturally incorporated in the LCAO coefficients of the MO, and reflected by the membership function
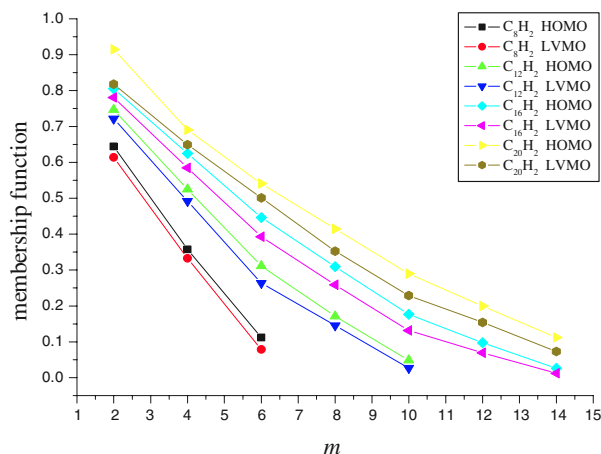
Figure 6. The membership functions in relation to the fuzzy translation for the HOMO and LUMO (at HF/STO-3G level) of various polyyne molecules.

although it has not been introduced directly into the function. However, the membership function for the molecular skeleton does not incorporate such effect, and so it depends on m smoothly (*i.e.*, linearly). Other molecules may also involve in the alteration of bond-lengths, and such effect may be merged into the atomic criteria of MO too. Such phenomenon means that the corresponding one-dimensional translation unit ought to include two inter-atomic distances. In other words, the one-dimensional lattice cell including two atoms, and m will be an even number for transformation $\hat{T} - m$. In this paper, therefore, we often analyze the case of even m.

The membership function related to the fuzzy translation transformation for some frontier MOs of the polyyne obtained at HF/STO-3G level is shown in figure 6. Each π-MO relates only to one AO from every atom. It is no sawtoohed as [7] if all of m are even numbers. As shown in figure 6, for the same polyyne molecule, the membership function of HOMO will be larger than that of LUMO. In addition, the membership function will decrease obviously with the increase of translation magnitude m. As the same m value, the smaller the polynne molecule (*i.e.*, smaller n) ought to be the less the membership function.

3.2. The membership functions for MOs of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$

Here the 16-carbon-polyyne ($C_{16}H_2$) and their cyano-derivatives with one or both ethynyls (-C $\equiv$ CH) substituted by -C $\equiv$ N, *i.e.*, H(C $\equiv$ C)$_7$(CN) or (C $\equiv$ C)$_6$(CN)$_2$, are taken as the prototypical. We also consider only transformation $\hat{T} - m$ with even m. To start with, as above we calculate and examine the membership functions of certain frontier MOs of $C_{16}H_2$ related to the trans-
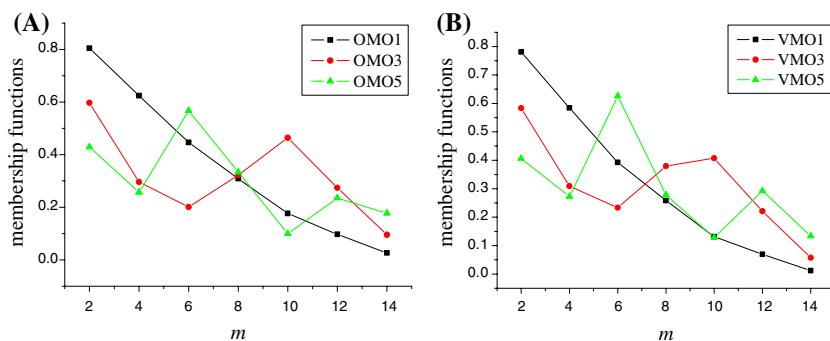
Figure 7. The membership functions related to the fuzzy translation transformations, for certain MOs of polyyne $C_{16}H_2$ at HF/STO-3G level.

Table 1
The membership functions for some MOs of $C_{16}H_2$ in relation to the fuzzy translation transformations*

	OMO			VMO		
m in $\hat{T} - m$	OMO-1&2	OMO-3&4	OMO-5&6	VMO-1&2	VMO-3&4	VMO-5&6
0	1	1	1	1	1	1
2	0.75685	0.59399	0.52261	0.68042	0.53877	0.51878
4	0.80483	0.59718	0.42912	0.78071	0.58329	0.40628
6	0.62460	0.29615	0.25652	0.58446	0.30924	0.27251
8	0.44659	0.20081	0.56732	0.39285	0.23367	0.62540
10	0.30915	0.32205	0.33387	0.25865	0.37986	0.27840
12	0.17653	0.46439	0.09980	0.13146	0.40719	0.12788
14	0.09709	0.27389	0.23544	0.06931	0.22104	0.29262
16	0.02637	0.09534	0.17715	0.01193	0.05757	0.13376

*All of the MOs in this table are two-fold degenerate.

formation at HF/STO-3G level, and show in table 1 and figure 7. Utilizing the data in table 1, we can readily write the Zadeh formulae [16, 17] for various MOs. In figure 7(A), the membership functions for the occupied MO (OMO) near the HOMO are shown, where OMO1 denotes the degenerate HOMO, OMO3 the degenerate OMO next to OMO1 (HOMO), and OMO5 the degenerate OMO next to OMO3. In figure 7(B), however, the membership functions for the virtual MO (VMO) near the LUMO are shown, where VMO1 is the degenerate LUMO, VMO3 is the degenerate VMO next to VMO1 (LUMO), VMO5 is the degenerate VMO and next VMO3. It is notable that these MOs are two-fold degenerate (for both their energy and membership function), and so the even suffixes may be omitted. Interestingly, figures 7(A) and (B) are similar to each other for OMO and VMO with the same suffix.

