

The fuzzy symmetries for linear tri-atomic B...A...C dynamic systems

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Abstract Based on our previous study on the elementary characterization of the fuzzy symmetry, we inquired the static state fuzzy symmetry of some molecules and their molecular orbitals (MO). Now we will analyze the fuzzy symmetry of some simple linear tri-atomic dynamic systems in connection with the reaction. Three related transformations will mainly be studied in detail. These three transformations are (1) the space inversion transformation about the mid-atom as the center, (2) the reaction reversal transformation in relation to the reaction $B + AC \rightarrow BA + C$ and (3) the joint transformation of the above two. We examined the variation for the internal configuration of these systems owing to the operation of above three transformations, and then establish methods to calculate the fuzzy symmetry characterization, such as the membership functions for the MOs of such linear tri-atomic dynamic systems in relation to these transformations. We examined the variation regularity in relation to the fuzzy symmetry characterization for the MOs of these systems along the intrinsic reaction coordinate (IRC) and dividing line. The variation regularity and the distribution for the fuzzy symmetry characterization in related internal configuration coordinate space are also analyzed. An IRC-scale is suggested for internal configuration coordinate space in this paper.

Keywords Linear tri-atomic dynamic system · Fuzzy symmetry · Reaction reversal transformation · IRC scale

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1 Introduction

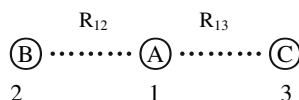
In theoretical chemistry, research on fuzzy symmetry is an interesting field. Important results have been obtained [1–5]. In our previous work [6–11], based on the study of the fuzzy symmetry characterization of molecules and molecular orbitals (MOs), we have analyzed the fuzzy symmetry of the static molecules and their MOs. Now we will study the fuzzy symmetry related to simple reaction dynamic systems and start with the simplest linear tri-atomic system. For the symmetry of such systems, many papers have been published. Among them, *the conservation rule of orbital symmetry* by Woodward and Hoffmann (W–H rule) [12] is important. By means of the quantum field theory, we have analyzed W–H rule [13, 14] for the symmetry in relation to sigmatropic reaction. We pointed out that there is not any perfect point group symmetry, but only the perfect symmetry transformation in relation to the joint (combined or union) reaction reversal and some point symmetry transformation. The simplest system with such kind of symmetry is the H_3 -system. Since the first potential energy surface of linear H_3 -system [15] was announced, there are a lot of papers in relation to this system and other linear tri-atomic system $B \cdots A \cdots C$ published [16, 17]. They are mainly concerned with the work of the potential energy surface that relates with the reaction: $B + AC \rightarrow BA + C$. Now we will analyze the subject in relation to this symmetry. For the H_3 system or the tri-atomic $B \cdots A \cdots C$ system with the same B and C atom, there are not any point group symmetry in general. But using the atomic distances of AB and AC as the internal configuration coordinates, the related potential energy surface ought to be provided with the reflection symmetry about the dividing surface (dividing line—the diagonal line in above internal configuration coordinate plane). Such symmetry about the dividing surface will not show in the corresponding potential energy surface of the linear tri-atomic $B \cdots A \cdots C$ system with different B and C atoms.

In this paper we will analyze the symmetry and fuzzy symmetry for linear tri-atomic $B \cdots A \cdots C$ system by means of some typical examples. In addition, the point group symmetry transformation, the reaction reversal transformation and their combination [13, 14] will be studied. Here reaction reversal transformation means that the relate system with the initial state ought to be reflected to a new state about the dividing surface (or line) [17, 18] as a mirror. Generally speaking, such transformation is a kind of symmetry transformation for the whole potential surface, but not for such dynamic system, itself. The reaction reversal transformation may be denoted as \hat{R} . In some cases, it may often unite with a certain point group transformation \hat{G} to form a new joint symmetrical transformation $\hat{G}\hat{R}$ for the dynamic system-self. In this paper \hat{G} is usually the space inversion transformation \hat{P} .

2 Computation Detail

The atomic positions in the linear $B \cdots A \cdots C$ system are specified from A, B and C by 1, 2 and 3, respectively, as shown in Fig. 1, and the atomic distances by R_{12} and R_{13} , respectively.

Fig. 1 The linear three-atomic B···A···C system and atomic numbering



Since the atomic intervals in the system may be varied, the atomic criteria (Y) are depended not only on the atomic intrinsic property but also on the atomic related position (internal configuration coordinate). For the linear B···A···C tri-atomic system, the atomic related position may be determined by atomic intervals R_{12} and R_{13} . The atomic criteria may thus be denoted as follows:

$$Y_A = Y_A(R_{12}, R_{13}), \quad (1a)$$

$$Y_B = Y_B(R_{12}, R_{13}), \quad (1b)$$

$$Y_C = Y_C(R_{12}, R_{13}). \quad (1c)$$

For this system, both atomic related positions (R_{12} and R_{13}) and atomic criteria (Y_A , Y_B , Y_C) ought to change under the operation of transformation \hat{G} :

$$\hat{G}(R_{12}, R_{13}) = (R_{G12}, R_{G13}) \quad (2a)$$

$$\hat{G}(Y_A, Y_B, Y_C) = (Y_{GA}, Y_{GB}, Y_{GC}) \quad (2b)$$

If \hat{G} is the space inversion transformation \hat{P} about the A atom as the centre, then:

$$\hat{P}(R_{12}, R_{13}) = (R_{P12}, R_{P13}) = (R_{13}, R_{12}), \quad (3a)$$

$$\hat{P}(Y_A, Y_B, Y_C) = (Y_{PA}, Y_{PB}, Y_{PC}) = (Y_A, Y_C, Y_B). \quad (3b)$$

If \hat{G} is the reaction reversal transformation \hat{R} , then:

$$\hat{R}(R_{12}, R_{13}) = (R_{R12}, R_{R13}) \quad (4a)$$

$$\hat{R}(Y_A, Y_B, Y_C) = (Y_{RA}, Y_{RB}, Y_{RC}) \quad (4b)$$

In general, the internal configuration coordinates and the atomic criteria of initial and final state can not be interrelated by simple ways due to the operation of \hat{R} . On the other hand, for the union (or joint) transformation, $\hat{P}\hat{R} = \hat{R}\hat{P}$:

$$\hat{P}\hat{R}(R_{12}, R_{13}) = (R_{PR12}, R_{PR13}) = (R_{R13}, R_{R12}) \quad (5a)$$

$$\hat{P}\hat{R}(Y_A, Y_B, Y_C) = (Y_{PRA}, Y_{PRB}, Y_{PRC}) = (Y_{RA}, Y_{RC}, Y_{RB}) \quad (5b)$$

As we known [7, 8], the membership functions (μ) for a certain molecule or MO system in relation to the operation of transformation \hat{G} may be calculated. For our system, $\mu(\hat{G})$ may be calculated as:

$$\mu(\hat{G}) = (Y_A \wedge Y_{GA} + Y_B \wedge Y_{GB} + Y_C \wedge Y_{GC}) / (Y_A + Y_B + Y_C) \quad (6a)$$

If the normalization criterion is introduced, the denominator in Eq. 6a would equal to one, and the equation would be simplified as:

$$\mu(\hat{G}) = (Y_A \wedge Y_{GA} + Y_B \wedge Y_{GB} + Y_C \wedge Y_{GC}) \tag{6b}$$

Therefore, the membership functions of the transformations \hat{P} , \hat{R} and $\hat{R}\hat{P}$, would become, respectively:

$$\mu(\hat{P}) = Y_A \wedge Y_{PA} + Y_B \wedge Y_{PB} + Y_C \wedge Y_{PC} = Y_A + 2Y_B \wedge Y_C \tag{7a}$$

$$\mu(\hat{R}) = Y_A \wedge Y_{RA} + Y_B \wedge Y_{RB} + Y_C \wedge Y_{RC} \tag{7b}$$

$$\begin{aligned} \mu(\hat{P}\hat{R}) &= Y_A \wedge Y_{PRA} + Y_B \wedge Y_{PRB} + Y_C \wedge Y_{PRC} \\ &= Y_A \wedge Y_{RA} + Y_B \wedge Y_{RC} + Y_C \wedge Y_{RB} \end{aligned} \tag{7c}$$

If atoms B and C are different, all of these membership functions would be less than one if Eqs. 7a–c are used. If B and C are the same while $R_{12} \neq R_{13}$ and $Y_B \neq Y_C$ are true, the membership functions would not be the same, but if $Y_B = Y_{RC}$ and $Y_C = Y_{RB}$ are true, the corresponding membership functions in relation to transformation $\hat{P}\hat{R}$ would be equal to one. In other words, there is some symmetry in relation to the joint reaction reversal and parity transformation ($\hat{P}\hat{R}$) for such system [13, 14], but the membership functions for both \hat{R} and \hat{P} are not equal to one. That is, there is no accurate symmetry for \hat{R} and \hat{P} , but only fuzzy symmetry for them. If B and C are different, the system has only some related fuzzy symmetry in relation to $\hat{P}\hat{R}$.

Now we turn to determine the various atomic criteria for the dynamic system. In the theoretic chemistry region, σ MO occupied by single electron (σ SMO) and its neighbour σ MOs, occupied and virtual (noted as σ OMO-1 and σ VMO-1, respectively) are more interesting. We suggested that the atomic criterion for a certain MO may be assigned to the square or summation of square for one or more LCAO coefficients according to the MO composition of the AOs [7, 8]. This scheme may also be applied to our present system. However, it is noteworthy that in the dynamic systems the LCAO coefficients depend on the internal configuration coordinate of the system. Therefore, the atomic criteria for various internal configuration coordinate conditions will be different.

Now we consider a certain state J, corresponding to the point (R_{12}, R_{13}) of the internal configuration coordinate plane for the linear tri-atomic B...A...C system, and the state J will be changed to state GJ under transformation \hat{G} , i.e, the state J transform to state GJ. Now we analyze the space inversion transformation ($\hat{G} = \hat{P}$) about atom A as the symmetrical centre. As shown in Fig. 2, after the operation of space inversion transformation ($\hat{G} = \hat{P}$), the linear tri-atomic system B...A...C ought to be changed

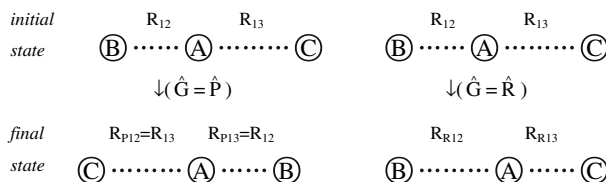


Fig. 2 The linear three-atomic B...A...C system under operations \hat{P} and \hat{R}

from the initial state J to the final state PJ, and B and C will commute, and so will R_{12} and R_{13} (i.e., $R_{P12} = R_{13}$; $R_{P13} = R_{12}$). If B and C are the same moreover the R_{12} equals R_{13} , the final state and the initial state may be identical; such system will have the usual space inversion symmetry, and the membership function in relation to transformation \hat{P} will equal unity. For the majority cases, however, the membership functions in relation to \hat{P} will be less than one. The reaction reversal transformation ($\hat{G} = \hat{R}$) is also shown in Fig. 2. From the initial state J to the final state RJ, no commutation exists between neither B and C nor R_{12} and R_{13} . If the initial state J belongs to intrinsic coordinate (IRC) path, the intrinsic reaction coordinate value (x_J -IRC) may be obtained using quantum chemical programs such as Gaussian [19]. The intrinsic reaction coordinate value (x_{RJ} -IRC) for the final state RJ ought to be the opposite number of x_J -IRC, i.e.,

$$(x_{RJ}\text{-IRC}) = -(x_J\text{-IRC}). \quad (8)$$

According to state RJ, we may obtain R_{R12} and R_{R13} . In general, R_{R12} and R_{R13} are different from R_{P12} and R_{P13} , respectively. That is:

$$R_{R12} \neq R_{P12} = R_{13}, \quad (9a)$$

$$R_{R13} \neq R_{P13} = R_{12}. \quad (9b)$$

If B and C are same atoms, (R_{R12}, R_{R13}) and (R_{P12}, R_{P13}) may be the equivalence. For such case, the dividing curve (line) would be the diagonal line in the internal configuration coordinate (R_{R12}, R_{R13}) space. For states in the dividing line, membership functions in relation to both transformations \hat{P} and \hat{R} ought to equal one, whereas for states elsewhere, the membership functions in relation to both \hat{P} and \hat{R} ought to be less than one even though they may be equal.

