

A Minimum Asymmetry Index for Measuring Asymmetry of the Electron Density Distribution

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Abstract

An asymmetry index (AI) is introduced to measure deviation of the electron density distribution in a molecule from any given symmetry. This AI is calculated by summing all point-wise differences between electron density distributions before and after symmetry operation. A minimum asymmetry index (MAI) rule is also introduced to evaluate uniquely the extent of asymmetry of a molecule with respect to any reference symmetry operation. This MAI rule prescribes where to locate the reference element of symmetry. The overall MAI for a given molecule with respect to a certain symmetry point group is calculated by averaging over AIs of all symmetry elements appearing in its character table. The proposed AI and the MAI rule are used to measure electron density asymmetry of the NX_3 , NX_2Y/NXY_2 and $NXYZ$ ($X, Y, Z = H, F, Cl, Br$) series of molecules referenced to the C_{3V} symmetry.

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1. Introduction

Most properties of the molecules depend on their symmetry. Determination of the point group of a molecular structure based on the nuclear geometry is quite straightforward and unique, but quantitative estimate of the extent of the electron density asymmetry is an

important and difficult problem. Quantification of chirality is important in pharmaceutical chemistry, chiral chromatography, chemical informatics, and kinetics of reactions. Quantitative asymmetry indices may have critical roles in finding structure-function relations, which can be used to solve a lot of problems in synthesis, catalysis, pharmacy, and material science. One of the most important applications of an asymmetry index is in nanoelectronic and nanophotonic sciences in which interaction of individual molecules with light is important. Because of the dependence of the optical rotation of molecules on their (electron density) chirality, finding a proper index measuring electron density asymmetry can help to establish a quantitative relation between optical rotation and chirality.

Attempts towards quantification of symmetry are reported first by Salem et al. by defining chirality forces as the differential interaction energy between two chiral tetrahedral molecules, once with the same and once with opposite chiralities [1]. Avnir et al. have then reported a lot of works in quantification of chirality. They introduced a relatively new method (named continuous symmetry and chirality measures, CSM, and CCM) to measure molecular symmetries beyond the well-defined known molecular point groups, which is based on the dynamic rotational properties of molecules [2], without considering electron density. The CSM and CCM are defined as the minimum distance that the principle vectors of the molecular fixed frame should be displaced to reach the point group of the nearest achiral (symmetric) structure. These measures are proposed as the asymmetry scales [3-7]. This method has been generalized to include symmetries of vectors, matrices, operators and functions [8]. By calculating CCM, correlations between chirality and several properties of helicenes have been derived [9]. The symmetry of tetra-coordinated copper complexes has been analyzed in terms of quantitative continuous symmetry. This methodology has been developed to estimate the degree of proximity of the molecular nuclear structure to a selected symmetry point group and has been used to analyze the electronic structure of molecules [10,12].

Pseudo-symmetry analysis method is used to measure symmetry of the molecular orbitals consisting of d orbitals in four-coordinate complexes based on the analytical functions [13] without evaluating and analysis of the numerical values of electron density. The pseudo-symmetry of molecular orbitals of a family of polycyclic aromatic compounds are also investigated based on the nuclear point group theoretical concepts without introducing any asymmetry index [14]. A chirality measure based on electron density clouds is described for the first time by Mezey [15] based on the Hausdorff concept of distances between sets and applied to quantify the structural differences between the two left-handed and the right-

handed partners of each chiral pair by computing the Hausdorff distance between the two enantiomorphous configurations [16,17]. In addition, different approaches are adopted by other researchers to quantify chirality [18-22]. Quantification of symmetry and chirality in various areas of science are reviewed and their relation with similarity and order of the system are discussed by Petitjean [23].

As can be seen in the above mentioned cases, almost all of the attempts in quantification of chirality are based on nuclear symmetry, while, most of the molecular properties depend on electron density distribution and its symmetry/asymmetry. A descriptive and representative index is thus needed to measure the extent of the asymmetry of the electron density.

Here, we introduce an asymmetry index (AI) for the electron density distribution applicable to all kinds of molecules. The main problem with the definition of such asymmetry index arises from the fact that location of the symmetry elements in a symmetric molecule is trivial and a routine task, while there is no criterion for the location of these elements in an asymmetric molecule. Presently, there is no well-defined method for setting the *would be* symmetry elements; mainly the molecular frame of the corresponding symmetric molecule is used to define the symmetric elements. In the present work, a minimum asymmetry index (MAI) is introduced as the criterion for the position and orientation of the symmetry elements with respect to which the extent of asymmetry is being measured. These AI and MAI are examined for prototypical NX_3 , NXY_2 and $NXYZ$ ($X,Y,Z=H,F,Cl,Br$) series of molecules.