Now we examine polyyne $C_{16}H_2$ and its monocyano-derivative, $C_{15}NH$ and dicyano-derivative, $C_{14}N_2$. Figures 8(A) and (B) show the membership functions
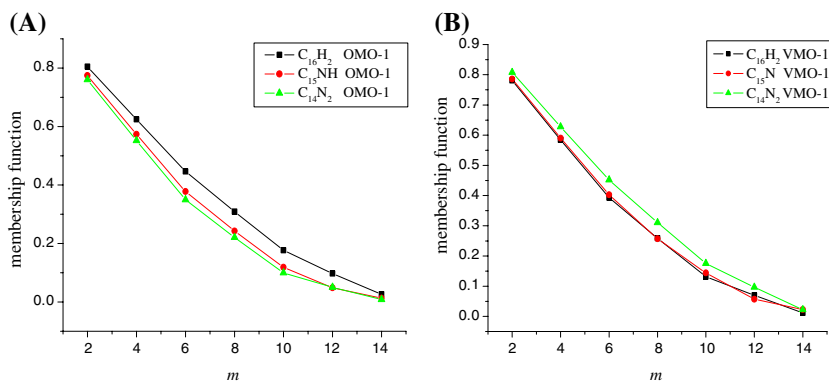
Figure 8. The plots of membership functions related to fuzzy translation transformation *vs.* the translation magnitude m, for the frontier MO (at HF/STO-3G level) of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$ for (A) OMO1 for HOMO, and (B) VMO1 for LUMO.

related to translation transformation $\hat{T} - m$ for the HOMO and LUMO of these compounds, respectively. The correlation curves of membership functions *vs.* m are similar to each other for these frontier MOs of these molecules. However, for the same m, the membership functions of HOMO decrease from $C_{16}H_2$, to $C_{15}NH$ and $C_{14}N_2$, whereas those of LUMO increase for the same order. Moreover, the membership function for the HOMO of $C_{15}NH$ is close to that of $C_{14}N_2$, but for the LUMO of $C_{15}NH$ is close to that of $C_{16}H_2$. Figure 9 shows the atomic criteria of these MOs, where the nitrogen atomic serial number is 0 in $C_{15}NH$, but it is 0 and 15 in $C_{14}N_2$. Other serial numbers are in connection with the carbon atom. As shown in the figure, the atomic criteria fluctuate with the rise and fall of m alternately for the most cases. This is similar to the case of a one-dimensional space fuzzy periodic lattice composed of two atoms, where the membership function related to translation transformation $\hat{T} - 2$ ought to be larger than that of other translations.

Figure 10 shows the plot of membership functions *vs.* m related to translation transformation $\hat{T} - m$ for certain other MOs in these molecules. It seems that for $C_{16}H_2$ and $C_{14}N_2$ the OMO and VMO with same suffixes are closer than do those for $C_{15}NH$. As mentioned above, the membership functions related to transformation $\hat{T} - m$ of the molecular skeleton and the MO is very different, in particular, those of non-frontier MOs. They often fluctuate *vs.* m. though they decrease monotonically with m for the frontier MO. This non-linearity is different from the dependence for the skeleton.

