Fuzzy symmetries for linear molecules and their molecular orbitals

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In this paper, the fuzzy symmetry of some prototypical linear molecules has been analyzed. The results show that some molecular orbitals (MOs) are less symmetrical but some others are more symmetrical than the molecular skeleton, which the MOs correspond to. The membership functions of space inversion for MOs are closely related to the chemical characteristics of the MOs. Sometimes, although the symmetry of a molecular skeleton is not obvious, however that of some MO is quite obvious. The membership functions of the fuzzy inversion symmetry depend on the choice of the position of the center of inversion. As compared to those of diatomic molecules and linear triatomic molecules, the linear polyatomic molecules in which a distinctive fuzzy symmetry of space translation may exist, and thus a significant effect on their properties can be expected.

KEY WORDS: fuzzy symmetry, linear molecules, molecular orbital

1. Introduction

At the end of last century, the establishment of fuzzy theory [1,2] attracted much attentions to many people in various regions, especially in the chemistry and chemical engineering. Though much more work concerning fuzzy theory focused on macroscopic aspects in chemistry, efforts have also been paid in microscopic theoretical chemistry. For example, Mezey and Maruani [3,4] have discussed the fuzzy symmetry caused by the displacement of some atoms in some specific molecules with symmetry of general point groups. Even some persons say, "are the concepts of chemistry all fuzzy?" [5]. However, the researches on the fuzzy characteristics of chemical symmetry are still poor.

As we known, most molecules aren't provided with the perfect symmetry in point group. For example, as one F atom of molecule $CF_2=CF_2$ is substituted

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by a Cl atom to form the molecule $CFCl=CF_2$, one excepts that the symmetry of the molecule $CFCl=CF_2$ will be seen as destroyed and displays the imperfect D2h when compared with that of $CF_2=CF_2$. However, the fuzzy symmetry related to the imperfect symmetry in microscopic theoretical chemistry is often denied or neglected. Instead, the so-called topological considerations [6] are put forward, therefore the related fuzzy symmetry is considered as common symmetry. In fact, our purpose is to construct such a generalized method to describe the fuzzy symmetry of various molecules and MOs by using fuzzy set theory [7]. In our pervious paper [8], we proposed the basic characterization of this method and analyzed the FCl as a simple example. Of course, there are a lot of fields ought to be analyzed by using this method. In this paper, we will probe into the fuzzy symmetries for linear molecules and their MOs. Some interesting phenomena will appear. As for the more complex molecules, we will discuss them in other follow-up papers.

The subject we are investigating concentrates on imperfect symmetry (or called fuzzy symmetry) of molecules and MOs. Since the imperfect symmetrical system can be seen as the result of the ideal-symmetrical system damaged in local part, from the viewpoint of fuzzy set theory [1,2] the damaged system should belong to a certain ideal symmetry group to some extent. The "grade of belonging" can be expressed using membership function, which takes the value between 0 and 1.

The fundamental question in designing a physically meaningful fuzzy set model is related to the choice of the membership function. If any atom J of a molecule M moves to the position of the atom GJ after the operation $\hat{G}$ of point group $\mathbf{G}$ is carried out, the membership function for molecule M in regards to operation $\hat{G}$ is defined as follows [7,8],

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

where Y_J and Y_{GJ} represent the atomic criteria of atoms J and GJ, respectively. We may choose the atomic numbers, electronic charges and so on as the criteria for M. Here the operation $x \wedge y$ is introduced, and the result of this operation is equal to the value of the smaller one of x and y.

The membership function for a MO can be defined similar as follows:

$$\mu_E(\hat{G}/\underset{\sim}{\mathbf{G}}; \Psi_\rho) = [\Sigma_J\Sigma_i(Y_{Ji} \wedge Y_{GJi})] / [\Sigma_J\Sigma_i(Y_{Ji})]$$
$$= \Sigma_J\Sigma_i[(a_\rho^*(J,i)a_\rho(J,i)) \wedge (a_\rho^*(GJ,i)a_\rho(GJ,i))]/\Sigma_J\Sigma_i[(a_\rho^2(J,i)\wedge a_\rho^2(GJ,i)], \tag{2}$$

where Ψ_ρ is the ρth MO, $a_\rho(J,i)$ is the linear combination coefficient of the ith AO on the Jth atom, and $a_\rho^*(J,i)$ is the conjugate one of $a_\rho(J,i)$. $a_\rho(GJ,i)$ and $a_\rho^*(GJ,i)$ have the similar meaning to $a_\rho(J,i)$ and $a_\rho^*(J,i)$, respectively. Where Y_{Ji} and Y_{GJi} are the criteria of the ith AO on the Jth and GJth atom, and they equal to $a_\rho^*(J,i)\, a_\rho(J,i)$ and $a_\rho^*(GJ,i)\, a_\rho(GJ,i)$, respectively. Further details of these criteria and membership functions may be available in ref [8].

In this paper, we will discuss the fuzzy symmetry of linear molecules. No matter what kind of linear molecule, it always holds the cylindrical symmetry along the chemical bond(s). First, we will discuss only the symmetry element, the center of inversion, for the linear molecules according to the internal configuration space. Taking the center of inversion and the identity into account, molecules can be classified to the point group $\mathbf{C_i}$, and corresponding to this group there are two kinds of irreducible representations, symmetrical (g) and asymmetrical (u) ones, which is often encountered in the study of molecular spectroscopy. Our previous research [8] reveal that the empirical AM1 method is often reliable for studying the fuzzy symmetry of molecules and MOs. Thus, we often use AM1 method in this paper. Of course, such analysis is not difficult to use other method in similar way. All the calculations have been performed using methods within Gaussian98 program [9].