2. Computation Method

Electron density in quantum mechanics is the probability of finding one electron in an infinitely small volume around each point and is calculated by

$$\rho(x, y, z) = n \sum_{\text{all } m_s} \int \cdots \int |\Psi(x, y, z, x_2, \dots, z_n, m_{s_1}, \dots, m_{s_n})|^2 dx_2 \cdots dz_n \quad (1)$$

where $\rho(x, y, z)$ is the electron density at the position (x, y, z) , n is the total number of electrons, Ψ is the n -electron wave function of the molecule, and the sum runs over all spin states m_s .

The asymmetry index (AI) for measuring asymmetry of the electron density with respect to the symmetry operation S is introduced as

$$I_S = \frac{\iiint |\Delta_S \rho(x, y, z)| dx dy dz}{\iiint \rho(x, y, z) dx dy dz} \quad (2)$$

in which the differential density $\Delta_S \rho$ is obtained by the geometrical transformation of the electronic density corresponding to the symmetry operation \hat{O}_S as

$$\Delta_S \rho(x, y, z) = \rho_S(x, y, z) - \rho(x, y, z) = (\hat{O}_S - \hat{E})\rho(x, y, z) \quad (3)$$

where $\hat{E}\rho(x, y, z) = \rho(x, y, z)$ is the original electron density of the molecule obtained from quantum mechanical computations, and $\rho_S(x, y, z)$ is its transformation under \hat{O}_S . The symmetry transformation operator \hat{O}_S is defined in terms of the symmetry operation S (associated with its corresponding symmetry element) belonging to the reference point group, PG , of interest based on which the asymmetry of the molecule is going to be evaluated. In Eq. (3), \hat{E} operator denotes the identity transformation. The proposed AI introduced in Eq. (2) is thus obtained based on the sum of all point-wise differences between the two electron densities before and after application of the symmetry operation S . In Eq. (2), division by the total number of electrons, $\iiint \rho(x, y, z) dx dy dz$, ensures normalization of the calculated index I_S (i.e. $I_S^{max} = 1$) to be thus comparable for different molecules with different number of electrons. The asymmetry index I_S quantifies deviation of the electron density distribution with respect to the certain symmetry operation S .

Selection of the position and direction of the symmetry elements in a symmetric molecule is obvious, but there has been no criterion for the location of these elements in an asymmetric molecule. The lack of a rule for location of the symmetry element results in numerous values for any proposed electron density AI, including ours, depending on the type and metrics of the molecule and the selection of the position and direction of the symmetry elements. In other words, the calculated AI cannot be unique, and thus AIs calculated for different molecules are not comparable. Here in this work, we propose a *minimum asymmetry index (MAI)* rule as the criterion for the selection of the best and unique position and orientation of the symmetry elements with respect to which the extent of asymmetry is going to be measured. In this rule, the MAI corresponding to a given symmetry S , for a certain molecule having electron density $\rho(x, y, z)$, is defined as:

$$I_{S,i} = \frac{\iiint |(\hat{O}_{S,i} - \hat{E})\rho(x, y, z)| dx dy dz}{\iiint \rho(x, y, z) dx dy dz} : I_S^{min} = \min\{I_{S,i}\} \quad (4)$$

where subscript i denotes all possible locations/orientations of the symmetry element S in the molecular fixed frame. The best positions and orientations of the symmetry elements are those closer to the center of mass of electron density. This fact limits the space, which should be searched for MAI.

To obtain the MAI of a molecule referenced to a certain reference point group PG , I_{PG}^{min} , a simple averaging is carried out on the MAI values corresponding to all operations S belonging to the PG of interest as:

$$I_{PG}^{min} = \frac{1}{g_{PG}} \sum_S I_S^{min} ; S \in PG \quad (5)$$

where I_S^{min} is defined and obtained by Eq. (4), and g_{PG} is the size (order) of the symmetry point group PG (according to its character table). Note that MAI of the symmetry elements belonging to one conjugacy class of the point group PG may not necessary be equal for the specific molecule under study. Such equality occurs only for molecules having the full PG symmetry. The position and orientation of all symmetry elements of a certain symmetry PG should be properly correlated. Otherwise, the asymmetry measure with respect to a certain PG would not be meaningful. This, however, does not forbid existence of other position/orientation for a symmetry element for which the individual MAI may be smaller than that of its position/orientation correspondent to other symmetry elements within the reference PG . Therefore, the MAI of an individual symmetry operation may be found in a different position from that when considered together with other operations of the PG of interest.

