



# Continuous group and electron-count rules in aromaticity

PRADEEP KUMAR\*

Department of Chemistry, Malaviya National Institute of Technology, Jaipur, Rajasthan 302 017, India  
E-mail: pradeep.chy@mnit.ac.in

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**Abstract.** In the present article a group theoretical approach has been used to explain different electron-count rules for aromaticity. A general group theoretical method is presented to derive and unite the different electron count rules (Hückel, Baird, Möbius, and Spherical aromaticity). It is shown that continuous groups play important role in understanding of these electron count rules.

**Keywords.** Aromaticity; group theory; continuous groups.

## 1. Introduction

In 1855 August Wilhelm Hofmann used the word 'aromatic' to classify a group of molecules with certain particular properties.<sup>1</sup> Much before quantum mechanics and even the notion of atom, August Kekule tried to explain those peculiar properties by proposing the resonance structures of benzene, which played a pivotal role in the development of the concept of aromaticity.<sup>2</sup>

Since then, it has been an important concept in chemistry.<sup>3-5</sup> It was traditionally attributed to the organic compounds. Initially, it was invoked to explain certain non-trivial reactivity and stability of certain compounds. For example, why does benzene undergo electrophilic substitution rather than addition like other alkenes. In modern science, the notion of aromaticity is no longer limited to organic compounds; it has now been already incorporated in other domains like metal clusters,<sup>6-8</sup> fullerenes,<sup>9,10</sup> photochemistry<sup>11</sup> and hydrogen bonded complexes.<sup>12</sup>

The concept of aromaticity was initially confined to the delocalization of electrons in pi ( $\pi$ ) orbitals, but now, it is known that electrons not only get delocalized in  $\pi$  orbitals but also in sigma ( $\sigma$ ) orbitals, hybrid orbitals and even in delta orbitals.<sup>13,14</sup> Besides orbitals, the geometry of molecule can also lead to different types of aromaticities. The Möbius aromaticity<sup>15-19</sup> can be a typical example. In spite of being found routinely in all elementary texts of organic chemistry, aromaticity is still a poorly understood and controversial concept.<sup>20</sup> One of the reasons might be that aromaticity is not a directly measurable property.<sup>21</sup> It manifests itself, in

terms of changes in structure, reactivity and stability of compounds. Consequently, a number of different indirect measures of aromaticity exist in literature like resonance energy, geometry based index,<sup>22</sup> information theoretic index,<sup>23</sup> nuclear independent chemical shift (NICS),<sup>24</sup> aromatic fluctuation index (FLU), etc.<sup>25,26</sup> It is generally an accepted fact that all kinds of aromaticities result from delocalization of electrons and all the indexes usually indicate the extent of this delocalization. Since the beginning, besides aromaticity index, electron-count rules were also used to identify the aromatic character of molecules.<sup>27</sup> The electron count rules usually give only qualitative description of aromaticity, while aromaticity indexes were designed to predict the aromaticity quantitatively. For example according to Hückel rule,<sup>3</sup> any planar cyclic molecule with  $4N + 2$  ( $N$  being a positive integer)  $\pi$ -conjugated electrons is called aromatic. Consequently, benzene and toluene both are aromatic according to Hückel rule, but  $4N + 2$  rule does not differentiate between them, whereas values of aromatic indexes, like ring current and resonance energy do differ for benzene and toluene. As soon as aromaticity in inorganic compounds had started to surface, a search for similar electron count rules like Hückel rule also started. For example, when fullerene was discovered and found to have some unusual properties like benzene, researchers tried to explain it on the basis of spherical delocalization of electrons.<sup>9,10</sup> It was obvious that Hückel rule can not be applied in fullerene or more generally to spherical molecules. Hirsch and co workers formulated the  $2(N+1)^2$  rules for spherical aromatic compounds.<sup>28</sup> Similarly, when aromaticity was found in Möbius type molecules, a  $4N$  rules for Möbius type molecules<sup>15-17</sup> had been formulated.