As shown in Fig. 3 clearly, the operation results for the joint transformation $\hat{P}\hat{R}$ are the same as those for $\hat{R}\hat{P}$. For the linear tri-atomic system $B \cdots A \cdots C$ with the same

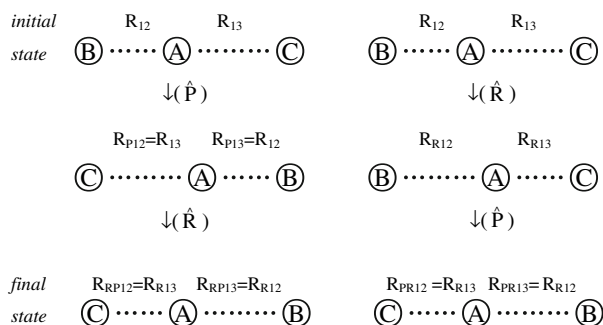


Fig. 3 The linear three-atomic $B \cdots A \cdots C$ system under joint operation $\hat{P}\hat{R}$

atoms B and C, we have:

$$R_{R12} = R_{P12} = R_{13} \quad (10a)$$

$$R_{R13} = R_{P13} = R_{12}, \quad (10b)$$

And so the final and initial states in Fig. 3 are the same. Therefore, there is the joint transformation $\hat{P}\hat{R}$ for such system, and its corresponding membership function equals one. If atoms B and C are different, the related membership function is less than one. On the other hand, for the system with the same atoms B and C the membership function in relation to \hat{R} or \hat{P} alone is usually less than one, except for those in the dividing surface, whereas the membership function in relation to the joint transformation $\hat{P}\hat{R}$ will be one no matter what the state belongs to dividing line or not.

Owing to the operation of \hat{R} , the initial state $\{R_{12}, R_{13}\}$ would change into the final state $\{R_{R12}, R_{R13}\}$ in general. For the linear tri-atomic system $B \cdots A \cdots C$ with the same atoms B and C, the final state (R_{R12}, R_{R13}) can be obtained by Eq. 10. Regardless the B and C are the same or not, for the states in the dividing surface, the \hat{R} ought to be equivalent to the identity transformation \hat{E} , and we may get the:

$$(R_{R12}, R_{R13}) = (R_{12}, R_{13}). \quad (11)$$

If the state in the IRC path, the final state (R_{R12}, R_{R13}) may be obtained by Eq. 8. However, the so-called general cases including states other than in the dividing surface and IRC path must also be examined. Only the IRC path and corresponding IRC value (x -IRC) can be obtained using Gaussian [19], but the dividing surface can not be obtained directly. If B and C are different, the related dividing surface may be not a straight line (i.e., not a one dimensional plan). How can we obtain the state generated by the operation of \hat{R} ? To start with, we examined Fig. 4, where Fig. (A) and (B) denote the two typical examples with B and C being and not being the same, respectively. In the figure, the vertical axis denotes the internal configuration coordinate (R_{12} and R_{13}) of the state, and the abscissa axis the IRC value. As shown in the figure, both R_{12} and R_{13} are the monotonic functions of the IRC value. R_{12} and R_{13} are monotonically increasing and decreasing, respectively. We may use the IRC values to denote R_{12} and R_{13} , and call them the IRC-scale of R_{12} and R_{13} . The IRC value is also the IRC-scale of IRC path itself. Corresponding to a certain state in the IRC path, R_{12} and R_{13} ought to be the same IRC-scale value. For the state outside of the IRC path, R_{12} and R_{13} IRC-scale values ought to be different. When both of these two IRC-scale values equal zero, this corresponds to the transition state. When B and C are the same, the curves of R_{12} and R_{13} ought to cross in the transition state. However, when B and C are different, the curves of R_{12} and R_{13} ought to cross not in the transition state.

We may use $R_{12}(a)$ and $R_{13}(a')$ to denote R_{12} and R_{13} both of which have the IRC-scale values a and a' , respectively. And use $\{R_{12}, R_{13}\}$ to denote any state of the linear tri-atomic $B \cdots A \cdots C$ system. Therefore the $\{R_{12}(a), R_{13}(a)\}$ and $\{R_{12}(a), R_{13}(b)\}$ ($b \neq a$) denote states in the IRC path and the outside of the IRC path, respectively. Under the operation of \hat{R} , the initial state $\{R_{12}(a), R_{13}(b)\}$ of the linear tri-atomic

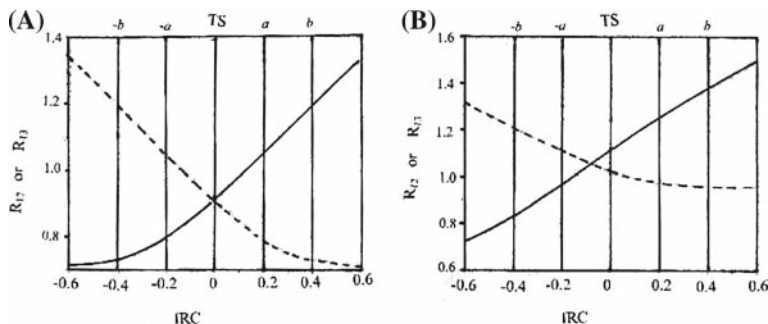


Fig. 4 Variation of the internal configuration coordinates for the linear three-atomic $B \cdots A \cdots C$ systems: R_{12} (solid curve) and R_{13} (dotted curve) along the IRC at HF/STO-3G. (A) HHH system; (B) HHF system ($R_{12} = R_{HH}$; $R_{13} = R_{HF}$)

$B \cdots A \cdots C$ system will be changed to:

$$\hat{R}\{R_{12}(a), R_{13}(b)\} = \{R_{R12}(a), R_{R13}(b)\} = \{R_{12}(-b), R_{13}(-a)\} \quad (12a)$$

If B and C are the same atoms, from inspection of Fig. 4(A) we have:

$$\hat{R}\{R_{12}(a), R_{13}(b)\} = \{R_{12}(-b), R_{13}(-a)\} = \{R_{13}(b), R_{12}(a)\} \quad (12b)$$

That is, $R_{12}(a)$ and $R_{13}(b)$ of the initial state will be commute under operation \hat{R} for systems with the same B and C atoms. For the initial state in the IRC path, Eq. 12a becomes:

$$\hat{R}\{R_{12}(a), R_{13}(a)\} = \{R_{R12}(a), R_{R13}(a)\} = \{R_{12}(-a), R_{13}(-a)\} \quad (13a)$$

If B and C are the same, we have:

$$\hat{R}\{R_{12}(a), R_{13}(a)\} = \{R_{12}(-a), R_{13}(-a)\} = \{R_{13}(a), R_{12}(a)\} \quad (13b)$$

The state in the dividing surface (line) ought to be unchanged due to operation \hat{R} . Using Eq. 12a, we found that state $\{R_{12}(a), R_{13}(b)\}$ in the dividing line satisfies a condition:

$$a = -b \quad (14a)$$

On the other hand, state $\{R_{12}(a), R_{13}(b)\}$ in the IRC path ought to satisfy a different condition:

$$a = b. \quad (14b)$$

As for the transition state (TS), i.e., the state at the point of intersection between the dividing line and the IRC path, this state must satisfy the following condition:

$$a = b = 0 \quad (14c)$$

Therefore, for TS, the reaction reversal transformation \hat{R} is equivalent to the identity transformation \hat{E} . Various states $\{R_{12}(a), R_{13}(a)\}$ in the IRC path may be obtained using program Gaussian [19]. According to Eq. 14a, the state in dividing line ought to be $\{R_{12}(a), R_{13}(-a)\}$. This may be a simplification and approximation method for the calculation of dividing surfaces. It is noticed that Eq. 14 is true whether B and C are the same or not.

For the initial state $\{R_{12}(a), R_{13}(b)\}$ of the linear tri-atomic B...A...C system, R_{12} and R_{13} will be commute under operation of the space inversion \hat{P} about A, i.e.,

$$\hat{P}\{R_{12}(a), R_{13}(b)\} = \{R_{P12}(a), R_{P13}(b)\} = \{R_{13}(b), R_{12}(a)\}. \quad (15)$$

This equation is similar to Eq. 12b. However, Eq. 12b may be true only for systems with the same B and C atoms, but Eq. 15 is true whether or no. In general, we have,

$$\{R_{P12}(a), R_{P13}(b)\} \neq \{R_{R12}(a), R_{R13}(b)\}. \quad (16a)$$

Only for the cases with the same B and C do we have,

$$\{R_{P12}(a), R_{P13}(b)\} = \{R_{R12}(a), R_{R13}(b)\} \quad (16b)$$

It must be pointed out that \hat{R} and \hat{P} are different transformations even if B and C are the same. Since in such case, the same B and C would commute under transformation \hat{P} , but they would not commute under transformation \hat{R} . This is important for the analysis of the fuzzy symmetry of MOs. The membership function in relation to a certain transformation ought to be connected with only the square term of the phase, the membership functions in related to \hat{R} and \hat{P} would be equal for systems with the same B and C. The analysis in connection with the representation component may differ evident. On the other hand, the membership functions of the system with different B and C ought to be unequal under \hat{R} and \hat{P} .

As for joint transformation $\hat{P}\hat{R}$, the initial state $\{R_{12}(a), R_{13}(b)\}$ of linear tri-atomic B...A...C system may be transformed as:

$$\begin{aligned} \hat{P}\hat{R}\{R_{12}(a), R_{13}(b)\} &= \hat{P}\{R_{R12}(a), R_{R13}(b)\} = \{R_{R13}(b), R_{R12}(a)\} \\ &= \hat{P}\{R_{12}(-b), R_{13}(-a)\} = \{R_{13}(-a), R_{12}(-b)\}. \end{aligned} \quad (17a)$$

For the system with the same B and C, using Eq. 16b, we have,

$$\hat{P}\hat{R}\{R_{12}(a), R_{13}(b)\} = \{R_{12}(a), R_{13}(b)\}. \quad (17b)$$

Therefore, for such system, the membership function related to the joint transformation $\hat{P}\hat{R}$ would be unity. In other words, the system stay unchanged under transformation $\hat{P}\hat{R}$, and the related representation would be pure (i.e., pure symmetrical or pure asymmetrical). For the system whose B and C are different, the membership function of corresponding joint transformation $\hat{P}\hat{R}$ will be less than one, and such system has only some fuzzy symmetry in relation to the joint transformation $\hat{P}\hat{R}$. The related representations would be not pure.