In the present work, the AIs corresponding to different symmetry operations associated with the C_{3V} reference symmetry point group are calculated for a number of NX_3 , NXY_2 / NX_2Y and $NXYZ$ ($X, Y, Z = H, F, Cl, Br$) molecules (Fig. 1) as prototypes, respectively with C_{3V} , C_S and C_1 point groups, thus all having C_{3V} reference symmetry. For this purpose, electron densities of these molecules have been computed at configuration interaction (CI) level of theory including singly excited determinants (CIS) using 6-31G basis set, over a three-dimensional space with 0.05 bohr steps. All quantum chemical computations

are carried out using G03 software [24]. The use of CIS allows accurate calculation of the excited state densities (to be used in the calculations of electric polarizability and hyperpolarizability tensors, and optical rotations intended for other independent works). Depending on the size of the molecule, boxes of $174 \times 174 \times 174$ to $300 \times 300 \times 300$ grid points, all with a criterion of $\rho(x, y, z) > 0.001 \text{ electron/bohr}^3$, are used.

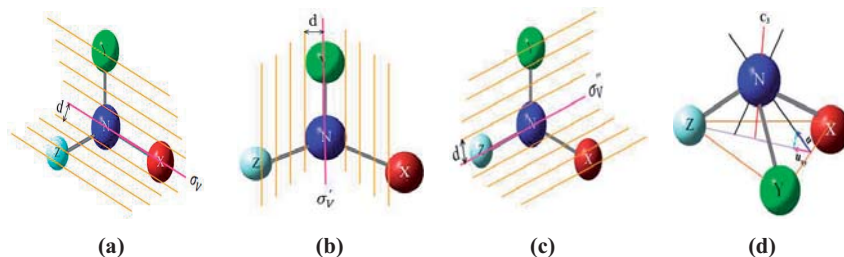


Figure 1: The reference σ_v , σ_v' and σ_v'' reflection planes and the C_3 rotation axis adopted for measuring electron density asymmetry index in the NXYZ families of molecules referenced to the C_{3v} symmetry.

The AIs are calculated using Eqs. 1-3 for different positions of the reflection plane and different orientations of the three-fold rotation axis (Fig. 1). The $I_{\sigma_v} / I_{\sigma_v'} / I_{\sigma_v''}$ MAIs for the $\sigma_v / \sigma_v' / \sigma_v''$ planes are obtained based on AI values calculated for the sets of planes parallel to the plane passing through the N-X / N-Y / N-Z bonds and the midpoint of the Y-Z / X-Z / X-Y sides (Fig. 1(a-c)), and the $I_{C_3^1} / I_{C_3^2}$ MAIs for the C_3^1 / C_3^2 axes are obtained based on the AI values calculated for the sets of C_3^1 / C_3^2 axes all passing through the N atom and a moving point on the line segment connecting the center of the X-Y-Z triangle and the midpoint of its Y-Z side (Fig. 1(d)).

Results obtained for the variation of the asymmetry indices I_{σ_v} and I_{C_3} with changes in the position/orientation of the symmetry elements σ_v and C_3 are shown in Figs. 2-4. The concept of MAI where the AIs are minimum ($I_{\sigma_v}^{min}$ and $I_{C_3}^{min}$) at certain positions and/or orientations of the reference symmetry element can be apprehended easily in these figures. Using the condition given in Eq. (4), the MAI values for the operations E , C_3^1 , C_3^2 , σ_v , σ_v' and σ_v'' are extracted, and are used to calculate the overall MAI values referenced to the C_{3v} point group using Eq. (5). These elemental and overall MAI values are reported in Table 1.

Note that because of similarity, and for brevity, only a limited number of graphs for the NX_3 , and $\text{NX}_2\text{Y}/\text{NXY}_2$ families of molecules are presented. This report is intended to present the idea of AI and MAI, and to demonstrate their application for a few prototype molecules as benchmark.