2. Fuzzy symmetries for non-hydride diatomic molecules

Now we discuss the irreducible representations of non-hydride heteronuclear diatomic molecules. Different from MOs of homo-nuclear diatomic molecules, generally, each MO of these non-hydride diatomic molecules (as listed in table 1) is neither symmetrical (g) nor asymmetrical (u) composition, but the result of the overlap, or called mix, of these two compositions. By comparing the content of the two compositions, symmetrical composition X_g and asymmetrical composition X_u, we define labels of the various fuzzy irreducible representations as follows: The fuzzy irreducible representation is labeled as $\widetilde{A}_g$ if the content of X_g is larger than that of X_u, labeled as $\widetilde{A}_u$ if X_g is smaller than that of X_u, and labeled as $\widetilde{A}_o$ if X_g is equal to that of $\widetilde{X}_u$, respectively.

In table 1, the MOs and their fuzzy symmetry of some non-hydride diatomic molecules are listed. From table 1, we can see that the symmetrical components X_g of the MOs is either near by one or by zero. Interestingly, as shown in figure 1, the trend of X_g of MOs is very similar for the different molecules. On the other hand, the membership functions vary also between zero and one, but the trend is somewhat differ for the various molecules. Generally, as the X_g or X_u vary a litter from 1, the corresponding membership functions may vary more. While as both the X_g and X_u near by 0.5, such as MO-1 and MO-2 of FCl, the membership function will be quite small. Generally, the effect of X_g and X_u to the membership functions is complex.

According to the idea of Zadeh [10], the fuzzy point group to which a MO of non-hydride diatomic molecules belongs can be expressed as:

$$\underset{\sim}{\mathbf{C_i}} = \frac{1}{\widehat{\mathbf{E}}} + \frac{\mu}{\widehat{\mathbf{P}}}, \tag{3}$$

Table 1
MOs and the related fuzzy symmetry of some non-hydride diatomic molecules.

	MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8
BN								
($\mu_Z = 0.833$)	σ[O]	σ[O]	π[O]	π[O]	σ[V]	π[V]	π[V]	σ[V]
Fuzzy irrep.	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$
X_g	0.8217	0.0569	0.0583	0.0583	0.9372	0.9809	0.9809	0.0132
$X_u = 1-X_g$	0.1783	0.9431	0.9417	0.9417	0.0628	0.0191	0.0191	0.9868
Membership Function	0.2371	0.8158	0.5312	0.5312	0.6635	0.7261	0.7261	0.7743
CO								
($\mu_Z = 0.857$)	σ [O]	σ [O]	π [O]	π [O]	σ [O]	π [V]	π [V]	σ [V]
Fuzzy irrep.	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$
X_g	0.8319	0.1462	0.0946	0.0946	0.8665	0.9547	0.9547	0.0054
$X_u = 1-X_g$	0.1681	0.8537	0.9054	0.9054	0.1356	0.0453	0.0453	0.9946
Membership Function	0.2575	0.8012	0.4146	0.4146	0.5807	0.5841	0.5841	0.2825
FCl								
($\mu_Z = 0.692$)	σ[O]	σ[O]	σ[O]	π[O]	π[O]	π[O]	π[O]	σ[V]
Fuzzy irrep.	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_u}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_g}$	$\underset{\sim}{A_u}$
X_g	0.6315	0.3528	0.9888	0.0922	0.0922	0.9304	0.9304	0.0060
$X_u = 1-X_g$	0.3685	0.6472	0.0118	0.9078	0.9078	0.0696	0.0696	0.9940
Membership Function	0.0380	0.0445	0.8147	0.4214	0.4214	0.4909	0.4909	0.8813
F$_2$								
($\mu_Z = 1$)	σ[O]	σ[O]	σ[O]	π[O]	π[O]	π[O]	π[O]	σ[V]
Irreducible representation	A_g	A_u	A_g	A_u	A_u	A_g	A_g	A_u
X_g	1	0	1	0	0	1	1	0
$X_u = 1-X_g$	0	1	0	1	1	0	0	1
Membership Function	1	1	1	1	1	1	1	1

*μ_z is the membership function of the molecule skeleton, calculated with the atomic number as the criterion. The following μ_z has the same meaning and will not be mentioned.

Where μ denoted the membership function in connection for inversion symmetry. For example, the fuzzy point group that MO-7 of CO belongs to can be expressed as follows,

$$\underset{\sim}{\mathbf{C_i}} = \frac{1}{\widehat{\mathbf{E}}} + \frac{0.584}{\widehat{\mathbf{P}}}. \tag{4}$$

The fuzzy irreducible representation of this MO can be expressed as $\underset{\sim}{A_g} = 0.955A_g + 0.045A_u$.

Have a care that the degenerate MOs, such as MOs 3 and 4 or 6 and 7, possess with not only the same energy but also the same fuzzy symmetry and fuzzy irreducible representation.
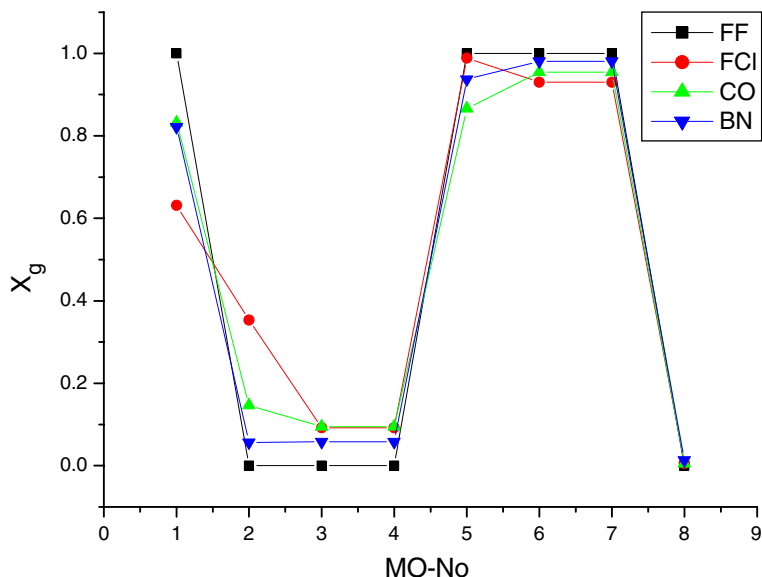
Figure 1. The symmetrical composition X_g of MOs for several diatomic molecules. The MOs are σ_{SS}, σ_{SS}^*, π_{PP}, π_{pp}, σ_{pp}, π_{pp}^*, π_{pp}^* and σ_{pp}^* in the order number of MO (MO-No) from 1 to 8, respectively. The MO-No and its energy order (from low to high) are consistent for CO and BN, but not for FCl and F_2.