\*For correspondence

Similar to close shell molecules, these electron count rule have also been formulated for open shell systems. Baird<sup>29</sup> was the first to formulate the  $4N$  rules for planar cyclic open-shell compounds similar to Hückel rule. After the discovery of spherical aromaticity in fullerene like molecules, Poater and Solá<sup>30</sup> had successfully formulated the  $2N^2 + 2N + 1$  rule for aromaticity in open shell spherical molecules. It warrants a mention here that stating the aromaticity rule does not always mean a complete understanding of the origin of these rules. For example, Hückel proposed his rule based on his LCAO-MO calculation which is popularly known as Hückel molecular orbital theory (HMO). Later Dewar<sup>31</sup> in the mid-1960s used perturbation theory to qualitatively derive and compare the formation energies to explain the Hückel rule. Recently, Miliordos explained the Hückel rule based on a particle on a cylinder model.<sup>32</sup> It is worth mentioning that Hückel molecular orbital theory was traditionally related to connectivity, therefore topological approach like graph theory gained popularity in explaining Hückel  $4N + 2$  rule. In this context, explaining Hückel rule based on a particle on a cylinder model gives a new way of thinking about aromaticity. In another example, although Heilbronner gave the  $4N$  rule for aromaticity in Möbius type molecules<sup>15</sup> based on simple HMO theory and later H. E. Zimmerman coined the term Möbius aromaticity,<sup>16,17</sup> a lot of effort was made in the recent past to understand the real origin of this  $4N$  rule. Miliordos solved a particle on Möbius strip problem<sup>32,33</sup> to unravel the mystery behind  $4N$  rule, whereas McKee *et al.*<sup>34</sup> used a more sophisticated HMO approach to understand this rule.

Initially, most of these rules were formed based on explicit *ab initio* calculations on different molecules. It is important to understand that these electron count rules are very general, as they just use a general kind of symmetry description of molecules. Therefore, instead for using *ab initio* approaches to explain these rules, symmetry based approaches might be more natural. Another importance of using the symmetry based approach is, it can give a connection between different electron count rules. For example, Rubin and Ordóñez<sup>35</sup> computed the eigenvalues and degeneracy of general  $n$ -dimensional spherical harmonics. One can clearly see there,  $n = 2$  case corresponds to Hückel rule, whereas  $n = 3$  case corresponds to Hirsch rule. In another case Poater *et al.*,<sup>36</sup> used electronic confined space analogy (ECSA) to show that  $4N + 2$  Wade-Mingos rule<sup>37,38</sup> for three dimensional closo boranes is equivalent to the  $4N + 2$  Hückel rule for polycyclic aromatic hydrocarbon.

Symmetry based approaches are nowadays gaining popularity in explaining these electron count rules.<sup>39–41</sup> B. A. Shainyan<sup>41</sup> used a physical symmetry, which he

called symmetry of space of states to shed light on the origin of electron count rules. Recently, it was shown that tubular aromaticity found in tubular boron clusters can be explained using particle in hollow cylinder model.<sup>42,43</sup> Same group used particle on a disk model, to explain aromaticity in planar boron cluster and coined the term disk aromaticity.<sup>44–46</sup> It is important to note that explaining aromaticity by solving classical text book problems like particle on sphere,<sup>28</sup> particle on disk,<sup>45,46</sup> particle on hollow cylinder<sup>42,43</sup> or particle on Möbius strip<sup>32,33</sup> are essentially symmetry based approaches. In all these problems, authors were trying to utilize, the underlying symmetry involved in electron delocalization space. Therefore, in explaining aromaticity rules, it appears natural to utilize the symmetry, directly, using group theory rather than solving differential equations.

In the present paper, the author explains different electron count rules, using the symmetry arguments based on group theory. The approach used here, is based on continuous groups, rather than point groups. Hopefully, the present work will complement other works that used symmetry based argument directly or indirectly, to explain aromaticity and will strengthen the symmetry based arguments, in exploring aromaticity.

## 2. Theory

Our chemical intuition says, that, aromaticity is actually the concept of extensive delocalization of electrons. The symmetry group of molecule, will depend on the structure of molecule. But, when electrons get truly delocalized, they will be in continuous symmetry. Consequently, when a molecule is aromatic, then the relevant electrons live in a different symmetry space. This delocalization space must be some continuous symmetry space. Therefore, continuous groups, not point groups should play important role in understanding of electron count-rules. It makes the study of aromaticity simple. Instead of solving full eigenvalue problems of actual Hamiltonians, one should solve text book kind of problems of continuous symmetry. For example, particle on a cylinder, particle on a sphere, etc. As mentioned in the introduction, similar approaches have been used to explain Hückel, Möbius, tubular, spherical and disk aromaticity. It is known that symmetry plays an important role in solving such kind of differential equations. In the context of electron count rules, this symmetry aspect of differential equations, become very important, as we are not looking for exact eigenvalues or eigenfunctions. Rather, we are in search of a general distribution of eigenfunctions. Lot of qualitative features about such kind of problems, can be understood, through group theory, without explicitly solving the differential equation. This can be illustrated by typical text book

solution of hydrogen atom. Hydrogen atom has a spherically symmetric potential. The angular part of the wave function turns out to be spherical harmonics. It is no coincidence that the spherical harmonics form the irreducible representation of the rotation group (particularly that of special orthogonal group, of order three, normally known as  $SO(3)$  group).