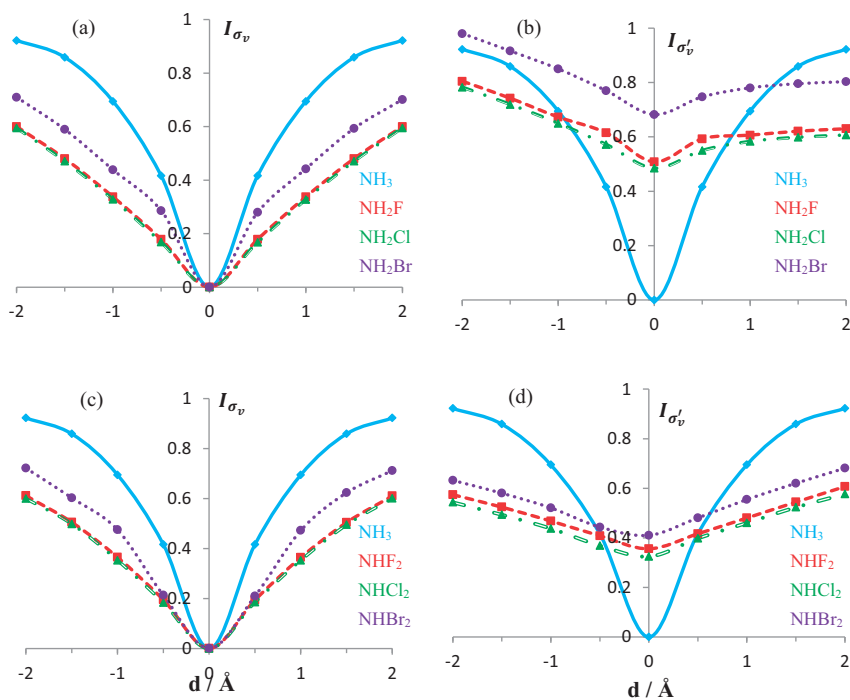


Figure 2: Asymmetry indices I_{σ_v} and $I_{\sigma'_v}$ corresponding to the σ_v (a & c) and σ'_v (b & d) reflection operations calculated for the $\text{NH}_2\text{X}/\text{NHY}_2$ ($\text{X}, \text{Y}=\text{F}, \text{Cl}, \text{Br}$) series of molecules using Eq. (3), as functions of the position of the parallel planes with respect to the one passing through the N atom (d , as defined in the text and demonstrated in Fig. 1(a-c)). The corresponding curves of the C_{3v} symmetric molecule NH_3 are given as references. Note the different values of MAI for different molecules when the plane does not belong to the C_s point group of the molecules.

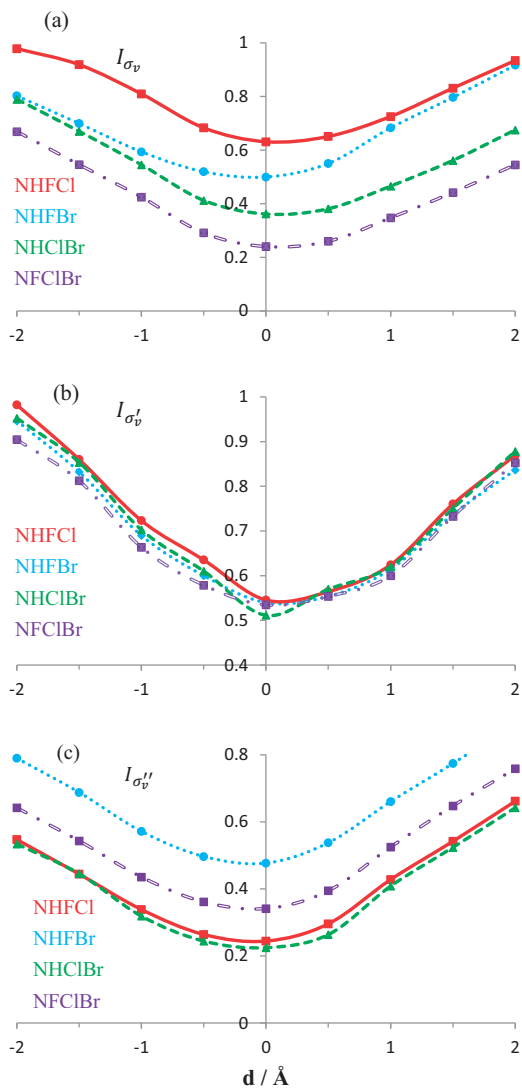


Figure 3: The same as Fig. 2, but for asymmetry indices corresponding to the σ_v (a), σ'_v (b) and σ''_v (c) reflection planes (Fig. 1(a-c)) for the NXYZ (X,Y,Z=H,F,Cl,Br) series of molecules. Note the different scales on the vertical axes and different values of MAI for different planes and molecules.