3.   Fuzzy symmetries for hydride diatomic molecules

Now we analyze the fuzzy symmetry of hydride diatomic molecules. Here, we take four hydrogen halide molecules [11,12] and lithium hydride [13,14] as prototypical ones. In table 2 the AM1 calculated results for these molecules have been listed. It can be seen from the first column of tables 1 and 2 that, compared with the non-hydride diatomic molecules, the membership functions of the hydride diatomic molecule skeletons are much smaller. This indicates that the fuzzy symmetry of inversion for each of these molecules is not obvious, especially for molecule including the larger halogen atom such as iodine and bromine. However, the membership functions for some MOs, such as the occupied MOs 2 and vacant MOs 5, are larger, that is to say the fuzzy symmetry of space inversion for these MOs is quite obvious. To be clear at a glance, we show the pictures of the MOs 2 in figure 2. One can see from figure 2 that the fuzzy symmetry of space inversion for MOs 2 is obvious. From table 2 we can see that the membership function of MO 2 of LiH is the smallest compared with those of HX skeleton, and the membership function of MO 2 of HX increases while that of the molecule HX decreases in the order of HF, HCl, HBr and HI. This indicates that although some symmetries of some molecules are not obvious, those of some MOs of these molecules may be obvious and significant, which is why some chemists are more interested in MOs than in molecule, itself.

Table 2
MOs and the related fuzzy symmetries of diatomic molecules HX (X = F, Cl, Br, I, Li).

	MO-1	MO-2	MO-3	MO-4	MO-5
HF					
($\mu_Z = 0.200$)	$\sigma[O]$	$\sigma[O]$	$\pi[O]$	$\pi[O]$	$\sigma[V]$
Fuzzy irrep.	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_u$
X_g	0.6129	0.7451	0.5	0.5	0.0074
Membership Function	0.0082	0.3506	0	0	0.8281
HCl					
($\mu_Z = 0.111$)	$\sigma[O]$	$\sigma[O]$	$\pi[O]$	$\pi[O]$	$\sigma[V]$
Fuzzy irrep.	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_u$
X_g	0.5434	0.8968	0.5	0.5	0.0026
Membership Function	0.0038	0.6948	0	0	0.8977
HBr					
($\mu_Z = 0.056$)	$\sigma[O]$	$\sigma[O]$	$\pi[O]$	$\pi[O]$	$\sigma[V]$
Fuzzy irrep.	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_u$
X_g	0.5783	0.8074	0.5	0.5	0.0006
Membership Function	0.0123	0.7580	0	0	0.9501
HI					
($\mu_Z = 0.037$)	$\sigma[O]$	$\sigma[O]$	$\pi[O]$	$\pi[O]$	$\sigma[V]$
Fuzzy irrep.	$\underset{\sim}{A}_u$	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_u$
X_g	0.4926	0.7423	0.5	0.5	0.0001
Membership Function	0.0001	0.9954	0	0	0.9908
HLi					
($\mu_Z = 0.500$)	$\sigma[O]$	$\sigma[V]$	$\pi[V]$	$\pi[V]$	$\sigma[V]$
Fuzzy irrep.	$\underset{\sim}{A}_g$	$\underset{\sim}{A}_u$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_o$	$\underset{\sim}{A}_u$
X_g	0.8320	0.4168	0.5	0.5	0.0890
Membership Function	0.2523	0.0955	0	0	0.8122

In order to obtain the X_g and X_u of each MO of the hydride diatomic molecules, we introduce two kinds of imaginary AOs which may be linear combined to replace the only s-AO of H atom. The introduced two imaginary AOs correspond to the s and pz AOs of X atom in the symmetry operation of the inversion. It can be seen from table 2 that, for MOs 3 and 4, the symmetrical and the asymmetrical components account are the same, i.e. $X_g = X_u = 0.5$. Accordingly, the irreducible representations for MOs 3 and 4 are labeled as $\underset{\sim}{A}_o$, while the corresponding membership functions are all zero. The underlying reason for this result is that the MOs 3 and 4 are formed from the p_y and p_z AOs of X atom (X = F, Cl, Br, I, Li) only, and not related to H atom.

MOs 1, 2 and 5 are more significant from the viewpoint of bonding. However, the three MOs play different roles for bonding: MO-1 is mainly composed of s-AO of X atom, thus the X_g is nearly equal to X_u, i.e. $X_g \approx X_u = 0.5$,
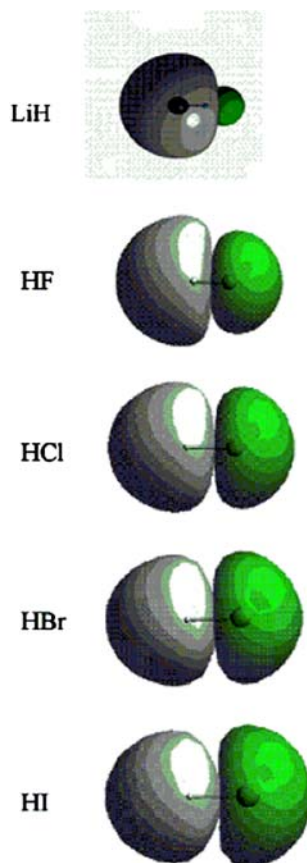
Figure 2. The MOs 2 of LiH and HX (X = F, Cl, Br, I). The fuzzy symmetry of all the MOs 2 is obvious. The membership function of MO 2 of LiH is the most small compared with those of HX. The membership function of MO 2 of HX increases while that of the molecule HX skeleton decreases in the order of HF, HCl, HBr and HI.

and the membership function is very small. This indicates that MO-1 contributes little to the bonding. MO-2 is the σ-BMO with $X_g > 0.5 > X_u$, indicating that the symmetrical component is crucial. While, MO-5 is the vacant σ^*-ABMO with $X_g < 0.5 < X_u$, indicating that the asymmetrical component is the majority. On the other hand, we note that the membership functions of MOs 2 and 5 increase in the order of HF, HCl, HBr and HI, which can be more clearly seen in figure 3. This implies that the fuzzy symmetry of space inversion for these MOs 2 and 5 becomes obvious in this order.