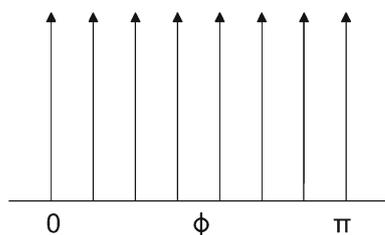
In the present article, symmetry based approach is used, instead of solving the differential equations. For the present analysis, there are two important aspects in the explanation of electron-count rules: first, to recognize the symmetry of the space in which electrons get delocalized; second, the symmetry of the orbitals involved in the delocalization process. Once, these two symmetries are recognized, we have to look for the irreducible representations of that group that accommodates these two symmetries. Within that group, the stable configuration corresponds to aromaticity whereas unstable configuration corresponds to antiaromaticity. This general methodology is illustrated in the next section by applying it to various classes of aromaticity.

### 3. Results and Discussion

#### 3.1 Hückel and Baird aromaticity

The molecules belonging to this class, have cylindrical symmetry for delocalized electrons. We can represent the cylinder on a two dimensional  $R^2$  plane (Figure 1) in the rotational angle space ( $\phi$ ).

In this plane, the cylindrical symmetry corresponds to the translational symmetry in  $\phi$ . The relevant group for cylindrical symmetry is special orthogonal group of order two i.e.,  $SO(2)$ , whose irreducible representations can be represented by  $\exp(-im\phi)$  where  $m = 0, \pm 1, \pm 2$  etc. The values of  $m$  are obtained from the boundary condition, which requires that, after a  $2\phi$  translation, a vector should be back onto the original vector. Now, if the orbitals involved in delocalization are  $\pi$  orbitals, we can use an inversion symmetry in conjunction with  $SO(2)$  symmetry. Consequently the resultant symmetry group will be a direct product of  $SO(2)$  and



**Figure 1.** The representation of cylinder in 2-d Space. The vectors are used to indicate the different points on cylinder's cross section.

$\sigma_h$  i.e.,  $SO(2) \otimes \sigma_h$ , which will be  $D_{\infty h}$  (after including inversion) group. The character table for  $D_{\infty h}$  point group is shown in Table 1.

This point group has two sets of, one dimensional as well as, two dimensional representations. One set with positive character for inversion (g) and other one with negative character (u). The  $\pi$  orbitals will belong to ungerade (u) set of one as well as two dimensional representations. The molecular orbital diagram, under this symmetry, is shown in Figure 2.