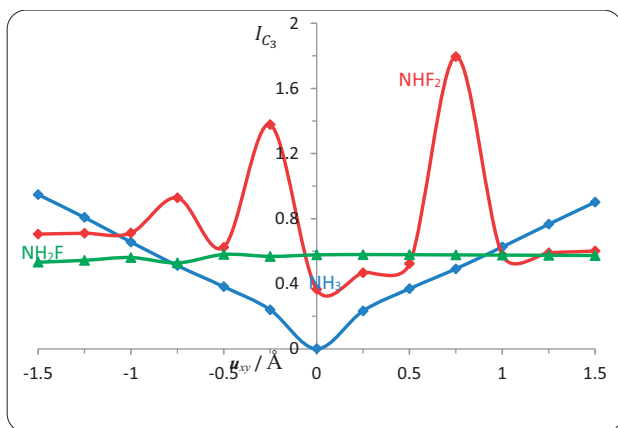


Figure 4: The same as Fig. 2, but for the variation of the asymmetry index $I_{C_3} = I_{C_3^2}$ with the orientation of the C_3 axis (defined in the text and demonstrated in Fig. 1(d)), measured in terms of the projection u_{xy} of the unit vector u ($|u|=1\text{\AA}$, lying along the C_3 axis) on the xy plane containing the XYZ triangle.

3. Results and Discussion

In the calculations of the asymmetry indices, only frontier orbitals are taken into account for the evaluation of the electron densities (i.e. valence $1s$ orbital for H, valence ns and np orbitals for N, F and Cl, and valence $4s$, $4p$ and $3d$ electrons for Br). In other words, the nuclei and their non-valence electrons are considered as structureless cores in all transformations. This can be justified as most physical properties related to the asymmetry of the electron density, such as electric multiple moments, (visible light) optical activity and refractive index, depend on the configuration and distribution of the valence electrons only. Inclusion of all electrons, however, although changes the numerical values of the proposed AI and MAI indices, does not alter validity of their concept and their use as discriminating indices.

Table 1: The MAI (I_5^{min}) corresponding to the symmetry operations S of the C_{3V} reference symmetry point group obtained for the NX_3 , NX_2Y/NXY_2 and $NXYZ$ ($X, Y, Z = H, F, Cl, Br$) family of molecules using Eq. (4). The overall MAI, $I_{C_{3V}}^{min}$, is calculated using Eq. (5) based on the values of I_5^{min} obtained for all symmetry species of the C_{3V} point group (as given in its character table). For the NX_2Y/NXY_2 series of molecules, the σ_V is considered to be the plane bisecting the X-X/Y-Y side, and the C_3 and C_3^2 axes corresponds to this side also.