One may note that the behavior of HLi is different from that of HX (X = F, Cl, Br, I). For HLi, the MO-1 is bonding σ-MO with $X_g > 0.5 > X_u$, while MO-2 is antibonding σ-MO with $X_g < 0.5 < X_u$. The two MOs are the frontier orbitals, HOMO and LVMO, respectively. Moreover, compared with the MO-2
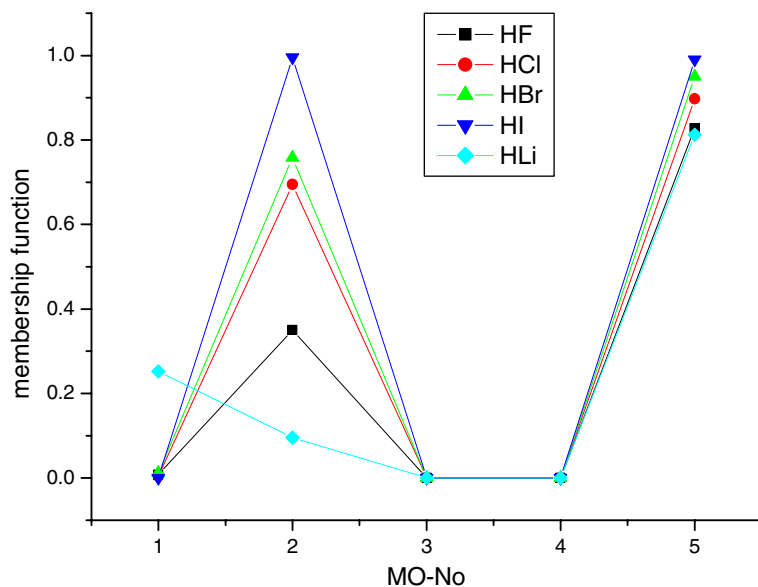
Figure 3. The membership functions of space inversion for the MOs of HX (X = F, Cl, Br, I) and LiH. The MOs are σ_{SS}, σ_{SSP}, π_{pp}, π_{pp} and σ_{SSP}^* in the order of MO-No from 1 to 5, respectively. In fact, the MOs -3 and -4 are the p_y-AOs and p_z-AOs, respectively, of both X and Li atoms.

of HX, the membership function of MO-2 of HLi is much smaller, which can also be seen from figure 3.

4. Fuzzy symmetries for linear triatomic molecules

The prototypical tri-atomic molecules under investigation are the XCN molecules, where X is hydrogen or halogen atom (correspondingly, XCN is hydrogen cyanide [15,16] or cyanogens halide [17,18]). We are still interested in the fuzzy symmetry of space inversion. For the linear tri-atomic molecules, the center of inversion can be set in two kinds of proper ways: one is set at carbon atom, and the other is set between atoms C and N. If the center of inversion is set at carbon atom, the atoms X, C, and N will move to the place of N, C and X in the original fashion of the molecule, respectively, under the operation of inversion. While if the center of inversion is set between the C and N, then the X, C and N atoms will move to the place of a pseudo-atom, N and C, respectively. Corresponding to the two kinds of centers of inversion, the related membership functions for these linear tri-atomic molecules are listed in table 3. It can be seen from table 3 that except for HCN, no matter the center of inversion is set at atom C or between atoms C and N, the trend of the membership functions μ_Z and μ_E is the same for the rest molecules XCN (X = F, Cl, Br, I), both decreasing in the order of FCN, ClCN, BrCN and ICN, though there are somewhat difference between μ_Z and μ_E for each molecule. It also can be seen from

Table 3

Membership functions of inversion for linear triatomic molecules XCN (X = H, F, Cl, Br, I) as the center of inversion is at atom C and between atoms C and N, respectively. (μ_Z and μ_E are the membership functions of the molecule skeleton, calculated with the atomic number and the total electron on atoms as the criterion, respectively).

XCN	The center of inversion is at atom C		The center of inversion is between atoms C and N	
	μ_Z	μ_E	μ_Z	μ_E
HCN	0.5714	0.5407	0.8571	0.8860
FCN	0.9091	0.9102	0.5455	0.5390
ClCN	0.6667	0.6735	0.4000	0.4089
BrCN	0.4167	0.4223	0.2500	0.2605
ICN	0.3030	0.3086	0.1818	0.1924

table 3 that both μ_Z and μ_E for molecules XCN (X = F, Cl, Br, I) obtained with the center of inversion set at the C atoms are greater than those as the center is set between the atoms C and N. In contrast, both μ_Z and μ_E for HCN obtained with the center of inversion set at the C atoms are smaller than those as the center is set between the atoms C and N. Therefore, for molecules XCN (X = F, Cl, Br, I) it is proper to set the center of inversion at carbon atom, while for HCN it is proper to set the center of inversion between atoms C and N.

Now we turn to discuss the fuzzy symmetries of MOs of these linear triatomic molecules. For XCN (X = F, Cl, Br, I), 12 MOs are formed from the combination of the outermost shell sp^3-AOs of X, C and N atoms. However, the character of fuzzy symmetry of MOs-1 and -2, which are the lowest in energy among the 12 MOs of each molecule, are neglected in tables 4 and 5.

From table 4 we can see that there are six occupied MOs (from MO-3 to MO-8) and four vacant MOs (from MO-9 to M-12) among the 10 MOs of FCN.

Table 4

The symmetrical compositions X_g content and the membership functions for MOs of FCN.