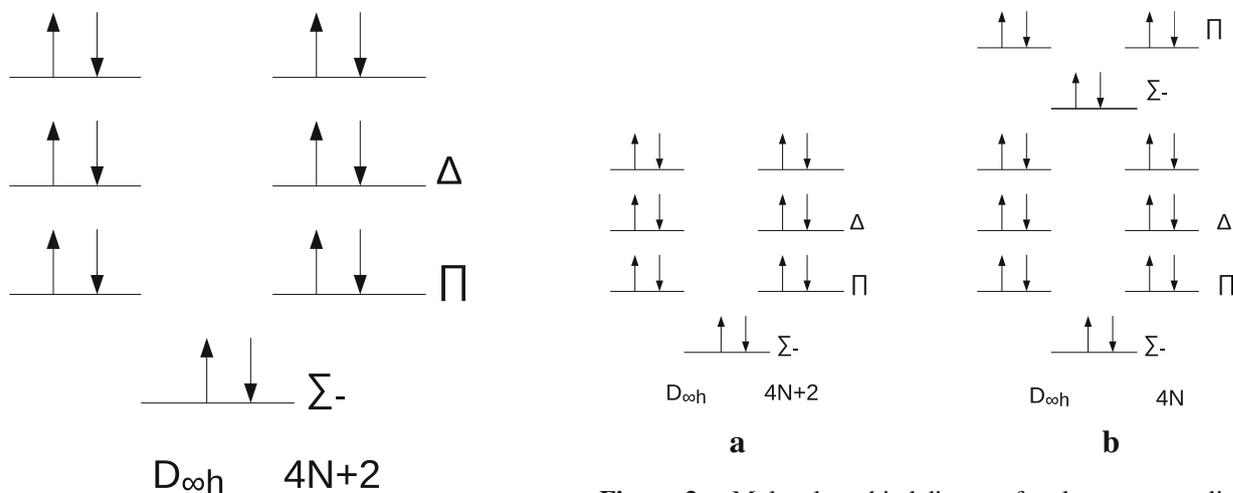
Now, if we are dealing with a closed shell molecule, we need a closed shell configuration for these orbitals. Using Pauli exclusion principle to fill up these orbitals, the closed shell configuration will correspond to  $4N + 2$  electrons for  $2N + 1$  orbitals. Therefore,  $4N + 2$  electrons are very natural for these closed shell molecules, in which electrons get delocalized within cylindrical space. It is interesting to note that, in molecules where more than one layer of atoms exist (Instead of molecules having a ring topology, they have a disk or tubular structure), more than one such set of orbitals may exist. Quantum mechanically it means, additional quantum numbers exist, besides the angular one. Consequently, the closed configuration can consist of  $4N + 2$  (Figure 3 a), or  $4N$  (Figure 3 b), depending upon the exact energy ordering of molecular orbitals.

This discussion, can easily be extended to the case, where electrons get delocalized in  $\sigma$  orbitals ( $\sigma$  aromaticity). Here again, one can use the  $D_{\infty h}$  point group, to derive the aromaticity rule. The rule for  $\sigma$  aromaticity will be the same, except the fact that  $\sigma$  orbital will correspond to the gerade (g) set of one as well as two dimensional representations. Consequently, electron count rule will be the same regardless of whether electron gets delocalized in  $\sigma$  or in  $\pi$  orbitals. The  $\sigma$  aromaticity and  $4N$  rule are not very apparent in organic molecules, as organic molecules usually have a ring topology and  $\pi$  delocalization. But in inorganic molecules, one can see it. For example, depending upon the number of boron atoms and overall charge, boron clusters can exist both in disk form and in tubular form.<sup>47</sup> There, depending upon the exact ordering of molecular orbitals the stable boron cluster may consist of either  $4N + 2$  or  $4N$  electrons.<sup>42-46</sup>

In case of open shell molecules, one needs to fill these molecular orbitals, in such a way that the resulting configuration need to be consistent with spin state of molecule. If the molecule is in triplet state, then total number of electrons will be  $4N + 2 + 2$ , where extra two electrons are unpaired electrons. So essentially,  $4N$  electrons will be optimal for both triplet and singlet states to exhibit aromaticity, famously known as Baird's rule.

**Table 1.** In the following table the symbols and numbers to the left and above the double lines refer to the  $D_{\infty h}$  point group. Below and to the right of the broken lines are species and characters of corresponding double group ( $D_{\infty h}^*$ ). The  $E(2\pi)$  represents the  $2\pi$  rotation operator while  $E(4\pi)$  is the  $2\pi$  rotation operator.

	$E(2\pi)$	$2C_{\infty}$	...	$\infty\sigma_v$	$i$	$2S_{\infty}$	...	$\infty C_2'$	$E(4\pi)$	...
$\Sigma_g^+$	1	1	...	1	1	1	...	1	1	...
$\Sigma_g^-$	1	1	...	-1	1	1	...	-1	1	...
$\Pi_g$	2	$2\cos(\phi)$	...	0	2	$-2\cos(\phi)$	...	0	2	...
$\Delta_g$	2	$2\cos(2\phi)$	...	0	2	$2\cos(2\phi)$	...	0	2	...
...	...	...	...	...	...	...	...	...	...	...
$\Sigma_u^+$	1	1	...	1	-1	-1	...	-1	1	...
$\Sigma_u^-$	1	1	...	-1	-1	-1	...	1	1	...
$\Pi_u$	2	$2\cos(\phi)$	...	0	-2	$2\cos(\phi)$	...	0	2	...
$\Delta_u$	2	$2\cos(2\phi)$	...	0	-2	$-2\cos(2\phi)$	...	0	2	...
...	...	...	...	...	...	...	...	...	...	...
$E_{\frac{1}{2}g}$	-2	$2\cos(2\phi/2)$	...	0	2	...	...	...	2	...
$E_{\frac{3}{2}g}$	-2	$2\cos(3\phi/2)$	...	0	2	...	...	...	2	...
$E_{\frac{5}{2}g}$	-2	$2\cos(5\phi/2)$	...	0	2	...	...	...	2	...
...	...	...	...	...	...	...	...	...	...	...