Series	NXYZ Molecule	Atoms			I_5^{min}					I_{PG}^{min}
		X	Y	Z	$I_{C_3}^{min} = I_{C_3^2}^{min}$	$I_{\sigma_V}^{min}$	$I_{\sigma_V}^{min}$	$I_{\sigma_V}^{min}$	I_E^{min}	$I_{C_{3V}}^{min}$
NX ₃	NH ₃	H	H	H	0.00021	0.00021	0.00021	0.00021	0.00017	0.00122
	NF ₃	F	F	F	0.00031	0.00030	0.00030	0.00030	0.00018	0.00170
	NCl ₃	Cl	Cl	Cl	0.00031	0.00031	0.00031	0.00031	0.00018	0.00173
	NBr ₃	Br	Br	Br	0.00012	0.00011	0.00011	0.00011	0.00011	0.00067
NX ₂ Y/ NXY ₂ X	NH ₂ F	F	H	H	0.49968	0.00039	0.49855	0.49855	0.00036	1.99721
	NH ₂ Cl	Cl	H	H	0.49707	0.00037	0.48477	0.48477	0.00047	1.96452
	NH ₂ Br	Br	H	H	0.68727	0.00044	0.68231	0.68231	0.00024	2.73984
	NF ₂ Cl	Cl	F	F	0.30267	0.00113	0.29968	0.29968	0.00113	1.20696
	NF ₂ Br	Br	F	F	0.47285	0.00040	0.53396	0.53396	0.00040	2.01441
	NCl ₂ Br	Br	Cl	Cl	0.30557	0.00080	0.30431	0.30431	0.00080	1.22136
	NHF ₂	H	F	F	0.35319	0.00033	0.35578	0.35578	0.00033	1.41860
	NHCl ₂	H	Cl	Cl	0.34613	0.00014	0.32446	0.32446	0.00014	1.34146
	NHBr ₂	H	Br	Br	0.42225	0.00044	0.40968	0.40968	0.00044	1.66474
	NFCl ₂	F	Cl	Cl	0.44281	0.00070	0.40392	0.40392	0.00070	1.69486
NFBr ₂	F	Br	Br	0.46174	0.00029	0.45399	0.45399	0.00029	1.83204	
NClBr ₂	Cl	Br	Br	0.26417	0.00042	0.26890	0.26890	0.00042	1.06698	
NXYZ	NHFCI	H	F	Cl	0.55244	0.49960	0.53960	0.47685	0.00034	2.62127
	NHFBr	H	F	Br	0.66181	0.63093	0.54543	0.24433	0.00045	2.74476
	NHClBr	H	Cl	Br	0.55505	0.36150	0.51131	0.22459	0.00047	2.09797
	NFCIbr	F	Cl	Br	0.48963	0.24067	0.53460	0.34141	0.00027	2.09621

The calculated MAI values reported in Table 1 show that when referenced to the C_{3V} symmetry, the I_S values are almost zero for all symmetry operations of the C_{3V} symmetric molecules NX_3 (NH_3 , NF_3 , NCl_3 and NBr_3) and for all symmetry operations belonging to the C_s symmetric molecules NX_2Y/NXY_2 (NH_2F , NHF_2 , ...). The infinitesimally small values obtained for these MAIs are due to the inherent computational errors in electronic structure calculations. These results justify definition of the MAI for measuring the extent of the asymmetry of the electron density of molecules, as it discriminates strictly between operations belonging to the molecule point group and other operations. Moreover, only the minimum value of I_S , MAI, can be considered as the quantitative measure of the asymmetry.

Results demonstrated in Figs. 2-4 and those reported in Table 1 show that asymmetry index decreases with increasing electronic spatial extent (i.e. size) of the X/Y/Z atom attached to the central atom N. For example, asymmetry index for NH_2F/NHF_2 is smaller than that for $NH_2Cl/NHCl_2$. By increasing spatial extent of the X/Y/Z atoms, the molecular electron density distribution is extended over a wider space and covers a larger portion of the volume between atoms X, Y and Z. This results in lower differences between the electron densities of the points before and after the symmetry operation (transformation), and thus results in a smaller value of AI.

The asymmetry indices obtained for the NXYZ series of molecules containing bromine atom(s) are larger because of contributions from the 3d orbital electrons to the differential electron density transformations evaluated in Eq. (3).

Fig. 2(a) shows dependence of the I_{σ_V} asymmetry index on the position of the reflection plane σ_V for the four molecules NH_2F , NH_2Cl , NH_2Br and NH_3 . It can be seen from this Figure that the AI is zero when the reflection plane superimpose the actual symmetry plane of the molecule. This validates our proposed minimum asymmetry index (MAI) rule. Fig. 2(b) shows the same dependence but for $I_{\sigma'_V}$ corresponding to another reflection plane (σ'_V) as shown in Fig. 1(b). As can be seen from Fig. 2(b), this AI also varies with the position of the plane. The asymmetry index $I_{\sigma'_V}$ vanishes for the C_{3V} molecule NH_3 since σ'_V is its symmetry (mirror) plane, while, it remains non-zero at all positions of the reflection plane for the two C_S molecules NH_2F , NH_2Cl and NH_2Br . At the minimum value of $I_{\sigma'_V}$, i.e. the corresponding MAI, the three C_S molecules NH_2F , NH_2Cl and NH_2Br are clearly discriminated. Interestingly, the MAI rule finds the NH_2Cl molecule at a lower symmetry as compared to NH_2F (with reference to the C_3 symmetry operation). Figs. 2(c) and 2(d) show the same dependence but for other sets of molecules (NHF_2 , $NHCl_2$, $NHBr_2$) having also NH_3

as the C_{3V} symmetric reference molecule. Trends observed for the AI corresponding to the planar symmetry calculated for other NX_2Y/NXY_2 series of molecule not shown in Fig. 2 are similar to that described above.