There is a space inversion symmetric centre in $C_{16}H_2$ and $C_{14}N_2$, and this centre will often be represented in their MOs. Consequently, the related membership function ought be one. As the fuzzy symmetric centre translates j inter-atomic distance units from the common symmetric centre, the membership function related to the fuzzy symmetry transformation of space inversion is equal
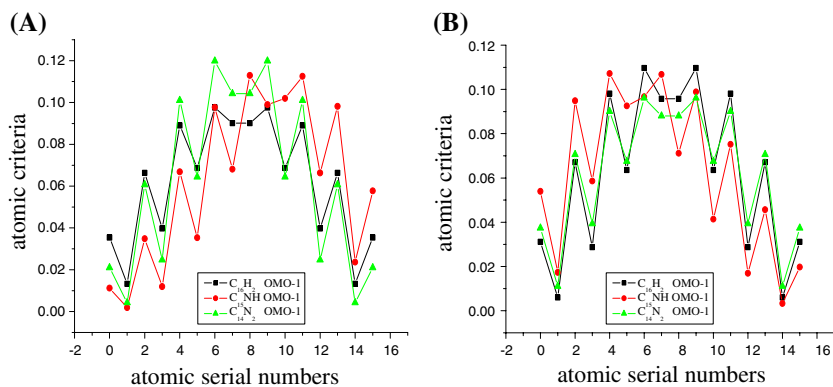
Figure 9. The plots of the AO criteria for the frontier MOs (at HF/STO-3G level) of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$ *vs.* atomic serial number (*cf.* figure 1). (A) OMO1 for HOMO, and (B) VMO1 for LUMO.
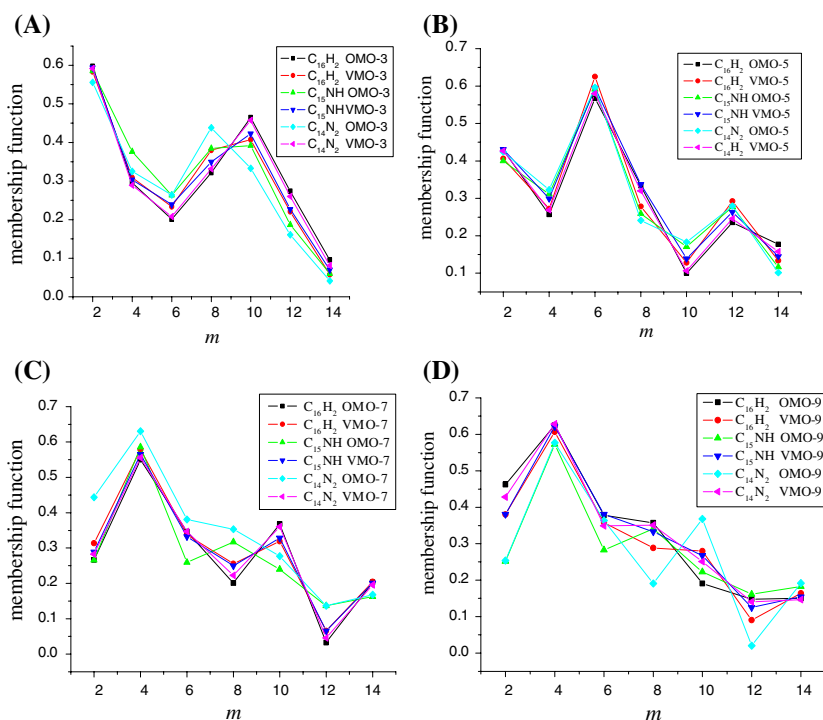

Figure 10. The plots of the membership functions related to fuzzy translation transformations *vs.* the translation magnitude *m*, for certain MOs of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$ at HF/STO-3G level. (A) OMO3 & VMO3, (B) OMO5 & VMO5, (C) OMO7 & VMO7, and (D) OMO9 & VMO9.

Table 2
The membership functions for some MOs of $C_{15}NH$ in relation to the fuzzy space inversion transformation*

OMO			VMO		
	The positions of main inversion center	membership functions		The positions of main inversion center	membership functions
OMO-1	(8,9)	0.8273	VMO-1	(6,7)	0.8916
OMO-3	(8,9)	0.8565	VMO-3	(6,7)	0.7746
OMO-5	(8,9)	0.8399	VMO-5	(7,8)	0.7743
OMO-7	(8,9)	0.6650	VMO-7	(7,8)	0.7803

*All of the MOs in this table are two-fold degenerate. The position of main inversion centre with $(i, i + 1)$ means the positions between the atomic serial numbers i and $i + 1$.

to that of $2j$ inter-atomic distance unit translation, which is similar to the case for the molecular skeleton with a symmetric centre.

$C_{15}NH$ does not have a common space inversion symmetric centre, and so we can only analyze the fuzzy space inversion symmetry according to a chosen symmetric centre. The membership functions of a certain MO would depend on the choice of the fuzzy symmetric centre. The fuzzy symmetric center with the maximal value of membership function may be called main symmetric centre. The membership functions of certain MOs of $C_{15}NH$ related to the fuzzy space inversion transformation of the main symmetric centre are showed in table 2.

4. The irreducible representation components

4.1. Computation detail

As regards to analyze the irreducible representation component for MOs, the first question is, what representation space will be expanded? In addition to the point group representation, we need to consider the space group representation. It is important that now we must consider the parallel translation group, its corresponding states and representations. In solid state physics, there are already some important results, in particular, the Bloch's theorem [18, 19]. According to this theorem, the state of the periodic space symmetry may be described by the Bloch function.

In the one-dimensional space (one-dimensional lattice) of a periodic unit length a, the eigenstate Φ_k related to the translation of m periodic transformation $\hat{T} - m$ is given below [20, 21],

$$\hat{T} - m\Phi_k = \exp(kmai)\Phi_k \tag{9}$$

where k is the wave vector, a number or a scalar in one-dimensional case. According to the Bloch theorem, the so-called Born-Karman boundary condition is

Table 3
The characters of parallel translation transformation group for one-dimensional lattice