By the way, as shown in Fig. 4, both R_{12} and R_{13} are monotonic functions of the IRC value, so we may introduce the IRC-scale to substitute the common nature scale (e.g. Å). Some examples will be given in the section below. It should be noted that using the IRC-scale to denote R_{12} and R_{13} will require them not too small in common nature scale, otherwise R_{12} and R_{13} may not correspond to any IRC-scale values.

3 The fuzzy symmetry for the transition state of the $B \cdots A \cdots C$ system

For the linear $B \cdots A \cdots C$ system, to start with, we may find the transition state (TS) using the Gaussian program [19], and analyze its related fuzzy symmetry. \hat{R} and the identity transformation \hat{E} are equivalent for TS. We will examine the fuzzy parity symmetry in relation to the space inversion transformation, \hat{P} . Using Gaussian program to find the related intrinsic reaction coordinate (IRC), we may then obtain the LCAO-MO coefficient of the system $\{R_{12}(a), R_{13}(a)\}$ point by point along the IRC path, and find their atomic criteria, Y_A , Y_B and Y_C according to the single point calculation. After that, we may obtain the state $\{R_{12}(-a), R_{13}(-a)\}$ under operation \hat{R} as well as related atomic criteria, Y_{RA} , Y_{RB} and Y_{RC} . Therefore, we can analyze the fuzzy symmetry along the whole IRC path. At last, we may extend to investigate the various states $\{R_{12}, R_{13}\}$ in the whole internal configuration coordinate space.

We first examine the fuzzy symmetry of TS. Since for TS, \hat{R} is equivalent as \hat{E} , so we have:

$$\hat{R}(R_{12TS}, R_{13TS}) = (R_{R12TS}, R_{R13TS}) = (R_{12TS}, R_{13TS}) \quad (18a)$$

$$\hat{R}(Y_{ATS}, Y_{BTS}, Y_{CTS}) = (Y_{RATS}, Y_{RBTS}, Y_{RCTS}) = (Y_{ATS}, Y_{BTS}, Y_{CTS}) \quad (18b)$$

and as $\hat{P}\hat{R}$ is equivalent to \hat{P} , we obtain:

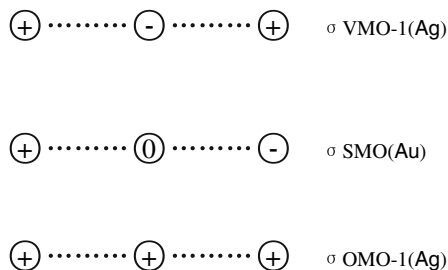
$$\hat{P}\hat{R}(R_{12TS}, R_{13TS}) = \hat{P}(R_{12TS}, R_{13TS}) = (R_{13TS}, R_{12TS}) \quad (19a)$$

$$\hat{P}\hat{R}(Y_{ATS}, Y_{BTS}, Y_{CTS}) = \hat{P}(Y_{ATS}, Y_{BTS}, Y_{CTS}) = (Y_{ATS}, Y_{CTS}, Y_{BTS}) \quad (19b)$$

For the same B and C, since, in general, $R_{12} \neq R_{13}$, and thus Y_B and Y_C are also different. However for TS, both $Y_{BTS} = Y_{RCTS} = Y_{CTS} = Y_{RBTS}$ and $R_{12TS} = R_{13TS}$ may be true. Therefore, for the whole skeleton and MOs, the membership functions in relation to $\hat{P}\hat{R} = \hat{P}$ ought to be unity, and the irreducible representations of the MOs would be pure. For example, σ SMO of TS of $H \cdots H \cdots H$ system belongs to the pure asymmetrical irreducible representation A_u , whereas σ OMO-1 and σ VMO-1 belong to the pure symmetrical one A_g , as shown in Fig. 5.

For other linear tri-atomic $B \cdots A \cdots C$ systems with the same B and C, e.g., the $H \cdots X \cdots H$ ($X = \text{halide atom}$), the σ SMO, σ OMO-1 and σ VMO-1 of TS also belong to pure symmetrical or pure asymmetrical irreducible representations. The σ MOs with pure symmetrical irreducible representations are formed by combining two sAOs of H

Fig. 5 MOs of the transition state of $H \cdots H \cdots H$ system and corresponding irreducible representations



atoms with the same phases and one s AO of X atom. The σ MOs with pure asymmetrical irreducible representations are formed and combined by means of two s AOs of H atoms with the different phases and one p_z -AO of X atom. The π MO is formed only by py - or px -AO of X atom. In essence, and they mainly keep the characteristic of the original AOs. For TS of $H \cdots F \cdots H$ system, the LCAO-MO in relation to σ OMO-1, σ SMO and σ VMO-1(α -spin), at the HF/STO-3G level, may be denoted respective as:

$$\begin{aligned}
 \Psi(\sigma \text{ OMO-1}) &= 0.4812\Phi(1F, 2pz) + 0.5252\Phi(2H, 1s) - 0.5252\Phi(3H, 1s) \\
 \Psi(\sigma \text{ SMO}) &= 0.1022\Phi(3F, 1s) - 0.5611\Phi(3F, 2s) + 0.7425\Phi(2H, 1s) \\
 &\quad + 0.7425\Phi(3H, 1s) \\
 \Psi(\sigma \text{ VMO-1}) &= 0.9581\Phi(1F, 2pz) - 0.5795\Phi(2H, 1s) + 0.5795\Phi(3H, 1s)
 \end{aligned} \tag{20a}$$

These MOs (β -spin), at the same level, may be denoted respectively as:

$$\begin{aligned}
 \Psi(\sigma \text{ OMO-1}) &= 0.7953\Phi(1F, 2pz) + 0.2799\Phi(2H, 1s) - 0.2799\Phi(3H, 1s) \\
 \Psi(\sigma \text{ SMO}) &= 0.0926\Phi(3F, 1s) - 0.5239\Phi(3F, 2s) + 0.7453\Phi(2H, 1s) \\
 &\quad + 0.7453\Phi(3H, 1s) \\
 \Psi(\sigma \text{ VMO-1}) &= -0.7191\Phi(1F, 2pz) + 0.7302\Phi(2H, 1s) - 0.7302\Phi(3H, 1s)
 \end{aligned} \tag{20b}$$

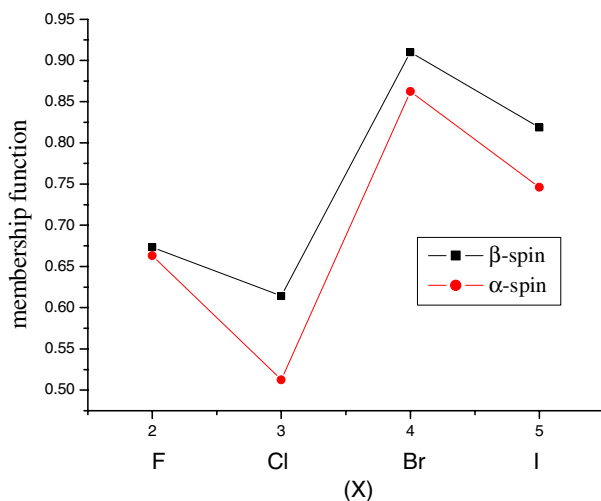
The membership function in relation to the joint transformation $\hat{P}\hat{R} = \hat{P}$ ought to be unity. For both α and β spin states, σ SMO is symmetrical, but σ OMO-1 and σ VMO-1 are asymmetrical. For calculation at other levels, the MO may differ in form, but all the membership functions related to $\hat{P}\hat{R} = \hat{P}$ will be unity. As for other X (Cl, Br, I) in the $H \cdots X \cdots H$ system, the TS would be similar. By the way, for the H_3 system, the σ SMO is asymmetrical, and the σ OMO-1 and σ VMO-1 are symmetrical. However, its membership function for $\hat{P}\hat{R}$ ought to be still unity. For the linear tri-atomic $B \cdots A \cdots C$ system, only if B and C are the same, the MOs of the transition state would belong to the pure symmetrical or pure asymmetrical irreducible representations.

For the TS of a $B \cdots A \cdots C$ system with different B and C, e.g., $H \cdots H \cdots F$, it will be more complicated—the representations that σ SMO, σ OMO-1 and σ VMO-1 belong to will be not pure symmetrical nor pure asymmetrical. However, \hat{R} and \hat{E} are still equivalent for TS, and the membership functions in relation to \hat{R} ought to be

Table 1 The membership functions for the MOs of the transition state of $H \cdots H \cdots X$ ($X = \text{halide atom}$) in relation to transformation $\hat{P}\hat{R} = \hat{P}$

	α -spin*			β -spin*		
	σ OMO-1	σ SMO-O	σ VMO-1	Σ OMO-1	σ SMO-V	σ VMO-1
HHF	0.6151	0.6632	0.8884	0.5235	0.6733	0.9338
HHCl	0.9137	0.5125	0.8458	0.4360	0.6140	0.9762
HHBr	0.9171	0.8623	0.7640	0.4064	0.9101	0.9725
HHI	0.4265	0.7462	0.7608	0.4875	0.8185	0.9388

* For σ SMO, the α -spin state is occupied, but the β -spin state is virtual

**Fig. 6** The membership functions of $H \cdots H \cdots X$ ($X = \text{halide atom}$) for σ SMO of the transition state at HF/STO-3G in relation to $\hat{P}\hat{R} (= \hat{P})$

unity. Equations 18 and 19 are true, too. The fuzzy symmetry in relation to \hat{P} may be analyzed as the common linear tri-atomic molecule [7]. As shown in Table 1, there are the membership functions in relation to $\hat{P}\hat{R} = \hat{P}$ (at HF/STO-3G level) for some σ MOs of $H \cdots H \cdots X$ system ($X = \text{halide atom}$) transition state. For various spin states of the same MO, the membership functions will be different. As shown in Fig. 6, there are the membership functions in relation to $\hat{P}\hat{R} = \hat{P}$ for σ SMO (two different spin states) of the $H \cdots H \cdots X$ ($X = \text{halide atom}$) TS.

Figure 7 shows the membership functions in relation to $\hat{P}\hat{R} = \hat{P}$ for σ OMO-2, σ OMO-1, σ SMO and σ VMO-1 of TS of the $H \cdots H \cdots F$ system (at the HF/STO-3G level). The irreducible representation components in relation to $\hat{P}\hat{R} = \hat{P}$ may also be different between different MOs. For the MOs of TS of the $H \cdots H \cdots X$ system, the representation components in relation to $\hat{P}\hat{R} = \hat{P}$ may be calculated using the method for the usual linear molecule, in principle.

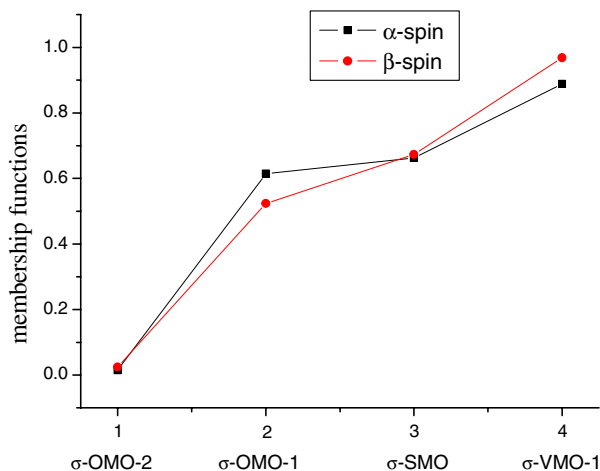


Fig. 7 The membership functions of $\text{H}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{F}$ system in relation to the transformation $\hat{P}\hat{R} = \hat{P}$ for σ OMO-2, σ OMO-1, σ SMO and σ VMO-1 of the transition state

4 The fuzzy symmetry for the $\text{H}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{H}$ system

4.1 The fuzzy symmetry of $\text{H}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{H}$ system in the IRC path and dividing line

Now we examine the linear tri-atomic H_3 system: $\text{H}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{H}$. That is the simplest system with joint point group transformation and reaction reversal symmetry [13, 14]. As mentioned above, its TS has the usual symmetrical center and the membership function in relation to \hat{P} ought to be unity and the corresponding MO irreducible representation will be pure symmetrical or pure asymmetrical. The irreducible representation of σ SMO is pure asymmetrical, but those of σ OMO-1 and σ VMO-1 are pure symmetrical.