Figs. 3(a), 3(b) and 3(c) show dependence of the I_{σ_V} , $I_{\sigma'_V}$ and $I_{\sigma''_V}$ asymmetry indices on the position of the reflection planes σ_V , σ'_V and σ''_V for the four asymmetric (chiral) molecules NHFCl, NHFBr, NHCIBr and NFCIBr. As can be seen from these figures, for all of these molecules, the MAI occurs around $d = 0$, i.e. when the plane passes the N-X, N-Y or N-Z bonds including its atomic centers (N,X), (N,Y) and (N,Z). Although passage of the planes from the two atomic centers, e.g. N and X, considerably decreases the AI, it is still expected to have the MAI somewhere else due to the difference between the remaining two atoms (e.g. Y and Z). Compatible with this expectation, the AI curves in Fig. 3 are all slightly asymmetric with respect to the $d = 0$ point (the MAI points fall somewhere between $d = 0$ and $d = \pm 0.5 \text{ \AA}$ positions).

Fig. 4 shows variation of the asymmetry index I_{C_3} with the orientation of the virtual C_3 rotation axis (shown in Fig. 1(d)) measured in terms of the projection u_{xy} of the unit vector u ($|u|=1\text{\AA}$, lying along the C_3 axis) on the plane containing the XYZ triangle, calculated for the NH_3 , NHF_2 and NH_2F molecules. Actually, in addition to the direction chosen and shown in Fig. 1(d), all possibilities of search paths should be considered for the change in the orientation of the C_3 axis in order to find the smallest MAI, regardless of the chemistry and geometry of the base triangle for searching the MAI. What are reported here are examples in order to describe the concept of MAI. As can be seen from this Figure, the relative values of this AI for these three molecules vary with the orientation of the rotation axis. More importantly, the MAI point of this I_{C_3} AI also can clearly discriminate these three molecules. This stresses the use of MAI rule for the unique evaluation of relative measures of asymmetries. Maxima and minima observed in the I_{C_3} asymmetry index curves denote passage of the corresponding symmetry element C_3 through the least and most concentrated electron density regions, respectively. The behaviors of the I_{C_3} AI for other molecules, which are not shown here for brevity, are more complex. However, their MAI points, which are reported in Table 1, remain reliably valid for uniquely ordering asymmetry of these families of molecules.

It should be noted here that the procedures for the calculation and finding MAI for $i = S_2$ and S_n symmetry operations (consisting more than one symmetry operation and involve more than one symmetry element) are basically the same, except that we should decide

position of which element (e.g. C_2 or σ_h in the case of S_2) should be optimized first. For all cases, including these compound operations, the set of positions with smaller value of MAI is intended and considered as the MAI.

4. Conclusion

A quantum mechanical asymmetry index (AI) is introduced to measure deviation of the electron density distribution from any symmetry. This asymmetry index is obtained based on the sum of all point-wise differences between the two electron density distributions before and after applying the geometrical transformation corresponding to the symmetry operation belonging to the reference symmetry point group of interest. The NX_3 , NX_2Y/NXY_2 and $NXYZ$ ($X, Y, Z=H, F, Cl, Br$) groups of molecules with the reference symmetry of C_{3V} have been used as prototype molecules for the calculation and analysis of AI. Results of these calculations show that AI decreases with the increase in the atomic number of the X, Y, and Y atoms of the molecule. Results also show that the AI values strongly depend on the position (or direction) of the operation elements such that relative values of the asymmetry index for different molecules vary considerably. A minimum asymmetry index (MAI) rule is introduced to estimate the extent of asymmetry of any given molecule with respect to any desired reference symmetry operations. This MAI rule prescribes where to locate or pass the operation element (e.g. center of inversion, axis of rotation, and plane of reflection) prior to the transformation.

The MAI values are obtained by calculating asymmetry indices corresponding to different positions of the planes of reflection and different orientations of the axis of rotation for different sets of the NX_3 , NX_2Y and $NXYZ$ molecules. The overall molecular MAI, I_{PG}^{min} , is introduced as an average of all elemental MAI corresponding to the symmetry operations belonging to the reference PG . This overall MAI can be used to quantify uniquely the extent of asymmetry of any given molecule with respect to any symmetry point group. The MAI rule provides a reliable and unique index to compare asymmetries of a pair or a group of molecules.

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