Parallel translation	$\hat{T}-0$	$\hat{T}-1$	$\hat{T}-2$	......	$\hat{T}-m$	......	$\hat{T}-(n-1)$
Irreducible representation		[where : $\varepsilon = \exp(2\pi i/n)$]					
Γ_0	1	1	1	......	1	......	1
Γ_1	1	ε	ε^2	......	ε^m	......	$\varepsilon^{(n-1)} = \varepsilon^*$
Γ_2	1	ε^2	ε^4	......	ε^{2m}	......	$\varepsilon^{2(n-1)} = \varepsilon^{2*}$
......	......	......	......	......	......	......	......
Γ_ν	1	ε^ν	$\varepsilon^{2\nu}$	......	$\varepsilon^{m\nu}$	......	$\varepsilon^{(n-1)\nu} = \varepsilon^{\nu*}$
......	......	......	......	......	......	......	......
Γ_{n-1}	1	$\varepsilon^{(n-1)} = \varepsilon$	$\varepsilon^{2(n-1)} = \varepsilon^{2*}$	......	$\varepsilon^{(n-1)m} = \varepsilon^{m*}$	......	$[\varepsilon^{(n-1)}] \times [\varepsilon^{(n-1)}] = \varepsilon$

used. For the one-dimensional lattice composed of n lattice points, the value of (kma) would be in $(-\pi, \pi)$. According to such boundary continuity, k will be $\nu(2/na)$, where ν is a positive integer, taking values of $0, 1, 2, \ldots, n-1$. In equation (9), term $\exp(kmai)$ becomes $\exp[m\nu(2\pi i/n)] \equiv \varepsilon^{m\nu}$, and is an eigenvalue of the wave-vector state Φ_k related to the $\hat{T}-m$ transformation, maybe called wave-parity [10, 20, 21]. The term Φ_k will then depend on ν uniquely. The wave-vector state Φ_k with discrete ν belongs to an irreducible representation, $\Gamma_{\nu'}$, related to the one-dimensional periodic parallel translation group. This group is an Abelian group, and so all of its irreducible representations are one-dimensional. The corresponding characters are shown in table 3. It is clear that this group and the C_n point group are isomorphic. This result means that the Born-Karman boundary condition have been introduced implicitly. Of course, the Born-Karman boundary condition is strictly correct only when n is infinite, and it is only an approximation for the finite molecule, *i.e.*, a finite n. It should also be noteworthy that the value field is a complex one. The state of wave vector corresponding to the one-dimensional irreducible representation ought to be the common eigenstate related to all symmetry transformations included in this parallel translation group. The eigenvalue (character) may be a complex.

Some states belonging to various irreducible representations may be degenerate. For example, two states belonging to Γ_ν and $\Gamma_{n-\nu}$ irreducible representations (table 3) may be degenerate. Both states are the eigen-states related to all symmetry transformations in the group, and some of their eigenvalues are indeed complex. However, for the real field when it is not the eigenstate for the symmetry transformation in corresponding parallel translation group to which it belongs, the two-dimensional irreducible representation will be introduced necessarily. As the degenerate states belong to Γ_ν and $\Gamma_{n-\nu}$ irreducible representation, that may be composed of states belonging to the two dimensional irreducible representation E_ν as the case for the C_6 point group [9] we exami-

ned. Since we are examining the irreducible representation in the complex field, the relative projection operators [22] ought to be a complex formula. We may start with the projection and then do the normalization for further analysis and calculation.

According to table 3, the projection operator related to Γ_ν irreducible representation may be shown as,

$$\hat{P}(\Gamma_\nu) = \sum_{m=0}^{n-1} \varepsilon^{-m\nu} \, \hat{T} - m, \tag{10}$$

where $\varepsilon^{-m\nu}$ is the complex conjugate of the eigenvalue related to $\hat{T} - m$, and the normalizing factor is ignored. We consider only one AO for each atom that is combined into the MO, Ψ_ρ as shown in equation (2). As the projection operator, $\hat{P}(\Gamma_\nu)$ in equation (10), acts on MO Ψ_ρ, the part of the MO that belongs to Γ_ν irreducible representation, $\Psi_\rho(\Gamma_\nu)$, can be obtained,

$$\Psi_\rho(\Gamma_\nu) = \hat{P}(\Gamma_\nu) \quad \Psi_\rho \sum_{m=0}^{n-1} \varepsilon^{-m\nu} \, \hat{T} - m \quad \Psi_\rho = \sum_{m=0}^{n-1} \varepsilon^{-m\nu} \, \hat{T} - m \left[\sum_{J=0}^{n-1} a_\rho(J)\phi(J) \right]$$

$$= \sum_{m=0}^{n-1} \sum_{J=0}^{n-1} a_\rho(J)\varepsilon^{-m\nu} \, \hat{T} - m\phi(J) \tag{11}$$

where,

$$\Psi_\rho \equiv \sum_{J=0}^{n-1} a_\rho(J)\phi(J) = \sum_{\nu=0}^{n-1} \Psi_\rho(\Gamma_\nu) \tag{12a}$$

$$\Psi_\rho(\Gamma_\nu) \equiv \sum_{J=0}^{n-1} a_\rho(J; \Gamma_\nu)\phi(J) \tag{12b}$$