Besides the TS, the states in IRC path, their membership functions in relation to \hat{P} will be less than one, and the corresponding irreducible representations will be not pure symmetrical nor pure asymmetrical. On the other hand, owing to such system has the perfect symmetry in relation to the joint transformation $\hat{P}\hat{R}$, the related membership function ought to be one for the states in the IRC path, and the corresponding MOs belong to pure symmetrical or pure asymmetrical irreducible representations. Different spin states of σ SMO belong to the pure asymmetrical irreducible representations, but those of σ OMO-1 and σ VMO-1 belong to the pure symmetrical one.

For the MOs of the state $\{R_{12}(a), R_{13}(a)\}$ in the IRC path calculated above, we may obtain their membership functions in relation to \hat{R} and \hat{P} . According to the calculation results for linear tri-atomic H_3 —system using Gaussian [19] at the HF/STO-3G level, we may further calculate these membership functions. In Fig. 8, (A)–(C) denote the membership functions respectively for σ SMO, σ OMO-1 and σ VMO-1 of the H_3 -system, in which α and β denote the corresponding spin states of related MOs, and R and P denote the membership functions respectively in relation to \hat{R} and \hat{P} . As shown in the figure, all the membership functions in relation to $\hat{P}\hat{R}$ are unity, and the membership

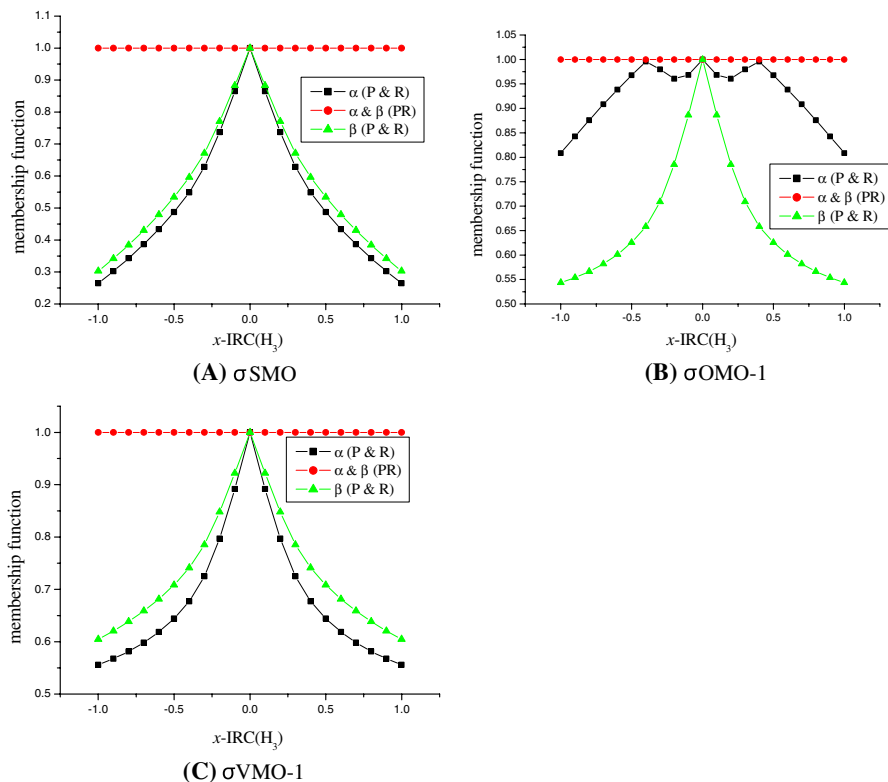


Fig. 8 Variation of the membership functions of $\text{H} \cdots \text{H} \cdots \text{H}$ system with IRC values along the IRC path for σSMO (A), $\sigma\text{OMO-1}$ (B), $\sigma\text{VMO-1}$ (C) with various spin states under transformations $\hat{P}\hat{R}$, \hat{R} and \hat{P}

functions in relation to \hat{R} and \hat{P} are equal for the same MO with the same spin state, although there are somewhat difference for the same MO with different spin states. For TS (IRC=0), all these membership functions are unity. This is always true for the linear tri-atomic $\text{B} \cdots \text{A} \cdots \text{C}$ system with the same B and C.

For the MOs of the $\text{H} \cdots \text{H} \cdots \text{H}$ system in the states along the IRC path, we may consider their irreducible representation (i.e., symmetrical and asymmetrical) components in relation to \hat{P} . Figure 9 denotes the variation of the irreducible representation components for the $\sigma\text{OMO-1}$, $\sigma\text{VMO-1}$ and σSMO of this system along the IRC path. For the states in the IRC, the IRC coordinate values (IRC-scale) are denoted as $x\text{-IRC}$. For $x\text{-IRC}=0$ (transition state), the related irreducible representations ought to be pure. For $\sigma\text{OMO-1}$ and $\sigma\text{VMO-1}$, their symmetrical representation component, $X(\text{G})=1$, and the asymmetrical one, $X(\text{U})=0$, but for the σSMO , $X(\text{G})=0$ and $X(\text{U})=1$. For other states, the irreducible representations will not be pure, yet their main representation components will usually be related to the same as for the transition state, i.e., for $\sigma\text{OMO-1}$ and $\sigma\text{VMO-1}$, the main representation components will be related to symmetrical, whereas for σSMO to asymmetrical. For such system, the irreducible representation components in relation to $\hat{P}\hat{R}$, which the MOs belong, ought to

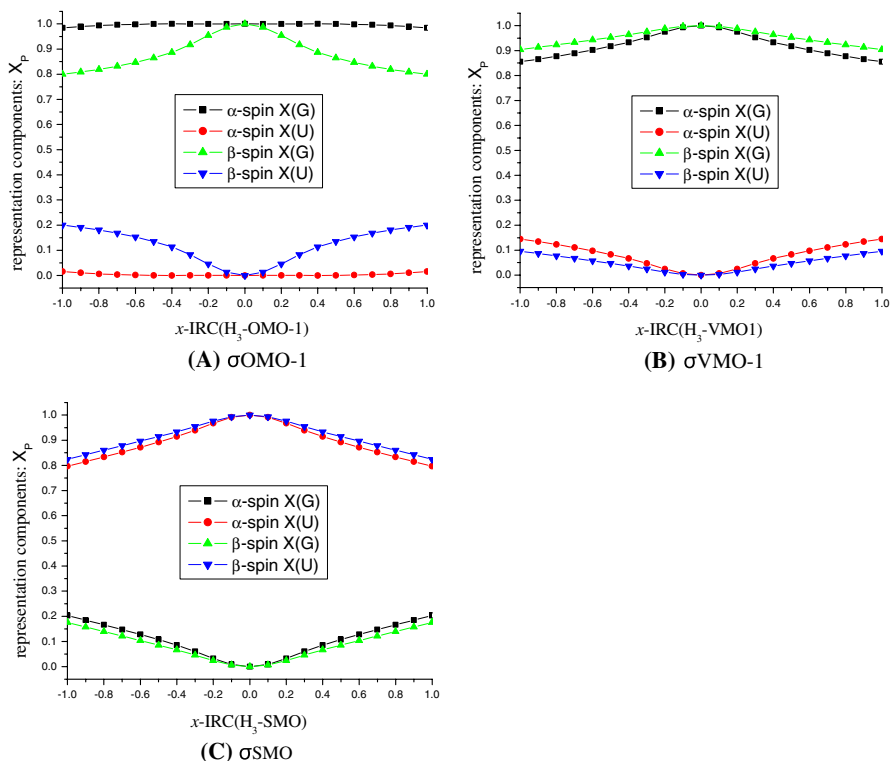


Fig. 9 Variation of the irreducible representation components of $\text{H}\cdots\text{H}\cdots\text{H}$ system along the IRC path for $\sigma\text{OMO-1}$ (A), $\sigma\text{VMO-1}$ (B), σSMO (C), with various spin state in relation to transformation \hat{P}

be either pure symmetrical or pure asymmetrical, the same as those for corresponding TS. This is, $X(\text{G}) = 1$ and $X(\text{U}) = 0$ for $\sigma\text{OMO-1}$ and $\sigma\text{VMO-1}$, meanwhile, $X(\text{G}) = 0$ and $X(\text{U}) = 1$ for the σSMO . For \hat{R} , there is no asymmetrical case, and so we will not be analyzed the related (symmetrical and asymmetrical) representation components. Interestingly, generally speaking, the $\text{H}\cdots\text{H}\cdots\text{H}$ system ($\text{IRC} \neq 0$) is provided with the $\hat{P}\hat{R}$ symmetry, but without the pure \hat{R} nor \hat{P} symmetry.

It is notable that transformations \hat{R} and \hat{P} are different. For TS, owing to the operation of \hat{P} , both the atoms and phases of MOs will change in relation to space inversion (Fig. 5). Under transform \hat{P} , atoms 2 and 3 and their orbital phases will be commute, but after operation \hat{R} , they will not. For the system with the same atoms 2 and 3, under the two transformations, the MO with symmetrical representation Ag will change in the same way, but the MO with asymmetrical representation Au will change differently. For the non-transition state system with the same atoms 2 and 3, the change due to the operation of both transformations include commutation between R_{12} and R_{13} . Under \hat{P} , both atoms 2 and 3 and their phases ought to commute, but under \hat{R} , atom 1 only moves between atoms 2 and 3, and the LCAO-MO coefficients may change in a way different from that under \hat{P} .

As for the states along the dividing line, the linear tri-atomic $B \cdots A \cdots C$ system with the same B and C, such as the $H \cdots H \cdots H$ system, has the perfect symmetry under space inversion transformation \hat{P} and reaction reversal transformation \hat{R} , corresponding to the identity transformation \hat{E} . Therefore the membership functions in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ ought to be unity.

4.2 The fuzzy symmetry for the internal configuration space of the linear $H \cdots H \cdots H$ system

Now, we examine the internal configuration states for the linear H_3 -system outside of the IRC path and the dividing line. For the linear H_3 -system, under space inversion \hat{P} about the middle H atom as the inversion centre, atoms 2 and 3 and their phases will be exchanged. Under operation \hat{R} , the initial state along the IRC path will be change about the TS as its centre, and so the x -IRC will be multiply with (-1) to form the unique final state. When the state outside of the IRC path, the final state under operation \hat{R} ought to be the reversal about the dividing surface (line) [13, 17] which is a super-surface cross cut to the IRC path orthogonally through the TS. The dividing surface may divide the internal configuration coordinate space into two parts: the reagent region and the product region. For the linear H_3 -system, the dividing surface is a one dimensional line, the diagonal line of R_{12} and R_{13} internal configuration coordinate plane with $R_{12} = R_{13}$. For such H_3 -system under operation \hat{R} , R_{12} and R_{13} will commute. For the fuzzy symmetry of this system outside of the IRC path, the MO-LCAO coefficients can be calculated point by point using Gaussian [19], and then the related criteria, membership functions and representation components can be obtained. After that, the corresponding contour map can be obtained using the grid method. It must be noted that for the various grid methods, the degree of approximation ought to be different and the related contour maps will be somewhat different, even if from the same grid method, due to the difference of the number and site (distribution) of the grid points selected in the calculation, the contour maps may be somewhat differ still.