	X_g		Membership function	
	C-center	CN-center	C-center	CN-center
MO-3(σ O)	0.7762	0.2880	0.5751	0.3616
MO-4(π O)	0.2011	0.3997	0.2880	0.1192
MO-5(π O)	0.2011	0.3997	0.2880	0.1192
MO-6(σ O)	0.2988	0.4304	0.4655	0.5452
MO-7(π O)	0.7455	0.1715	0.8875	0.5006
MO-8(π O)	0.7455	0.1715	0.8875	0.5006
MO-9(π V)	0.1033	0.9765	0.6016	0.8858
MO-10(π V)	0.1033	0.9765	0.6016	0.8858
MO-11(σ V)	0.9742	0.4481	0.9513	0.1199
MO-12(σ V)	0.3502	0.0714	0.6722	0.5894

Table 5
The symmetrical composition X_g for MOs of XCN (X = Cl, Br & I), the center of inversion is at atom C.

	ClCN	BrCN	ICN		ClCN	BrCN	ICN
MO-3(σ O)	0.7872	0.8867	0.9243	MO-8(π O)	0.8217	0.8003	0.7564
MO-4(π O)	0.0271	0.0011	0.0297	MO-9(σ V)	0.7385	0.6606	0.6225
MO-5(π O)	0.0271	0.0011	0.0297	MO-10(π V)	0.1142	0.1247	0.1450
MO-6(σ O)	0.2714	0.1868	0.1526	MO-11(π V)	0.1142	0.1247	0.1450
MO-7(π O)	0.8217	0.8003	0.7564	MO-12(σV)	0.3341	0.2869	0.3198
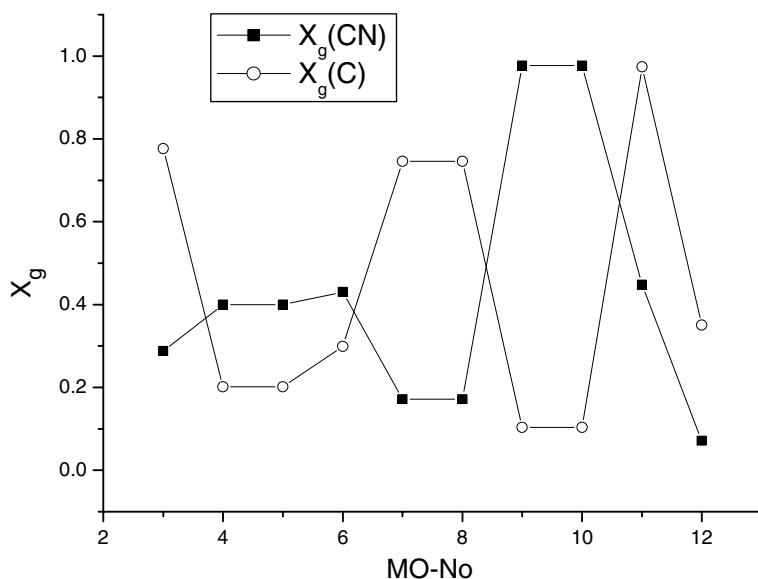
Figure 4. The X_g of MOs for FCN. X_g (C) and X_g (CN) are the result as the center of inversion is at carbon atom and between atoms C and N, respectively.

The MO pairs, i.e. MOs-4 & 5, MOs-7 & 8, and MOs-9 & 10 are degenerate π-MOs. The rest four are σ-MOs. The symmetric conposition (X_g) for the 10 MOs of FCN are list in columns 2 and 3 of table 4 and also shown in figure 4. From figure 4 we can clearly see that the X_g of different MOs behaviors quite different for the two kinds of centers of inversion: For some MO(s), such as MO-3, -7 -8 and -11, the X_g (C) (the center of inversion is at carbon atom) is much larger than the X_g (C-N) (the center of inversion is between the atoms C and N), while for some MO(s), such as MO-9 and -10, the X_g (C) is much smaller than X_g (C-N), and for some MO(s), such as MO-6, the difference of two Xs are not very obviously. In the last two columns of table 4 and also in figure 5, the membership functions for the 10 MOs of FCN are shown. One can see from
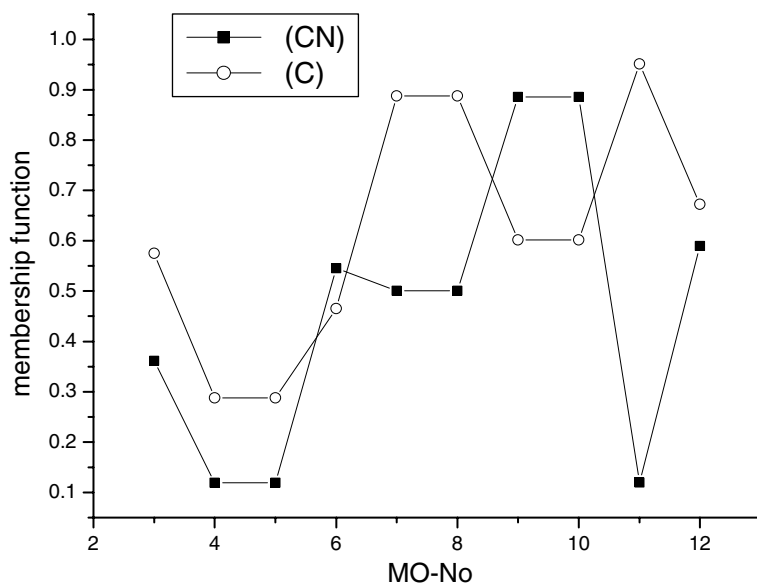
Figure 5. The membership functions of MOs for FCN.

figure 5 that, also, the membership functions behavior different for the two kinds of centers of inversion. Though for most MOs, the membership function μ_C (the center of inversion is at carbon atom) is much larger than the μ_{CN} (the center of inversion is between atoms C and N). However, as to the center of inversion at carbon atom for some MOs, such as the MO-9 &10, the μ_{CN} is larger than μ_C.