**Figure 2.** Molecular orbital diagram for electrons on cylinder.

**Figure 3.** Molecular orbital diagram for electrons on cylinder. (a) represents an arrangement where  $4N + 2$  rules applicable whereas (b) represents a configuration which complies  $4N$  rule.

### 3.2 Möbius aromaticity

Molecules belongs to this category have a Möbius topology. Although, theoretical prediction about Möbius aromaticity came much earlier, experimental observation of such molecules are still an active area of research.<sup>18,19,48</sup> Initially, the search for Möbius aromaticity were limited to annulenes, but recently, expanded porphyrins is gaining popularity<sup>19,49</sup> as potential candidates for Möbius aromaticity. The parametric equation for Möbius strip is as follows.<sup>33</sup>

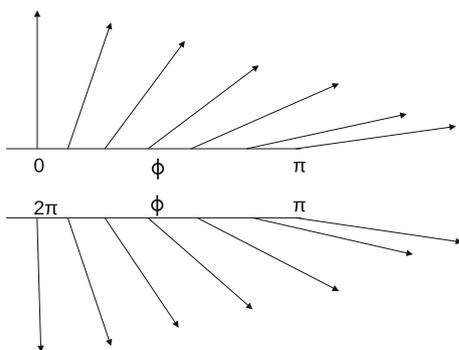
$$x = [R + s\cos(\pm\phi)]\cos(\phi) \quad (1)$$

$$y = [R + s\cos(\pm\phi)]\sin(\phi) \quad (2)$$

$$z = s \left[ \sin\left(\frac{\phi}{2}\right) \right] \quad (3)$$

If we wish to represent it on a  $R^2$  plane, it will look like Figure 4. It is evident from Figure 4, that the vectors not only translate, but also twist.

The translation in  $\phi$  direction and translation in  $z$  direction (which give rise to the twisting) can be separated. Therefore, the representations of Möbius space symmetry have two parts; one comes from invariance of translation in  $\phi$  direction, and, the other one comes



**Figure 4.** The Möbius strip in 2-d Space. The vectors are used to indicate the different points on Möbius strip.

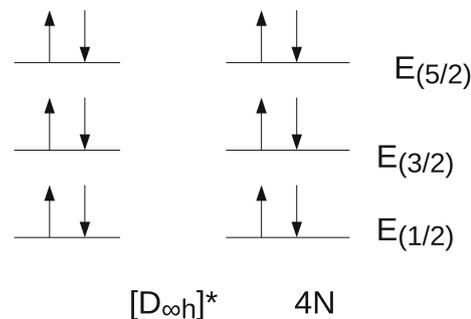
from invariance of translation in  $z$  direction. Mathematically, it will be of the form  $e^{\pm im\phi} e^{\pm icmz}$ . The particle on the Möbius strip has been solved analytically and the constant 'c' was found to be  $2/R$ .<sup>33</sup> The cylindrical symmetry can be applied to Möbius strip, with one major modification to the Hückel case; in case of Möbius strip the boundary condition involves a rotation of  $4\pi$ , not  $2\pi$ . Due to this boundary condition,  $m$  can take values  $0, \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \pm 2$ , etc. The half integer values of  $m$  make the Möbius strip interesting. In the case of Möbius strip, one should use the double group of  $D_{\infty h}$ , which means, the group relevant to Möbius aromaticity will be  $D_{\infty h} \otimes \text{spin-group}$ . The double group for  $D_{\infty h}$  is given in Table 1.<sup>50</sup> For double group, the identity element is  $4\pi$  rotation, not  $2\pi$  rotation. If electron delocalization takes place through  $\pi$  orbitals, we have to search for, that irreducible representation of this group in which  $\pi$  orbital belongs. On the Möbius strip, a  $2\pi$  rotation will change the phase of  $\pi$  orbital, that means the character corresponding to the  $2\pi$  rotation will be negative. If we see the characters of  $D_{\infty h}$  and the corresponding double group, it is evident that, the representations, which have negative character value, corresponds to half-integer values of  $m$ , not full integer values. It is clear from the orbital digram given in Figure 5, aromaticity rule for Möbius strip, will be  $4N$  ( $2N$  orbital), as this give rise to a closed configuration.