For some MOs (with certain spin state) of the H_3 linear system at HF/STO3G level, the membership functions and irreducible representation components in relation to \hat{P} may be used to produce the contour maps as shown in Figs. 10 and 11. In these figures, the abscissa and the vertical ordinate of the contour map are R_{13} and R_{12} , respectively. For both R_{13} and R_{12} , the grid points were selected with a gap value of 0.1, using the Kriging grid calculation method [20, 21]. In the membership function contour maps, the fluctuation may appear along the diagonal lines. However, according to the theoretic analysis or calculated for the state in the diagonal line using Gaussian [19], the membership functions always equal unity. It means that such fluctuation may be introduced by the approximation in the grid calculation method. As we increase the grid points in the dividing line, such fluctuation will be weakened and smoothed gradually. As the grid points increase to 10-fold for the dividing line, for the fluctuation in the most contour maps will be dampened or even removed completely. Generally speaking, the more grid points are used, the more accurate the grid method and results become, although the more work load is needed. In principle, such contour maps for the linear H_3 system should be symmetric about the diagonal line, but there may be

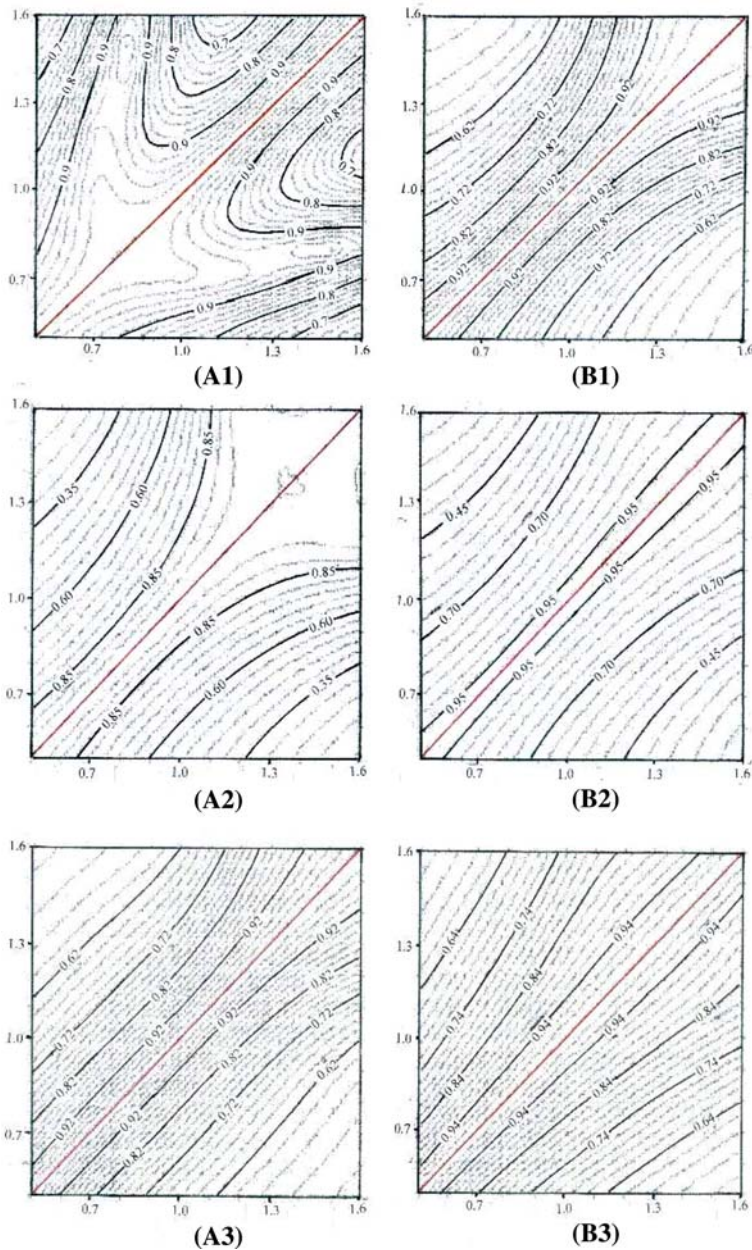


Fig. 10 The membership function contour maps of H_3 linear system for certain MOs in relation to \hat{P} (or to \hat{R}). Here X_j denotes MOs: $X = A$ and B denote α - and β -spin states, respectively; $j = 1, 2$ and 3 denote OMO-1, SMO and VMO-1, respectively

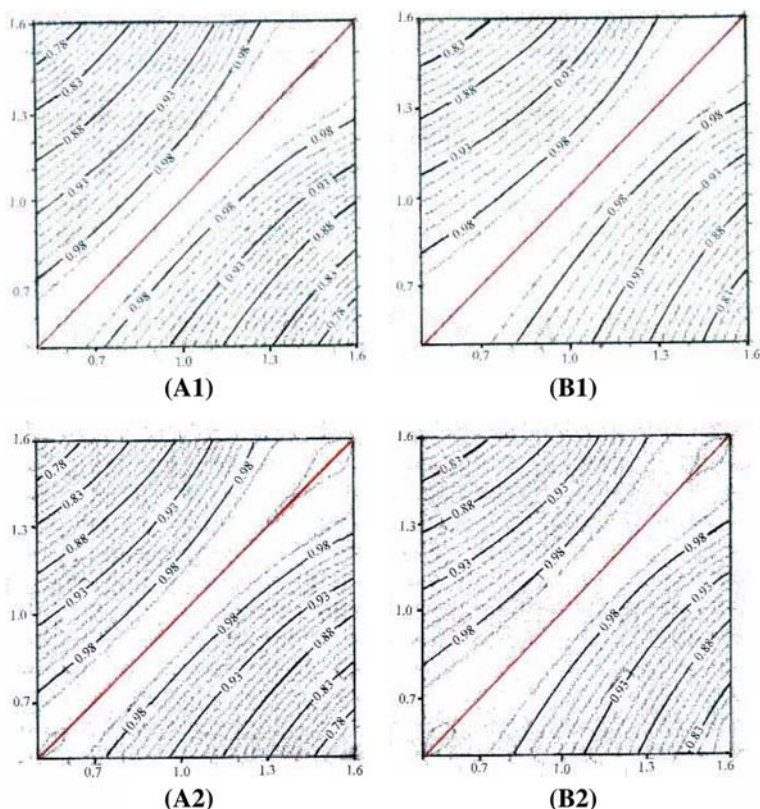


Fig. 11 The asymmetrical representation component X_u contour maps of H_3 linear system for SMO in relation to \hat{P} . For X_j , $X=A$ and B denote α - and β -spin state; j denotes different amounts of grid points: $j=1$, to increase the grid points along the dividing line

some small deviation due to the approximation of the grid method. Figure 10 shows the membership function contour map in relation to the space inversion transformation \hat{P} for some MOs of the H_3 -linear system. The diagonal line in the figure is the dividing line, and the whole contour map is provided with the symmetry about the dividing line.

This system has the whole perfect symmetry in relation to $\hat{P}\hat{R}$, so the corresponding membership functions would be always unity. The membership functions in relation to \hat{R} and \hat{P} ought to be equality, similar as in the IRC path.

Figure 11 shows the contour maps of asymmetrical representation component X_u in relation to transformation \hat{P} for the SMO of the H_3 -linear system, as for the diagonal line, the corresponding states would always be asymmetrical, that is, $X_u=1$.

For other MOs, e.g., OMO-1 and VMO-1, we may obtain similar main representation component contour map in relation to \hat{P} . For OMO-1 and VMO-1, the representations with more components in relation to \hat{P} would be symmetrical. But for SMO, there is asymmetrical. Since the H_3 -linear system is provided with the perfect symmetry in relation to $\hat{P}\hat{R}$, the corresponding representation ought to be pure symmetrical or pure

asymmetrical. Moreover, that is true not only for TS, but also for the whole internal configuration coordinate space. For \hat{R} , there is without the asymmetrical representation, we can not analyze the related representation component.

5 The fuzzy symmetry for H · · · F · · · H system

Now we analyse the H · · · F · · · H system, which, similar to the H · · · H · · · H system, is a tri-atomic B · · · A · · · C linear system with the same B and C. The TS of such system ought to have the perfect symmetry in relation to $\hat{R} = \hat{E}$ and $\hat{P} = \hat{P}\hat{R}$. The membership functions of this system in the TS and related MOs ought to be unity. When the system departs from the TS, that symmetry will be decreased. To start with, we examine the variation along the IRC path. Comparing with the H · · · H · · · H system, a F atom replaces the middle H atom. The HF/STO-3G MOs include the F *p*-AO contribution. The potential energy variation of this system at the level of theory along the IRC path is shown in Fig. 12(A). As shown in the figure, when x -IRC = 0 (i.e., TS), the related potential energy would be at the maximum. Such potential energy curve ought to be provided with symmetry about the TS. According to the internal configuration coordinate space along the IRC path, we may obtain the atomic normalizing criteria for corresponding MOs and obtain the membership functions in relation to transformations $\hat{P}\hat{R}$, \hat{R} and \hat{P} using Eq. 17. Figure 12(B)–(D) show the membership functions in relation to $\hat{P}\hat{R}$, \hat{R} and \hat{P} versus x -IRC, for σ SMO, σ OMO-1 and σ VMO with the two spin states, respectively.

Although these membership function curves versus IRC are symmetry about the TS, they are usually less than one, i.e., having no the perfect symmetry. As shown in Fig. 12, the following points can be inferred. First, for the TS with x -IRC = 0, the membership functions in relation to the above transformations and for related MOs are equal to one. Second, for these MOs, their membership functions in relation to $\hat{P}\hat{R}$ ought always to be unity for all x -IRC values, but their membership functions in relation to \hat{R} and \hat{P} will be unity only for x -IRC = 0 (TS), but less than one for other x -IRC values. In other words, for the linear tri-atomic B · · · A · · · C system with the same B and C, $\hat{P}\hat{R}$ is the perfect symmetry [13, 14], but \hat{R} or \hat{P} is not the perfect symmetry. Third, for the MOs with the same spin, the membership functions related \hat{R} and \hat{P} are equality, but they are different for the different spin. Fourth, even though for the linear tri-atomic B · · · A · · · C system with the same B and C, the corresponding reaction will not be perfect symmetric in relation to \hat{R} or \hat{P} , although the related membership function variation along the IRC path will still be provided with the symmetry about the TS centre.