Here $a_\rho(J)$ and $a_\rho(J; \Gamma_\nu)$ are the LCAO coefficients of Ψ_ρ and $\Psi_\rho(\Gamma_\nu)$, respectively. The irreducible representation component of Ψ_ρ in connection with the state $\Psi_\rho(\Gamma_\nu)$ ought to be:

$$X_\rho(\Gamma_\nu) = \frac{\displaystyle\sum_{J=0}^{n-1} a_\rho^*(J; \Gamma_\nu)a_\rho(J; \Gamma_\nu)}{\displaystyle\sum_{\nu=0}^{n-1}\sum_{J=0}^{n-1} a_\rho^*(J; \Gamma_\nu)a_\rho(J; \Gamma_\nu)} \tag{13}$$

where $a_\rho^*(J; \Gamma_\nu)$ is the conjugate of $a_\rho(J; \Gamma_\nu)$. Now we expand equation (11), using the Born-Karman boundary condition and comparing with equation (12b) to obtain $a_\rho(J; \Gamma_\nu)$, and then using equation (13) to obtain $X_\rho(\Gamma_\nu)$. This

is tedious but not too difficult to program. For simplifying the formula, we introduce the conjugate amount,

$$A_\rho(\Gamma_\nu) = \sum_{J=0}^{n-1} \varepsilon^{-J\nu} a_\rho(J) \tag{14a}$$

$$A_\rho^*(\Gamma_\nu) = \sum_{J=0}^{n-1} \varepsilon^{J\nu} a_\rho(J) \tag{14b}$$

Equation (13) may be simplified and denoted as,

$$X_\rho(\Gamma_\nu) = \frac{A_\rho^*(\Gamma_\nu) A_\rho(\Gamma_\nu)}{\sum\limits_{\nu=0}^{n-1} A_\rho^*(\Gamma_\nu) A_\rho(\Gamma_\nu)} \tag{15}$$

where the MO is not necessarily normalized. To start with the case of the common symmetric centre, we set n (figure 1) to an even number. As $n = 2q$, the centre will be between $(q-1)$th and qth atoms, and the LCAO-MO coefficients for the *Jth* and $(n-J-1)$*th* atoms ought to be equal in absolute value. Accordingly, another pair of conjugate amounts, $B_\rho(\Gamma_\nu)$ and $B_\rho^*(\Gamma_\nu)$, can be introduced,

$$A_\rho(\Gamma_\nu) = \varepsilon^{\nu/2} \sum_{J=0}^{n-1} \varepsilon^{-(J+\frac{1}{2})\nu} a_\rho(J) \equiv \varepsilon^{\nu/2} B_\rho(\Gamma_\nu) \tag{16a}$$

$$A_\rho^*(\Gamma_\nu) = \varepsilon^{-\nu/2} \sum_{J=0}^{n-1} \varepsilon^{(J+\frac{1}{2})\nu} a_\rho(J) \equiv \varepsilon^{-\nu/2} B_\rho^*(\Gamma_\nu) \tag{16b}$$

In the summation of $B_\rho(\Gamma_\nu)$, the complex coefficient before $a_\rho(n-J-1)$ would be $\varepsilon^{-(n-J-\frac{1}{2})\nu} = \varepsilon^{(J+\frac{1}{2})\nu}$; it is conjugated with that before $a_\rho(n-J-1)$. We can then readily collate these two terms and combine them into a real term and a pure imaginary term. If the common symmetric centre does not exist, the real and the pure imaginary terms may be obtained. Both $B_\rho(\Gamma_\nu)$ and $B_\rho^*(\Gamma_\nu)$ may be denoted as the summations of isolated real and pure imaginary terms.

$$B_\rho(\Gamma_\nu) = \text{Re}[B_\rho(\Gamma_\nu)] - \text{Im}[B_\rho(\Gamma_\nu)]i \tag{17a}$$
$$B_\rho^*(\Gamma_\nu) = \text{Re}[B_\rho(\Gamma_\nu)] + \text{Im}[B_\rho(\Gamma_\nu)]i \tag{17b}$$

The irreducible representation component $X_\rho(\Gamma_\nu)$ may then become the following,

$$X_\rho(\Gamma_\nu) = \frac{\text{Re}^2[B_\rho(\Gamma_\nu)] + \text{Im}^2[B_\rho(\Gamma_\nu)]}{\sum\limits_{\nu=0}^{n-1} \{\text{Re}^2[B_\rho(\Gamma_\nu)] + \text{Im}^2[B_\rho(\Gamma_\nu)]\}} \tag{18}$$

where the real and imaginary parts of $B_\rho(\Gamma_\nu)$ may be respectively denoted as:

$$\text{Re}[B_\rho(\Gamma_\nu)] = \sum_{L=0}^{q-1} a_\rho(L; \text{Re}) \cos[(L + \tfrac{1}{2})\pi\nu/q] \tag{19a}$$

$$\text{Im}[B_\rho(\Gamma_\nu)] = \sum_{L=0}^{q-1} a_\rho(L; \text{Im}) \sin[(L + \tfrac{1}{2})\pi\nu/q] \tag{19b}$$