For MOs of XCN (X = Cl, Br, and I), the X_g are shown in table 5 and figure 6. Figure 6 indicates that the X_g of the MOs for the three molecules behavior similarly in trend. This may result from the similar construction of these MOs for the three molecules.

In table 6, figures 7 and 8, the X_g and the membership functions of MOs for HCN are list. In majority not always, both the X_g (CN) and μ_{CN} are larger than X_g (C) and μ_C, respectively.

5. Fuzzy symmetries for linear polyatomic molecules

Except for diatomic molecules and triatomic molecules, linear molecules may be composed of many atoms, so-called the linear polyatomic molecules. As for linear polyatomic molecules, except for fuzzy symmetry of inversion, the fuzzy symmetry of one-dimensional translation may be analyzed. One-dimensional translation symmetry is the simplest symmetry in space groups, thus, from this point we can expand our research of fuzzy symmetry to fuzzy
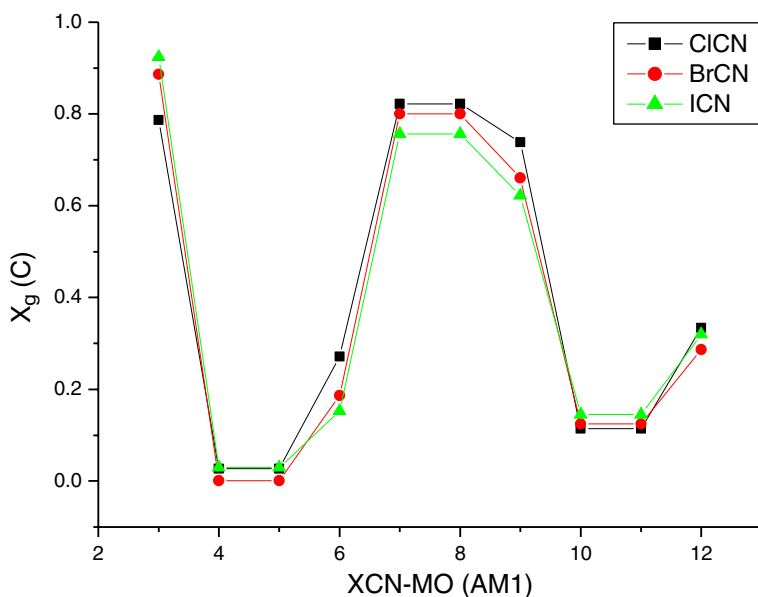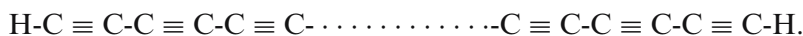
Figure 6. The symmetrical composition X_g of MOs for XCN (X = Cl, Br, I) molecules. Where XCN-AC denoted that the symmetric compositions X_g of MOs for XCN (X = Cl, Br, I) molecules are calculated at AM1 level and using the C-atomic position as the center of inversion.

Table 6
The symmetrical compositions X_g and the membership functions for MOs of HCN.

	X_g		Membership function	
	C-center	CN-center	C-center	CN-center
MO-1(σ O)	0.6501	0.9644	0.3278	0.6557
MO-2(σ O)	0.4741	0.0926	0.7790	0.7079
MO-3(σ O)	0.5398	0.6340	0.3795	0.3660
MO-4(π O)	0.2668	0.0011	0.4664	0.9328
MO-5(π O)	0.2668	0.0011	0.4664	0.9328
MO-6(π O)	0.2400	0.9996	0.5201	0.9598
MO-7(π V)	0.2400	0.9996	0.5201	0.9598
MO-8(σ V)	0.6970	0.5191	0.5647	0.1304
MO-9(σ V)	0.1889	0.0717	0.6659	0.6005

space groups. Here, we take linear polyyne molecule [19] as example to discuss fuzzy symmetry of one-dimensional translation in fuzzy space groups.

The polyyne, H-(C≡C)$_n$-H, can be outspreaded as follows,

$$\text{H-C} \equiv \text{C-C} \equiv \text{C-C} \equiv \text{C-} \cdots\cdots\cdots \text{-C} \equiv \text{C-C} \equiv \text{C-C} \equiv \text{C-H}.$$
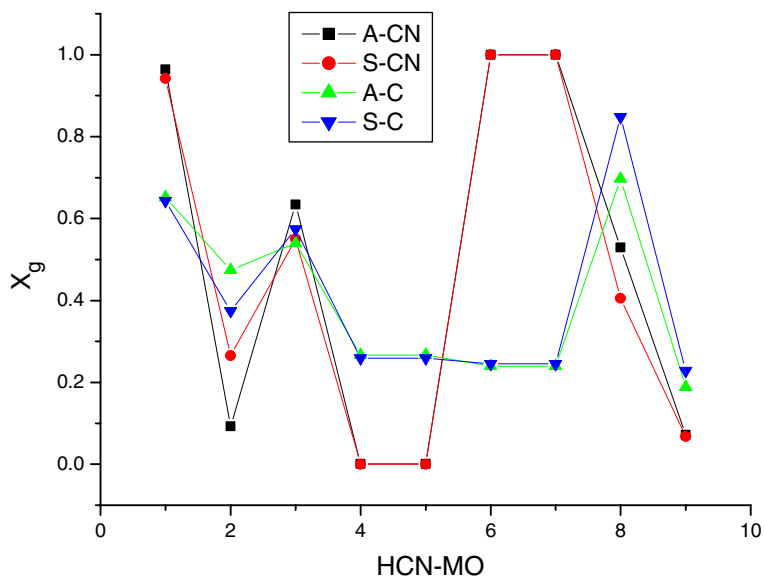
Figure 7. The symmetrical composition X_g of MOs for HCN molecules. Where A-C and A-CN denote that the symmetric compositions X_g of MOs for XCN (X = Cl, Br, I) molecules that are calculated at AM1 level using the C-atomic position and between the point at CN bond as the center of inversion, respectively. As for S-C and S-CN, they are denoted the same meaning as A-C and A-CN, except at STO-3G level. For various calculation level, these relationships are similar.
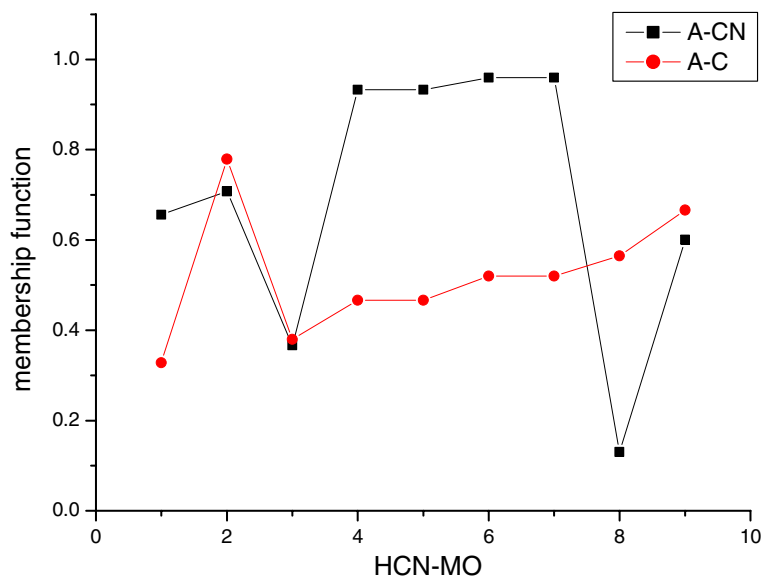