It should be noticed that \hat{R} and \hat{P} are different transformations. No matter whether B and C are the same or not, due to operation \hat{R} or \hat{P} , the system would be changed in general in a way that the related membership functions would be less than one. However, if B and C are the same, the related membership functions will be equal. Under operation $\hat{P}\hat{R}$ to such B · · · A · · · C system, we have:

$$R_{PR12} = R_{RP12} = R_{R13}, \quad R_{PR13} = R_{RP13} = R_{R12}. \quad (21a)$$

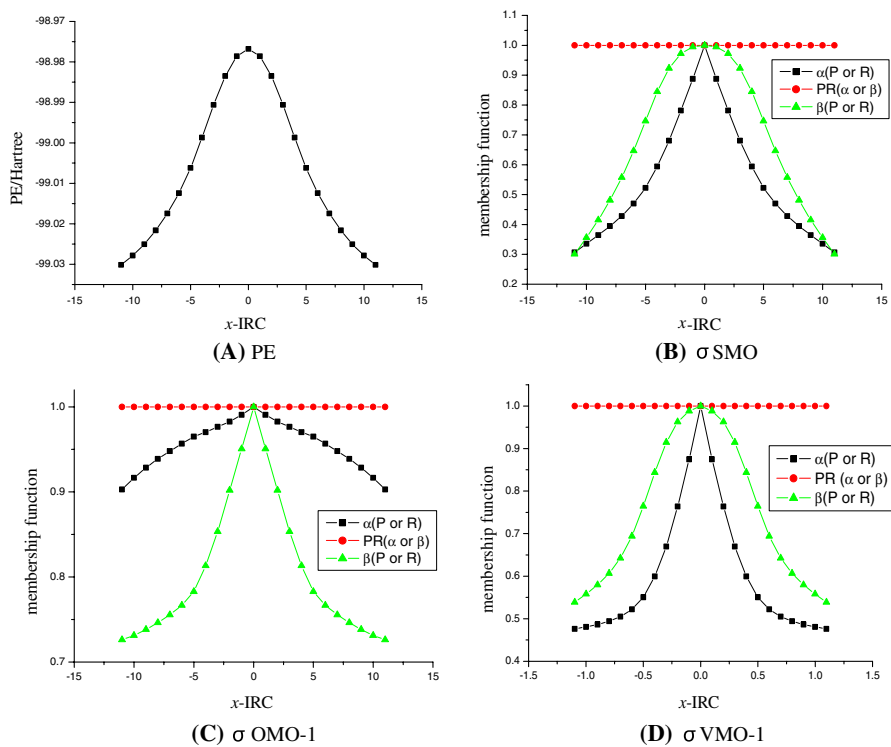


Fig. 12 The variation of certain properties for $\text{H}\cdots\text{F}\cdots\text{H}$ system along the IRC path: potential energy, PE (A), or the membership functions for σ SMO (B), σ OMO-1 (C) and σ VMO-1 (D) in two spin states in relation to transformations $\hat{P}\hat{R}$, \hat{R} and \hat{P} , respectively

Meanwhile atoms B and C would commute:

$$R_{\text{PR}12} = R_{\text{RP}12} = R_{\text{R}13} = R_{12}, \quad R_{\text{PR}13} = R_{\text{RP}13} = R_{\text{R}12} = R_{13} \quad (21b)$$

That is, such system will be restored under this operation of $\hat{P}\hat{R}$, and so the related membership function will be unity.

In order to describe the irreducible representation component, we may need to introduce the imaginary AOs as we did for the irreducible representation component of hydrogen halide MOs in relation to \hat{P} irreducible representation component [8], where H atom 1s-AO was combined with several AOs of the halide atom to form the MO. Using the imaginary AO method, for hydrogen halide molecules [8], we introduce more imaginary AOs which may be linear combined to replace the only 1s-AO of H atom. The introduced more imaginary AOs correspond to the various AOs of halide atom in the symmetry operation of \hat{P} , respectively. Similarly, we may analyze the MO irreducible representation components in relation to \hat{P} for $\text{H}\cdots\text{F}\cdots\text{H}$ system. The AOs of F atom will be combined with the AOs of the two H atoms, and, especially, the F p_z -AO will be related to two s -AOs of two H atoms. In this way, we may obtain the irreducible representation components for σ -SMO, σ -OMO1 and σ -VMO1 of the

system in relation to \hat{P} as shown in Fig. 13. The π MOs conserve the p -AO character of the middle F atom, their representations are pure asymmetrical, i.e., $X(U) = 1$ and $X(G) = 0$.

It is interesting, for the $H \cdots F \cdots H$ system, as shown in Fig. 13, that the main representation of σ SMO is symmetrical— $X(G) > X(U)$, but those of σ OMO-1 and σ VMO-1 are asymmetrical— $X(G) < X(U)$. Comparing with Fig. 9, we noted that, for the $H \cdots H \cdots H$ system, the main representation of σ SMO is asymmetrical $X(G) < X(U)$, but those of σ OMO-1 and σ VMO-1 are symmetrical $X(G) > X(U)$.

For the $H \cdots F \cdots H$ system along the IRC path, the related fuzzy symmetry for the internal configuration coordinate plane may be analyzed in the same fashion as for the $H \cdots H \cdots H$ system, the basic rules and many results are similar in essence, even though the corresponding calculation will be more complicated owing to the p -AO of mid F atom. Some difference and similarity in connection to the representation components for these two systems can also be seen as shown in Figs. 13 and 9.

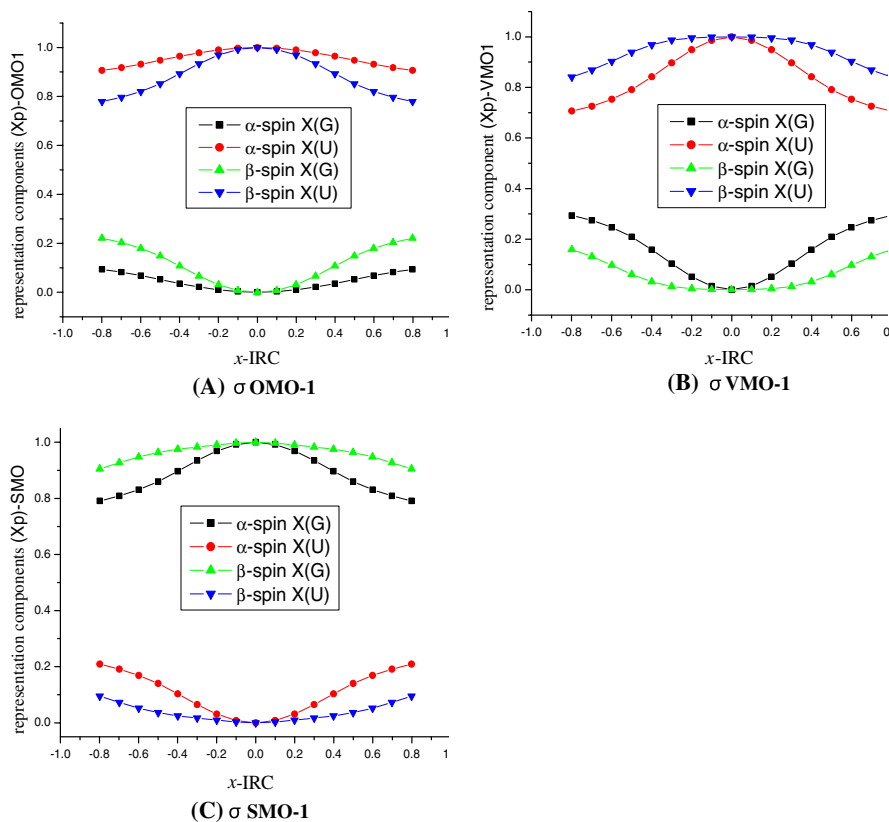


Fig. 13 Variation of the irreducible representation components of $H \cdots F \cdots H$ system along the IRC path for (A) σ OMO-1, (B) σ VMO-1 and (C) σ SMO with two spin states in relation to transformation \hat{P}

6 The fuzzy symmetry for the $H \cdots H \cdots F$ system

6.1 The fuzzy symmetry for the IRC path and the dividing line of $H \cdots H \cdots F$ system

Now we examine the linear tri-atomic $B \cdots A \cdots C$ system with different B and C atoms. In this system, there is no perfect $\hat{P}\hat{R}$ symmetry. Therefore, the membership functions for the related MOs in relation to $\hat{P}\hat{R}$, \hat{R} and \hat{P} ought to be less than unity. For TS, the relationships, $\hat{P}\hat{R} = \hat{P}$ and $\hat{R} = \hat{E}$, are still true. For such system, the membership functions in relation to $\hat{P}\hat{R}$ and \hat{P} versus the IRC path curves would intersect at TS, and the membership functions in relation to \hat{R} would be unity at TS. Taking this system, $H \cdots H \cdots F$, as an example, we show the internal configuration coordinates $R_{12}(R_{HH})$ and $R_{13}(R_{HF})$ vs the IRC path in Fig. 4(B). For TS, R_{12} and R_{13} are unequal. The potential energy along the IRC path will be maximal in TS, but it is non-symmetrical about TS. For the MOs of such system, there are not perfect symmetry in relation to transformations $\hat{P}\hat{R}$, \hat{R} and \hat{P} , and so we may only analyze their fuzzy symmetry.

We first analyze the fuzzy symmetry of the MOs of the $H \cdots H \cdots F$ system along the IRC path in relation to the $\hat{P}\hat{R}$, \hat{R} and \hat{P} . For x -IRC $\neq 0$ (i.e. not TS), the corresponding state of such system will change due to operation \hat{R} : one state in the IRC path ought to change to another one in the path. The IRC values of the final state and of initial state would be opposite (different by a merely negative sign). According to Fig. 4(B), we may note values of R_{12} and R_{13} corresponding to the final state from initial state under operation \hat{R} , whereas the corresponding system under operation \hat{P} may be treated as the ordinary point symmetrical transformation. We may then calculate the related MOs using Gaussian [19] as well as the atomic criteria. Furthermore, we may obtain the membership functions in relation to $\hat{P}\hat{R}$, \hat{R} and \hat{P} . Figure 14 shows the results using HF/STO-3G, and the membership functions of σ SMO (two spin states) of the system along the IRC path in relation to \hat{R} and \hat{P} . The potential energy is maximal at TS (x -IRC = 0). Although the membership function reach the maximum in relation to \hat{R} at TS (x -IRC = 0), the maximum in relation to \hat{P} occurs at other state (x -IRC $\neq 0$). Moreover, the membership functions in relation to \hat{R} and \hat{P} are unequal. Figure 15 shows the membership functions for σ SMO (two spin states) of the linear tri-atomic $H \cdots H \cdots F$ systems along the IRC path in relation to $\hat{P}\hat{R}$, \hat{R} and \hat{P} . It should be noted that there are not perfect symmetry in relation to $\hat{P}\hat{R}$, and so the corresponding membership functions will be less than one.

Figures 16 and 17 show the membership functions in relation to $\hat{P}\hat{R}$, \hat{R} and \hat{P} respectively for σ OMO-1 and σ VMO-1 (two spin states) of the system along the IRC path. Although the variation curves of various MOs are considerably different, comparing with Fig. 15, we note the following common features. First, the membership functions in relation to $\hat{P}\hat{R}$ and \hat{R} versus IRC path are symmetrical about TS (x -IRC = 0), but they are not in relation to \hat{P} . Moreover, in relation to $\hat{P}\hat{R}$ and \hat{P} the membership functions are equality at TS. Furthermore, the membership function in relation to \hat{R} equals one at TS.

The membership functions for various MOs along the dividing line in relation to \hat{R} ought to be unity because \hat{R} corresponding to the identity \hat{E} , and those in relation to \hat{P} and $\hat{P}\hat{R}$ are equal as shown in Fig. 18 for σ SMO (two spin states).