Here, the coefficients before the trigonometric functions reflect the symmetrical and asymmetrical components related to the common space inversion transformation, and may be obtained from the LCAO-MO coefficients a_ρ (L) and a_ρ (GL), GL $= n - L - 1$, as we did in *ref.* [6]. When the symmetrical representation is related to the common inversion transformation, $a_\rho(L;\text{Re})$ would be zero; and when the asymmetrical one is related to, $a_\rho(L;\text{Im})$ would be zero. According to the symmetrical and asymmetrical states, $\Psi_\rho(\Gamma_\nu; g)$ and $\Psi_\rho(\Gamma_\nu; u)$, in connection with representation Γ_ν, corresponding representation components for Ψ_ρ ought to be respectively as follows:

$$X_\rho(\Gamma_\nu; g) = \frac{\text{Im}^2[B_\rho(\Gamma_\nu)]}{\sum\limits_{\nu=0}^{n-1} \{\text{Re}^2[B_\rho(\Gamma_\nu)] + \text{Im}^2[B_\rho(\Gamma_\nu)]\}} \tag{20a}$$

$$X_\rho(\Gamma_\nu; u) = \frac{\text{Re}^2[B_\rho(\Gamma_\nu)]}{\sum\limits_{\nu=0}^{n-1} \{\text{Re}^2[B_\rho(\Gamma_\nu)] + \text{Im}^2[B_\rho(\Gamma_\nu)]\}} \tag{20b}$$

As above, we consider the polyyne of linear polymer molecule as a one dimensional fuzzy lattice in which the unit cell contains only one atom. If each lattice is constructed by s atoms, and the LCAO coefficient for the i-th AO ($i =$ 1 to Ai) of the A-*th* atom (A = 1 to s) in the J-*th* lattice (J = 0 to $n' - 1$) in the ρ-*th* MO (Ψ_ρ) is $a_\rho(J, A, i)$, then replacing equation (12), this MO may be denoted as:

$$\Psi_\rho \equiv \sum_{J=0}^{n'-1} \sum_{A=1}^{s} \sum_{i=1}^{Ai} a_\rho(J, A, i)\phi(J) = \sum_{\nu'=0}^{n'-1} \Psi_\rho(\Gamma_{\nu'}) \tag{21a}$$

$$\Psi_\rho(\Gamma_{\nu'}) \equiv \sum_{J=0}^{n'-1} \sum_{A=1}^{s} \sum_{i=1}^{Ai} a_\rho(J, A, i; \Gamma_{\nu'})\phi(J) \tag{21b}$$

The irreducible representation components related to the fuzzy parallel translation group above may be used further, but the summation running over J will be replaced by over J, A, and i. It is notable that for such case there are sn' atoms, whereas the number of both lattice points and irreducible

representations for the fuzzy group is only n'. Of course, we may still examine the irreducible representation components related to the fuzzy space inversion symmetrical transformation.

Now we will examine some prototypical molecules. The results will be strictly correct for the infinite lattice owing to the Born-Karman boundary condition. Since the molecule is not very small, the desirable results are often approximate. The related methods ought to be used for larger molecules via programming.