Figure 8. The membership functions of MOs for HCN molecules. Where A-C and A-CN denoted that the membership function of MOs for HCN molecules are calculated at AM1 level moreover using the C-atomic position and between CN position as the center of inversion, respectively.

In this molecule, between the two terminal H atoms, there are $l = n/2$ C≡C units connected by C-C single bonds. If l is even number, the center of inversion is at the middle point of the central C-C single bond. While if l is odd number, the center of inversion is at the middle point of the central C≡C triple bond. Obviously, the symmetry about inversion for polyyne is common symmetry.

Here, we will stress the fuzzy symmetry of space translation in space groups. Corresponding to the translation operation (labeled as $\hat{T}$) toward right by distance of two neighbored carbon atoms (the difference in length between single bond and triple bond is ignored), the membership function can be deduced as follows,

$$\mu_{YT} = \left[\sum_J (Y_J \wedge T_{TJ})\right] / \left[\sum_J (Y_J)\right] = \left[\sum_J (Z_J \wedge Z_{TJ})\right] / \left[\sum_J (Z_J)\right] \quad (4a)$$

$$= [(n-1)Z_C + 2Z_H] / [nZ_C + 2Z_H] = (6n-4)/(6n+2) = \mu_{ZT} \quad (4b)$$

Accordingly, as $n = 2, 4, 6, 8, 10\ldots\ldots$, the values of μ_{ZT} are 0.5714, 0.7692, 0.8421, 0.8800, 0.9032$\ldots\ldots$ This indicates that even n is not very large, the molecule may make out that there is the fuzzy symmetry about operation $\hat{T}$. On the other hand, it can be expected that some properties of polyyne may be affected by its fuzzy symmetry about space translation. The relationship between total energies (TE) and membership functions of polyyne molecules with different n (or l) is an example, as shown in figure 9. Where the total energies calculated at RB3LYP/cc-pVDZ level are from Ref [20]. Corresponding to operation, $\hat{T}$-m, translate toward by m-fold of the distance of the neighbored carbon atoms, we can get:

$$\mu_{YT-m} = \left[\sum_J (Y_J \wedge Y_{T-mJ})\right] / \left[\sum_J (Y_J)\right] = \left[\sum_J (Z_J \wedge Z_{T-mJ})\right] / \left[\sum_J (Z_J)\right]$$
$$(5a)$$

$$= [(n-m)Z_C + 2Z_H] / [nZ_C + 2Z_H] = (6n-6m+2)/(6n+2) = \mu_{ZT-m}.$$
$$(5b)$$

It is obvious that for the same n, i.e. the same polynne, the bigger the m, the less the membership function is, and for the same $m > 0$, i.e. the same translation, the less the n, the less the membership function.

As for the polynne MOs, owing to the criteria for various C-atoms are different, the membership function for translation-symmetry is more complex than that of its molecular skeleton. In chemistry, the frontier and near-frontier MOs are more important. There are some π-MO in polynne. As the directions of the z-axis and molecular principle axis are the same, such π-MO may be denoted as:

$$\Psi = a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3 + a_4\Phi_4 + \cdots + a_n\Phi_n, \quad (6)$$

where the Φ_J and a_J are the p_{x-} (or p_{y-}) AO of J-th C-atom and corresponding LCAO coefficient, respectively. In relation to this MO, the criterion is $Y_J =$
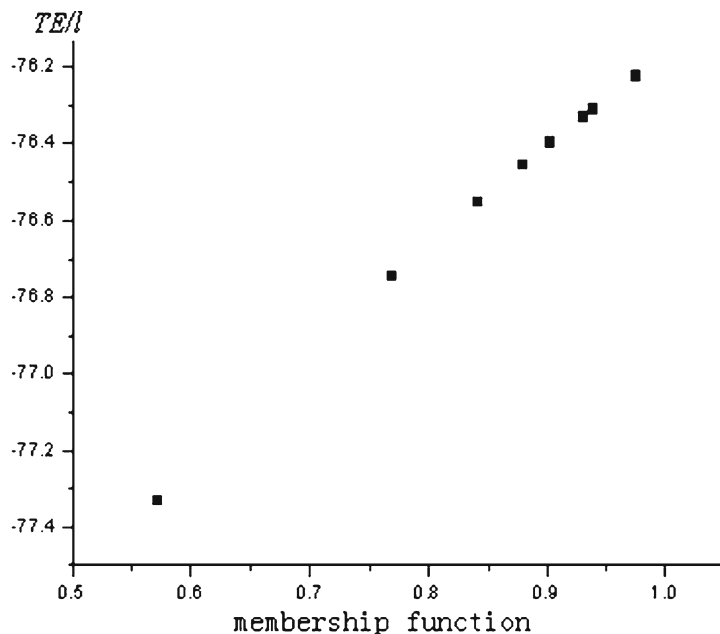
Figure 9. The linear relationship between *TE/l* and membership functions of polyyne molecules for translation operation $\hat{T}$. Where *TE* and *l* are the total energies and the C≡C unit number, respectively.