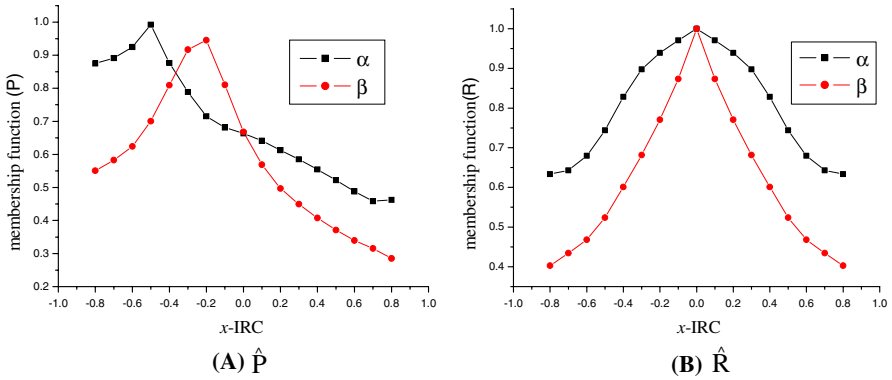


Fig. 14 Variation of the membership functions of $H \cdots H \cdots F$ system along the IRC path for σ SMO in two spin states in relation to \hat{P} (A) and \hat{R} (B)

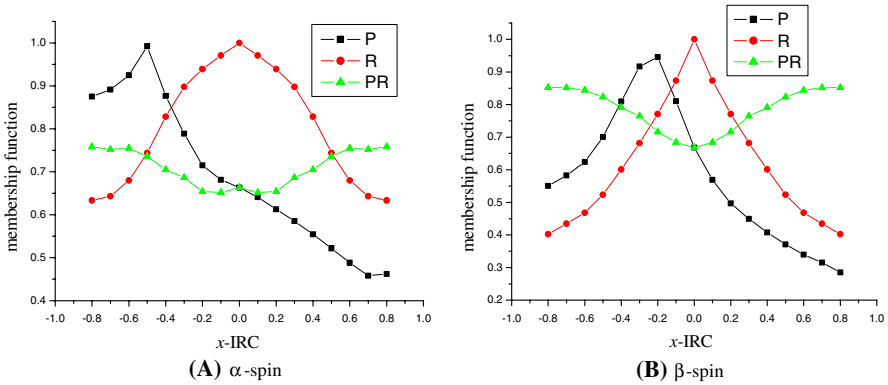


Fig. 15 Variation of the membership functions of $H \cdots H \cdots F$ system along the IRC path for σ SMO in (A) α -spin and (B) β -spin states in relation to \hat{P} , \hat{R} and \hat{PR}

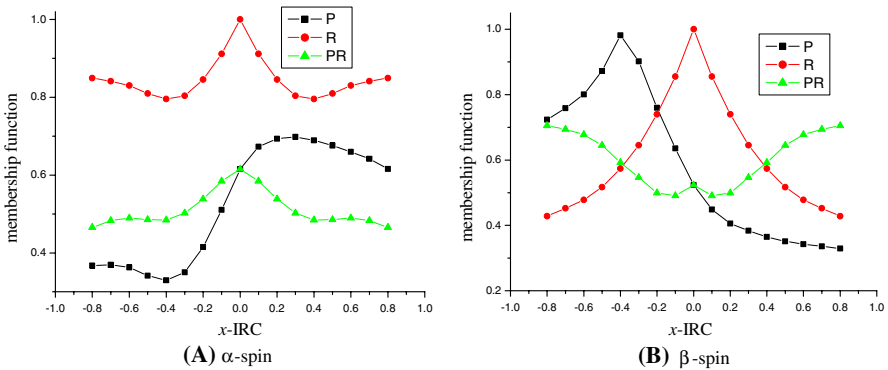


Fig. 16 Variation of the membership functions of $H \cdots H \cdots F$ system along the IRC path for σ OMO-1 in (A) α -spin and (B) β -spin states in relation to \hat{P} , \hat{R} and \hat{PR}

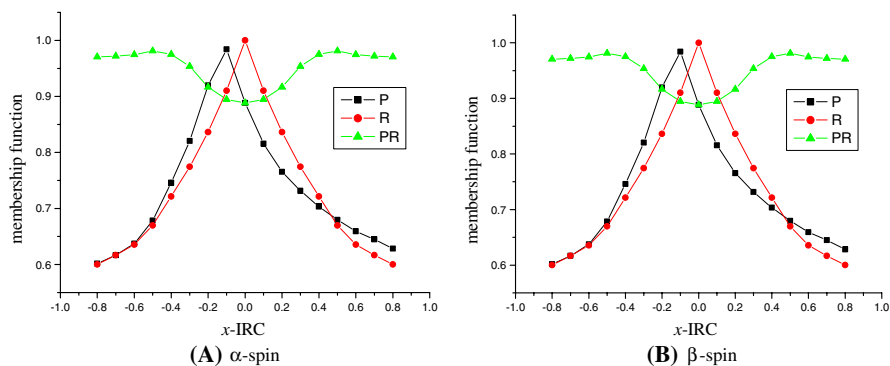


Fig. 17 Variation of the membership functions of $H \cdots H \cdots F$ system along the IRC path for σ VMO-1 in (A) α -spin and (B) β -spin states in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$

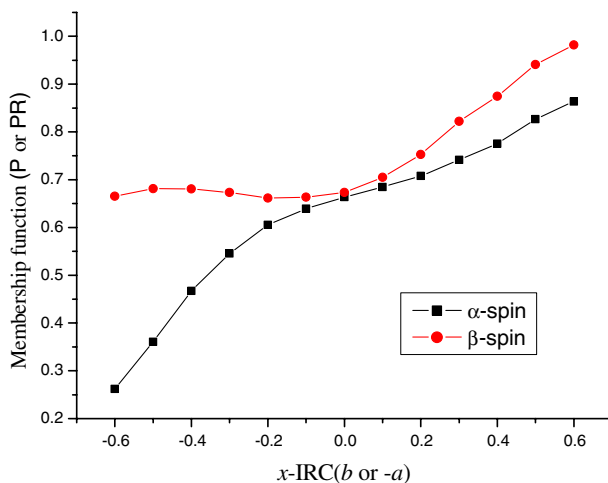


Fig. 18 Variation of the membership functions of $H \cdots H \cdots F$ system along the dividing line for σ SMO in α -spin (black) and β -spin (red) states in relation to \hat{P} and $\hat{P}\hat{R}$: the membership function in relation to \hat{R} equal to one along the dividing line

For the MOs of linear tri-atomic $H \cdots H \cdots F$ system, their irreducible representation components in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ may be examined in principle, but there may be some various methods for this purpose, and some of them may obtain some similar but not quite same results. Further work should be done, we will not discuss them here. A summary on the fuzzy symmetry characteristics in connection to the linear tri-atomic $B \cdots A \cdots C$ systems with the same B and C (such as $H \cdots H \cdots H$ and $H \cdots F \cdots H$) and different B and C atoms (such as $H \cdots H \cdots F$) is shown in Table 2.

Table 2 Variation of the membership functions of $B \cdots A \cdots C$ system for the MOs on the IRC path and dividing lines under transformations \hat{P} , \hat{R} and $\hat{P}\hat{R}$

Transformation	Same B and C atoms	Different B and C atoms
<i>On the IRC path</i>		
Membership functions: \hat{P}	Symmetry about the transition state in the IRC-scale Same as that in relation to \hat{R}	No symmetry about the transition state in the IRC-scale No same as that in relation to \hat{R}
Membership functions: \hat{R}	Symmetry about the transition state in the IRC-scale Same as that in relation to \hat{P}	Symmetry about the transition state in the IRC-scale Not same as that in relation to \hat{P}
Membership functions: $\hat{P}\hat{R}$	Equal to one	Symmetry about the transition state in the IRC-scale
<i>On the dividing line</i>		
Membership functions: \hat{P}	Equal to one	No symmetry about the transition state in the IRC-scale Same as that in relation to $\hat{P}\hat{R}$
Membership functions: \hat{R}	Equal to one	Equal to one
Membership functions: $\hat{P}\hat{R}$	Equal to one	No symmetry about the transition state in the IRC-scale Same as that in relation to \hat{P}

6.2 The fuzzy symmetry for the internal configuration space of the linear $H \cdots H \cdots F$ system

For the membership functions of any internal configuration state in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ for the linear tri-atomic $H \cdots H \cdots F$ system, we may obtain the final internal configuration states about these transformations according to Eqs. 12–19. We may calculate the MO-LCAO coefficients for the states before and after the operation using Gaussian [19], and then obtain the atomic criteria and the membership functions related to the transformations. Using the calculated results, we can compute point by point the values of these membership functions to form the contour map according to Kriging grid method [20, 21]. The contour maps of the membership function in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ for the SMO (two spin state) of the system are shown in Fig. 19. As for other MOs, the treatment is similar and omitted here. For convenient to analysis, the IRC-path and dividing line (curve) are also shown in Fig. 19. Comparing with the Fig. 10 (the H_3 system as the example for the linear tri-atomic $B \cdots A \cdots C$ system with same kinds atoms B and C), the membership functions in relation to \hat{R} and \hat{P} the contour maps are different for $H \cdots H \cdots F$ in Fig. 19, and the membership functions in relation to $\hat{P}\hat{R}$ are not always unity.

On the other hand, as shown in Figs. 14–17, for the MOs of this system, the membership functions curves in relation to \hat{R} and $\hat{P}\hat{R}$ along the IRC path are symmetry about the TS. Why is such symmetry not shown in Fig. 19? The cause is that we used the common nature scale (e.g. angstrom) in Fig. 19 whereas the IRC scales is used in Figs. 14–17. In fact, as shown in Fig. 19, although there is not the symmetry obviously, for the membership functions in relation to \hat{R} and $\hat{P}\hat{R}$ the contour maps, the membership function seems somewhat well-distribution about the dividing curve.

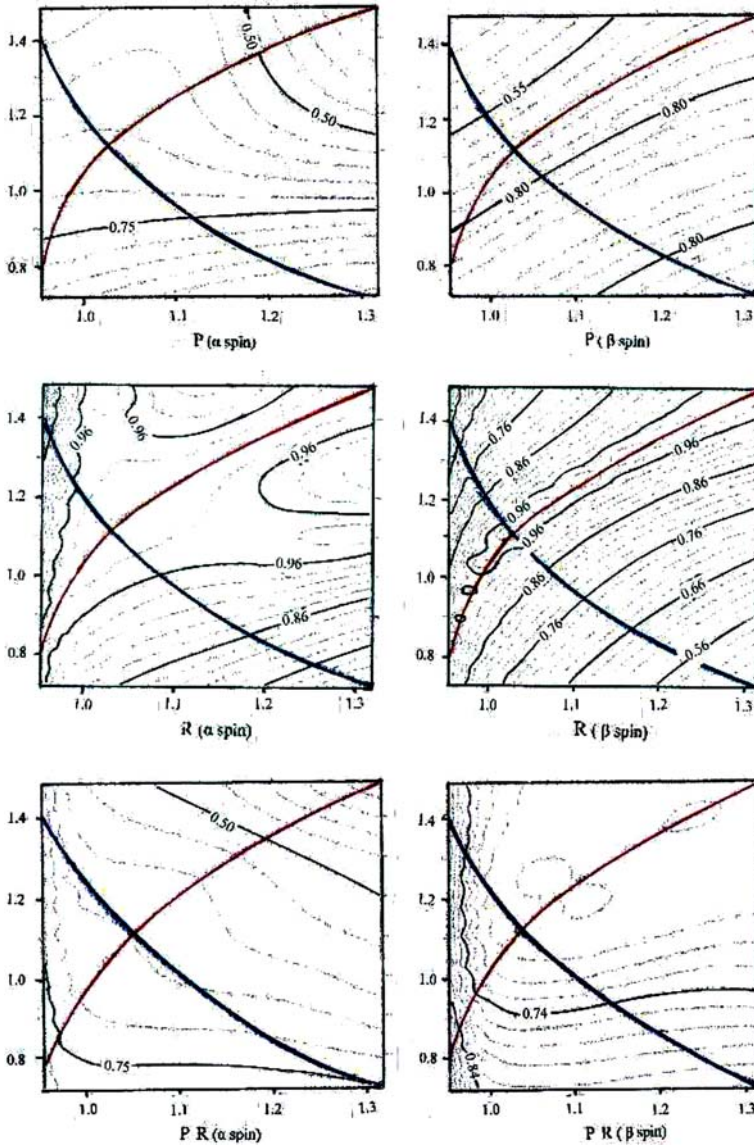


Fig. 19 The membership function contour maps in relation to the \hat{P} , \hat{R} and $\hat{P}\hat{R}$ for SMO (α and β spin states) of linear $H \cdots H \cdots F$ system corresponding to various internal configurations. The common nature scale (the Cartesian coordinate scale) is used for the internal configuration coordinate R_{12} (ordinate) and R_{13} (abscissa). The blue and red curves denote the IRC-path and dividing line, respectively