It is important to note that, this rule is for  $\pi$  aromaticity.

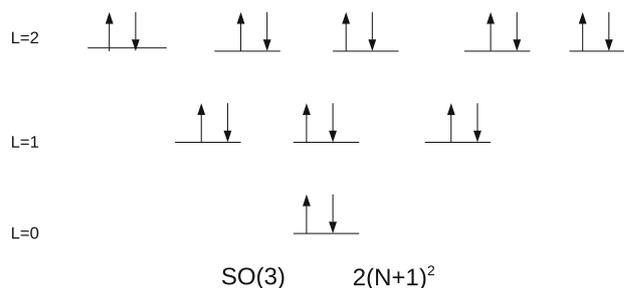
The  $\sigma$  orbital do not change phase on  $2\pi$  rotation, hence it belongs to full as well as half-integer value of  $m$ . Consequently, the  $\sigma$ -aromaticity rule for Möbius strip will be  $4N + 2$  as it was for Hückel case.

### 3.3 Spherical aromaticity

For spherical molecules like fullerene, electron delocalization space is a sphere, which belongs to  $SO(3)$



**Figure 5.** Molecular orbital diagram for electrons on Möbius strip.



**Figure 6.** Molecular orbital diagram for electrons on sphere.

symmetry group. If we include inversion symmetry, the relevant group become  $SO(3) \otimes C_i$ , which is the  $O(3)$  group. The spherical harmonics can be used to represent the irreducible representations of this group. It is evident from Figure 6 that, in this case, the orbitals will be counted as 1, 3, 5, 7 —, which will be total  $(N + 1)^2$  orbitals where  $N$  is an integer.

If we fill electrons, using Pauli principle, the closed shell will be formed with  $2(N + 1)^2$  electrons. Therefore, the electron-count rule for spherical molecules will be  $2(N + 1)^2$ . Let us analyze the open shell spherical molecule. In this case, when HOMO is half filled, then it corresponds to a stable configuration i.e., aromatic. If we count, this number will be 1,5,13,25— which mean  $2N^2 + 2N + 1$  for an electron spin of  $S = N + \frac{1}{2}$ .

Three dimensional aromaticity in literature can be divided into the two groups one as “Spherical aromaticity” and other one as “Spatial aromaticity”.<sup>7,8,41,51,52</sup> The word spherical aromaticity is reserved for fullerene like molecules which obeys strictly  $2(N + 1)^2$  and  $2N^2 + 2N + 1$  rule for closed shell and open shell systems respectively, whereas word spatial aromaticity is applicable to various cage-like compounds. As mentioned earlier, the tubular aromaticity, which is a spatial aromaticity, obeys the generalized Hückel rule. In this context, the  $SO(3)$  group is useful only for spherical aromaticity not for spatial aromaticity. Most of the times

one needs to map the spatial aromaticity to some continuous symmetry. For example, as mentioned in the introduction, Poater *et al.*,<sup>36</sup> had successfully mapped the three dimensional aromaticity in closo borane to Hückel like cylindrical symmetry space.

#### 4. Conclusion

Based on the group theory, the present analysis concludes that the origin of all electron-count rules are the same. It assumes that, electrons are moving freely in the molecules. Therefore, continuous groups play an important role in deciding the electron-count rules. It was also observed that these electron count rules also depend on the type of orbitals. For example, in case of Möbius aromaticity electron count rules are opposite for  $\sigma$  and  $\pi$  orbitals. Group theoretical methods give a nice way to incorporate the symmetry of orbitals into the electron delocalization symmetry space. Here, we have successfully classified different types of aromaticities in terms of irreducible representations of continuous groups, except spatial aromaticity.

Finally, It is also worth mentioning that Group theory is a well-developed mathematical theory. Therefore, we believe that besides unifying different electron-count rules, it will be useful to shed more light on different questions related to aromaticity. For example, to derive electron-count rules, the present analysis assumes a complete delocalization of electron, but we know that, aromaticity per se does not required a complete delocalization. There are also incidence that a perturbation can increase or decrease the aromaticity character of system. In such cases, whether Group theory can be helpful or not, is a matter of further investigation.

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