aJ^2 for J-th C atom, and it is zero for H atoms. Corresponding to $\hat{T}$-m, the membership function is:

$$\mu_{YT-m} = \left[\sum\nolimits_{J} (Y_J \wedge Y_{T-mJ}) \right] \Big/ \left[\sum\nolimits_{J} (Y_J) \right] = \left[\sum\nolimits_{J}^{n-m} (Y_J \wedge Y_{m+J}) \right] \Big/ \left[\sum\nolimits_{J} (Y_J) \right]$$
$$= \left[\sum\nolimits_{J}^{n-m} (a_J^2 \wedge a_{m+J}^2) \right] \Big/ \left[\sum\nolimits_{J} (a_J^2) \right], \tag{7}$$

where the $\sum_{J}$ and $\sum_{J}^{n-m}$ are denoted the summation range being $(1, n)$ and $(1, n - m)$, respectively. For example, the polynne $C_{16}H_2$ at HF STO-3G level, both the HOMO and LVMO are degenerated π-MO. According to equation (7), the $\hat{T}$-m, membership functions for these MO are shown in figure 10. Similar to the case of the molecular skeleton, the membership function decreases as m increases yet, however the decrement curves are not linear as equation (5) predicted, they are sawtooth-like. This phenomenon arises as a result of the alternating single- and tri- bonds. In fact, there are two C (and two inter-atomic distances) in one unit, then we ought to consider $\hat{T}$-m, with even number m.

In addition to the translation symmetry, there are the common space inversion symmetry with membership function equal one. As for fuzzy inversion symmetry, the symmetry element (i.e. the center of inversion) may be selected by not
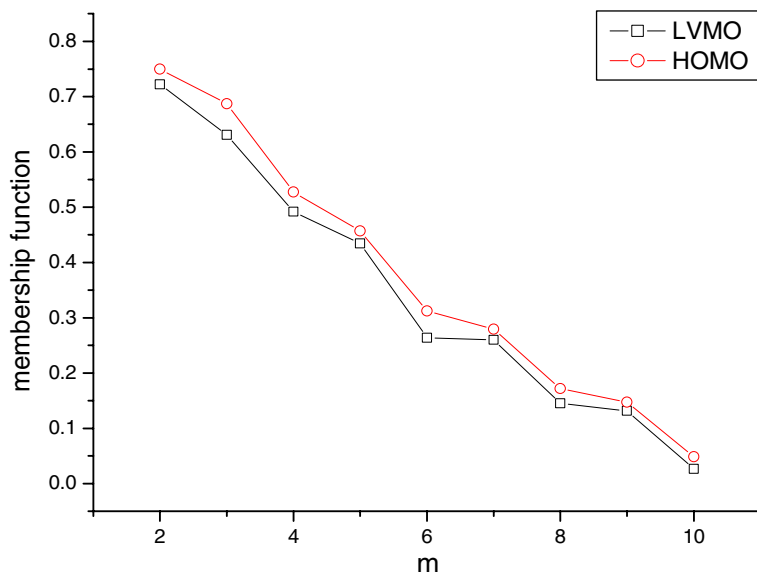
Figure 10. The membership functions for HOMO and LVMO of polynne $C_{16}H_2$, corresponding to the translation operation $\hat{T}$-m.

only one way. In these cases, there are some inter-relationship between the symmetry of fuzzy inversion and fuzzy translation.

It is expected that the fuzzy symmetry of polyyne molecules have many significant characteristics, which intrigues us to make further efforts to work on them. However, in this paper, we just briefly present the commonness and peculiarities of polyyne molecules compared with other linear molecules as far as the fuzzy symmetry is concerned.

6. Conclusions

In previous paper [8], we discussed the fuzzy symmetry of molecule and MO. Moreover, we also introduced their fuzzy characterization and gave some simple application example. Based on these results, in this paper, we have analyzed the fuzzy symmetry of some diatomic molecules, linear tri-atomic molecules and linear polyyne molecules. The main points in this text are listed as follows:

1. As to non-hydride diatomic molecule, the membership function of fuzzy space inversion parity is not too small. While the symmetry composition and membership functions of its MOs depends on their chemical characteristics, and some trends of such dependent relationships are similar for various molecules.

2. All the hydride diatomic molecules HX (X = F, Cl, Br, I) have lower symmetry about space inversion due to the great difference in size of atoms H and X. Consequently, the membership function of the space inversion parity is very small. While the symmetry about space inversion parity for some MOs of the molecule may be not very small. For same kind of MO and molecular skeleton of HX, the sequence of membership function values may differ. For various HX, the membership function and the characterization of MO are interrelated. As for HLi, though there are 1s-AO of H and sp^3-AO of Li to form five MOs, but where only one MO is occupied BMO. The MO-2 of LiH is empty and its membership function for space inversion symmetry is less than that of HX, obviously.

3. For common symmetry, the corresponding symmetry element ought to be only one selected way, however for fuzzy symmetry, there may be not only. As the example, we choose the center of inversion for the hydrogen cyanide and cyanogens halide and analyze their selection positions. In connection to the various selection positions the corresponding membership functions are different. Generally speaking, the symmetry element should be chosen according to the question to resolve. The corresponding membership functions depend on the position of the center of inversion.

4. For polyynes, H-(C≡C)$_n$-H, even n is not very large, the molecule may be provided with the fuzzy symmetry of space translation, and corresponding membership function may be over 0.9. Moreover, it can be expected that some properties of polyyne may depend on the membership functions of this fuzzy symmetry.

Acknowledgments

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