4.2. The irreducible representation components for MOs of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$

We took $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$ as the example of the one dimensional lattice in which each unit lattice contains two atoms (CC or CN), and considered the πMO. This reduces equation (21) as A_i is 1 and no summation over i is needed, and s and n' are 2 and 8, respectively. In this parallel translation group, the minimum unit length is the distance between two consecutive lattices, *i.e.*, two diatomic distance units, one single and one triplet bond lengths. There are eight cells including 16 AOs to form a fuzzy one dimensional crystal. For the corresponding fuzzy parallel translation group, there are eight irreducible representations, $\Gamma_{\nu'}$ ($\nu' = 0$ to 7; $\Gamma_0 = \Gamma_8$). According to the method described above, we calculated the irreducible representation components for the πMOs of these molecules. Figure 11(A) show the results related to the frontier MO of these molecules. For the HOMOs of these three molecules, the representation components related to $\Gamma_{\nu'}$ with $\nu' = 2$ and 6 are maxima. For their LUMOs, the representation components with $\nu' = 1, 3, 5$ and 7 are maxima. As the space inversion transformation for $C_{16}H_2$ and $C_{14}N_2$, the HOMOs belong to the pure symmetrical representation (G), but the LUMOs belong to the pure asymmetrical representation (U). For $C_{15}NH$ without the common space inversion symmetry, the MOs may include both symmetrical and the asymmetrical components, simultaneously, and their main representations ought to be the same as the pure representations of the corresponding MOs of $C_{16}H_2$ and $C_{14}N_2$ related to the space inversion. Figure 11(B) shows the representation components related to the fuzzy parallel translation and the fuzzy space inversion for the frontier MOs of $C_{15}NH$, *i.e.*, the products of the representation components related to these two fuzzy groups. As for figure 12, the irreducible representation components related to the parallel translation group for some other π-MOs of these three molecules are shown. It is notable that the maxima of representation components occur either at (1) $\nu' = 2$ and 6 or (2) $\nu' = 1, 3, 5$ and 7. For π-MOs far from the frontier MO, they belong to case (2). As the representation components related to the space inversion in $C_{16}H_2$ and $C_{14}N_2$, the representation of the MO is pure symmetrical or pure asymmetrical, denoted by (G) or (U)
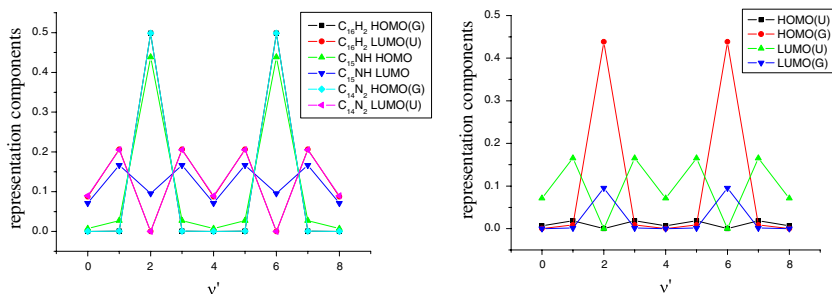
Figure 11. The plots of irreducible representation components *vs.* v': (G) and (U) denote symmetry and asymmetry corresponding to space inversion, respectively. (A) related to the fuzzy parallel translation for frontier MOs of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$, (B) related to both fuzzy space inversion and fuzzy parallel translation for frontier MOs of $C_{15}NH$.
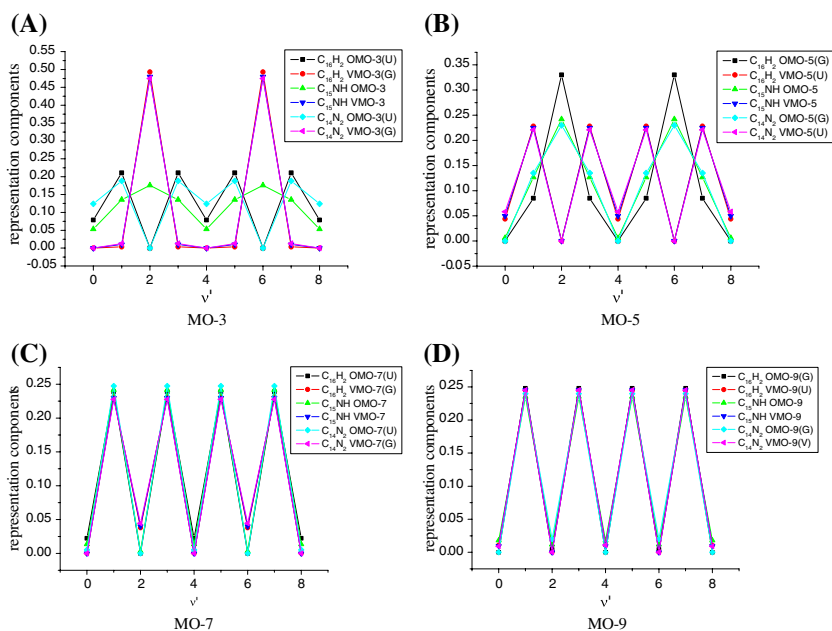

Figure 12. The plots of irreducible representation components *vs* v' for some MOs of $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$, where (G) and (U) denote symmetry and asymmetry related to space inversion, respectively.

respectively in figure 12. For the MOs of $C_{15}NH$, both symmetrical and asymmetrical components appear in their fuzzy representation simultaneously, but other main representations ought to be similar to the pure representations of corresponding MOs in $C_{16}H_2$ and $C_{14}N_2$.

5.   Conclusions

In this paper, we have analyzed the fuzzy group (set) of the molecular space symmetry. To start with, we touched upon the one-dimensional translation fuzzy space set of the linear molecule. The difference between point and space groups lies in that the former is finite group, but the latter infinite group. For the fuzzy point groups, we consider mainly the fuzzy characterization due to the difference between original and symmetry transformed atoms. For the space group, the fuzzy characterization introduced also arises from the difference between infinite and finite nature. We focus on and analyze here only the one-dimensional translation transformation of polyynes and their cyano-derivatives. The space group has widely been applied to solid state physics, and some of the results are cited here. The main conclusions include the following.

1. The calculation method for the membership functions of the fuzzy translation symmetry transformation related to the molecular skeleton has been established. The membership function approaches to one for medium molecules, and it will approach to 0.9 for the molecule of more than tenfold of the translation length. Therefore, if the molecule is not too small, use of the fuzzy translation symmetry ought to be reasonable. In crystallography, the dimension of a crystal is much larger than that of a unit cell, the relative membership function ought to be close to one. We may thus analyze the problem as an infinite translation symmetry in a crystal. However, the corresponding fuzzy sets of the parallel translation symmetry transformation are not fuzzy groups.

2. For homologous molecules, there are certain relationships between their property and membership functions of the parallel translation symmetry transformation. The causes for these relationships are a piece of very interesting future work.

3. For polyynes (C_nH_2) and related mono- and dicyano-derivatives ($C_{n-1}NH$, $C_{n-2}N_2$), the membership functions related to the parallel translation symmetry transformation are similar. For a certain translation length, their plot of membership functions *vs.* the molecular magnitude (n) become nearly to one curve.