According to the natural scale, both IRC path and dividing line are not straight lines in Fig. 19. If we present the contour maps of the membership functions in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ in the IRC scale, we can have Fig. 20, where the blue diagonal lines are the IRC paths and the red diagonal lines are the dividing lines. The intersection point of these two diagonal lines and the origin point of the coordinate system ought to be connected with the TS. Since R_{12} and R_{13} are monotonically increasing and decreasing respectively along with the IRC, the initial (reactant) and final (product) states of this reaction system lie in the upper right and lower left parts of the internal configuration coordinate space, respectively. Similar to Figs. 14–17, for the MOs of such system, there is the symmetry about the dividing line for the membership functions in relation to \hat{R} and $\hat{P}\hat{R}$. However, there is not such symmetry for the membership functions in relation to \hat{P} .

In addition, the membership functions in relation to \hat{R} in the dividing line would be always unity, but there is some fluctuation in Fig. 20 due to the error introduced in the grid calculation.

By the way, using the nature and IRC scales, we can get the potential energy contour maps of linear HHF system with somewhat different shapes (Fig. 21). Although the intersection points of the IRC path and dividing lines are the TS and saddle points for both these two scales, however the IRC-path and dividing lines are the straight lines in IRC-scale case, and the curves (not straight) in nature scale case, respectively.

7 Conclusions

In our previous papers on the molecular fuzzy symmetry, we analyzed some static and stable molecules for which the related configuration is usually only one. In this paper, we analyze some simple linear tri-atomic dynamic systems in which there are usually many related configurations, and their corresponding fuzzy symmetry characteristics would be complicated. Besides the conventional point symmetry transformations, a special transformation called reaction reversal had been analyzed. The $H \cdots H \cdots H$, $H \cdots F \cdots H$ and $H \cdots H \cdots F$ systems are analyzed in detail. The main conclusion includes the following.

1. The configuration of the linear tri-atomic system $B \cdots A \cdots C$ may be changed owing to the operation of some common transformations: space inversion (\hat{P}), reaction reversal (\hat{R}) and their joint transformation ($\hat{P}\hat{R}$) which are somewhat similar to \hat{P} and \hat{R} , but different in essence.
2. For the linear tri-atomic $B \cdots A \cdots C$ system with the same B and C atoms, there is no space inversion (\hat{P}) nor reaction reversal (\hat{R}) symmetry, but there is joint $\hat{P}\hat{R}$ symmetry. For systems with different B and C, we may analyze their fuzzy symmetry in relation to \hat{P} , \hat{R} or $\hat{P}\hat{R}$.
3. For the linear tri-atomic $B \cdots A \cdots C$ system, we chose AB and AC atomic distances (i.e. R_{13} and R_{12} , respectively) as the internal configuration space coordinates. For R_{12} and R_{13} , we used both the Cartesian coordinates scale and the IRC (intrinsic reaction coordinate) scale. In the IRC-scale, the transition state (TS) will lie in the origin in the internal configuration space. Through such origin, there are two diagonal lines corresponding to the IRC-path and dividing line. For the initial

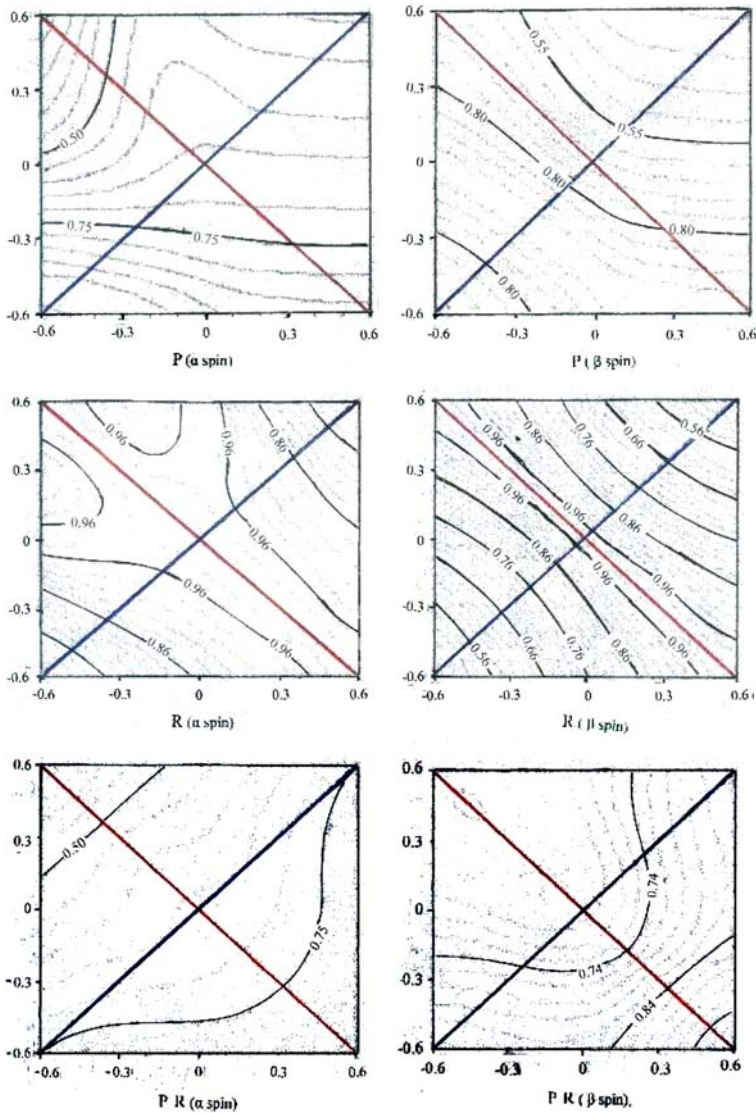


Fig. 20 The membership function contour maps of linear H...H...F system in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ for SMO in α and β spin states corresponding to various internal configurations. The IRC scale is used for the internal configuration coordinates R_{12} (vertical ordinate) and R_{13} (abscissa). The blue and red diagonal lines denoted the IRC-path and dividing line, respectively

and final configuration states under operation \hat{P} , \hat{R} and $\hat{P}\hat{R}$, we obtained the atomic criteria of MOs and the membership functions in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ for the linear tri-atomic system

4. For the TS, \hat{R} corresponds to the identity (\hat{E}), and so the membership functions in relation to \hat{P} and union $\hat{P}\hat{R}$ are equality. For the system with the same B and C, the TS would possess the perfect symmetry in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$. For systems

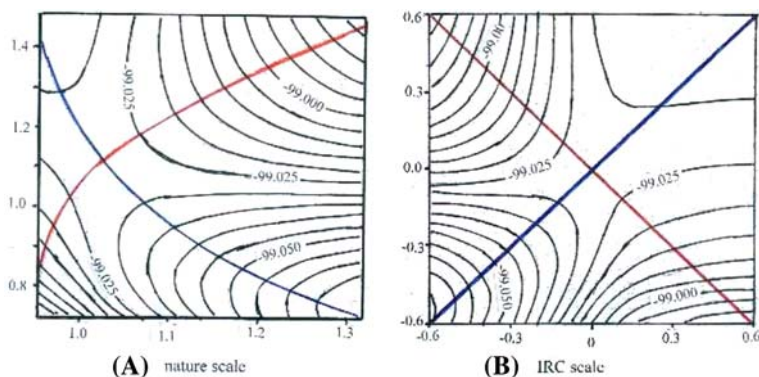


Fig. 21 The potential energy contour maps of linear $H \cdot H \cdot H \cdot F$ system corresponding to various internal configurations. The common nature scale and the IRC scale are used in figures (A) and (B), respectively. The intersection point of blue (IRC path) line and red (dividing) line denoted the TS

with different B and C, the TS will have only the fuzzy symmetry in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$. We examined the TS of the linear $H \cdot H \cdot H \cdot X$ ($X = F$) system as an example.

5. For the system with the same B and C, e.g., $H \cdot H \cdot H \cdot H$ and $H \cdot H \cdot F \cdot H$, we discussed their membership functions in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ along the IRC path and dividing line. These systems have the perfect symmetry in relation to $\hat{P}\hat{R}$, so the membership functions in relation to $\hat{P}\hat{R}$ would be unity and invariable along both IRC-path and dividing line. The membership functions in relation to \hat{P} and \hat{R} along the IRC-path are equal, less one and provide with the symmetry about the TS. For different spin states of the same MO, the related membership functions are slightly different. Since all configurations along the dividing line have the perfect symmetry in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$, so the corresponding membership functions will be unity.
6. For the dividing line, since \hat{R} equals the identity transformation \hat{E} , the eigenvalue will always be one. On the other hand, corresponding to \hat{R} , there is not possible a state with the eigenvalue = -1, we can not examine the related irreducible representation components. However, we examined this in relation to \hat{P} and $\hat{P}\hat{R}$. For the linear tri-atomic $B \cdot A \cdot C$ system with the same B and C atoms, there is the perfect symmetry in relation to $\hat{P}\hat{R}$, and the related membership functions shall be unity. The corresponding irreducible representation, same as that of the related TS, is pure. For $H \cdot H \cdot H \cdot H$ and $H \cdot H \cdot F \cdot H$ systems, their SMOs belong to the asymmetrical and symmetrical representations, respectively, and both their OMO-1 and VMO-1 belong to the symmetrical and asymmetrical ones, for various systems respectively.
7. For the linear tri-atomic $B \cdot A \cdot C$ system with different B and C atoms, such as $H \cdot H \cdot H \cdot F$, we analysed the membership functions in the IRC-scale in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ along the IRC path, where the membership functions for \hat{R} and $\hat{P}\hat{R}$ are provided with the symmetry about the TS. The membership functions along the dividing line in relation to \hat{R} are always unity, and those in relation to \hat{P} and $\hat{P}\hat{R}$ are equal.

8. For the system with different B and C atoms, such as $H \cdots H \cdots F$, we also examined the membership functions in relation to \hat{P} , \hat{R} and $\hat{P}\hat{R}$ in the internal configuration space. Since the common nature scale is not convenient to show corresponding symmetry titles, we focused on the IRC scale to examine the membership functions, which gives interesting results. In the IRC-scale, the membership functions in relation to \hat{R} and $\hat{P}\hat{R}$ are provided with the symmetry about the dividing surface (line), but not in relation to \hat{P} .

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