4. For polyynes (C_nH_2) and dicyano-derivatives ($C_{n-2}N_2$), there is the common space inversion symmetry, but for the monocyano-derivatives ($C_{n-1}NH$) there is not such symmetry. In the latter case, they were analyzed in terms of the fuzzy space inversion symmetry.

5. For the MOs in these molecules, due to their alternating single- and triple- bonds, two atoms were chosen in a unit, and the membership functions related to the translation only with the even number

of the inter-atomic distances were analyzed. For the frontier MOs, the membership functions related to the parallel translation transformations increase with the molecular size (n) increase, but decrease with the translation distance (m). As for even m, the corresponding change curves are smooth. For the same polyyne, the membership functions of HOMOs are slightly larger than those of LUMOs.

6. For the prototypical molecules, $C_{16}H_2$, $C_{15}NH$ and $C_{14}N_2$, the membership functions of frontier occupied OMO-j and virtual VMO-j related to the translation transformation are similar for the same j, in particular, for $C_{16}H_2$ and $C_{14}N_2$, but not for different j.

7. For the eigenstates and eigenvalues, the Bloch theorem which is based on the Born-Karman boundary condition was used. It is adopted for our not-too-small molecules. Using the project operator method in complex number field, we calculated the representation components of their frontier orbitals corresponding to fuzzy parallel translation symmetry. The corresponding irreducible representation components of $C_{16}H_2$ are very similar to those of $C_{14}N_2$, but less similar to those of $C_{15}NH$.

8. Owing to the space inversion symmetry of $C_{16}H_2$ and $C_{14}N_2$, their MOs are either symmetrical or asymmetrical, *i.e.*, their representation components being one or zero. For example, the HOMOs of $C_{16}H_2$ and $C_{14}N_2$ are symmetrical, but their LUMOs asymmetrical. For $C_{15}NH$, which does not have common space inversion symmetry, its MOs include both symmetrical and asymmetrical representation components. However, its main representations are the same for those 'pure' representations of corresponding MOs for $C_{16}H_2$ and $C_{14}N_2$.

Acknowledgments

References

[1] P.G. Mezey and J. Maruani, Mol. Phys. 69(1) (1990) 97.
[2] P.G. Mezey and J. Maruani, Int. J. Quantum Chem. 45 (1993) 177.
[3] R. Chauvin, J. Math. Chem. 16 (1994) 245.
[4] R. Chauvin, J. Math. Chem. 16 (1994) 257.
[5] X.Z. Zhao and X.F. Xu, Acta Phys. Chim. Sci. 20 (2004) 1175 (in Chinese).
[6] X.Z. Zhao, X.F. Xu, G.C. Wang, Y.M. Pan and Z.S. Cai, Mol. Phys. 103 (2005) 3233.
[7] X.F. Xu, G.C. Wang, X.Z. Zhao, Y.M. Pan, Y.X. Liang and Z.F. Shang, J. Math. Chem. 41(2) (2007) 143.

[8] X.Z. Zhao, X.F. Xu, G.C. Wang, Y.M. Pan, Z.F. Shang and R.F. Li, J. Math. Chem. 42(2) (2007) 265.

[9] X.Z. Zhao, G.C. Wang, X.F. Xu, Z.C. Li, Y.M. Pan, R.F. Li and Z.F. Shang, J. Math. Chem. (File No A2225) DOI:10.1007/s10910-006-9210-x.

[10] X.Z. Zhao, X.Z. Yi, D.R. Guan, X.F. Xu, G.C. Wang, Z.F. Shang, Z.S. Cai, Y.M. Pan, J. Mol. Struct. (THEOCHEM) 713 (2005) 87.

[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel *et al.*, Gaussian 98, revision A.3 (Gaussian, Inc., Pittsburgh PA, 1998).

[12] K. Fukui, T. Yonezawa and H. Shingu, J. Chem. Phys. 20 (1952) 722.

[13] U. Molder, P. Burk, I.A. Koppel, Int. J. Quantum Chem. 82 (2002) 73.

[14] M.Q. Jiang, *The Rule of Homologous Linearity of Organic Compounds* (Science Press, Beijing, 1980) p234 (in Chinese).

[15] W.S. Xiao, *Basic Fuzzy Mathematics and its Application*. (Aircraft Industry Press, Beijing, 1992) pp. 201–204 (in Chinese).

[16] L.A. Zadeh, Inform and Control 8B (1965) 338.

[17] R.E. Bellmann, L.A. Zadeh, Manag. Sci. 17 (1970) 13141.

[18] C. Kittel, Introduction of Solid State Physics. Chapter 7 (John Wiley & Sons Inc., NY, 2005).

[19] F.Bloch, Z. Phys. 52 (1928) 555.

[20] X.Z. Zhao, *Application of Symmetry Principle in Field Theory to Chemistry* (Science Press, Beijing, 1986) (in Chinese).

[21] X.Z. Zhao, Z.S. Cai, G.C. Wang, Y.M. Pan, B.X. Wu, J. Mol. Struc. (THEOCHEM) 586 (2002) 223.

[22] F.A. Cotton, *Chemical Application of group Theory*, Chapter 6 (Wiley, New York, 1999).