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TO DISCUSSION

## Rules for Counting Electrons and Three-dimensional Aromaticity

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The aromaticity concept is one of the most mysterious in chemistry. For planar cyclic systems with a closed conjugation system the aromaticity requirement is the fulfillment of the  $4n + 2$  Hückel rule formulated at the beginning of nineteen thirties [1]. The rule determines the number of the p-electrons in the aromatic systems (2, 6, 10, 14, ...) which remarkably coincides with the number of electrons on the closed electron subshells of atoms (*s*, *p*, *d*, *f*, ...). Recently Hirsch suggested another rule of counting electrons,  $2(n + 1)^2$ , for fullerenes and other cage-like structures possessing three-dimensional aromaticity [2–5]. The number of electrons determined by Hirsch rule corresponds to the number of electrons on the filled electron shell of an inert gas (2, 8, 18, 32, ...) and differs from the number of electrons on the closed subshells of atoms (although sometimes coincides with it). Therefore two fundamental problems arise: (1) Why just  $4n + 2$  or  $2(n + 1)^2$  and why they are so remarkable; (2) Does any connection exist between these numbers. The only statement possible with respect to these numbers notwithstanding the objects they describe is that both numbers are even; yet  $4n + 2$  is not simply even, but a doubled uneven number, whereas it is not the case with  $2(n + 1)^2$ .

Let us consider the problem disregarding for some time the particular chemical nature of the molecules under discussion, and examine the number of irreducible states in an arbitrary *n*-dimensional states *independent of the nature of objects within*, namely, let us consider a *space of states*. In a zero-dimensional space obviously a single state is possible: a point. In a one-dimensional space three irreducible states are possible: a point, a vector with a positive direction, and a vector with a negative direction. In keeping with this reasoning in two-dimensional and three-dimensional spaces five and seven irreducible states

respectively are possible (in the latter event these are: “point”, “to the left”, “to the right”, “up”, “down”, “forward”, and “backward”). These options exhaust the possibilities of our three-dimensional space whence follows a somewhat unexpected conclusion that the mentioned types of the electron shells (*s*, *p*, *d*, and *f*) close the number of the possible sublevel types, and the existence of *5g* (and moreover *6h*) electrons, and consequently of *g*-elements (starting from no. 121, eka-actinium, tentative symbol Ubu, unbiunium) is impossible.

In the general case the number of irreducible states in an *n*-dimensional space equals  $2n + 1$ . Returning now to the rule of counting electrons and considering just the electrons as the objects in the arbitrary *n*-dimensional space we know that they should obey Pauli principle (maximum two electrons in each state), and the number of electrons for every closed electron subshell should be equal to  $2(2n + 1) = 4n + 2$ . Now taking into consideration that any *n*-dimensional space includes all the (*n*–*k*)-dimensional subspaces, then the number of electrons filling all the subshells will be expressed by a sum over all  $k \leq n$  and in keeping with the linear series formula proves to be  $2(n + 1)^2$ :

$$\sum_{k=0}^n [4(n - k) + 2] = 2(n + 1)^2$$

Interestingly, at even *n* the number of electrons by Hirsch rule  $2(n + 1)^2$  coincides with the number of electrons by Hückel rule  $4m + 2$  at  $m = 1/2n(n + 2)$ .

Initially the Hückel rule was introduced for planar systems, and the Hirsch rule, for the systems of three-dimensional aromaticity. But whether all planar systems obey the Hückel rule, and whether all systems of the

three-dimensional aromaticity fit to the Hirsch rule? Strictly speaking, no. Although there are no exclusions from the  $4n + 2$  rule when correctly applied. There are some examples of the formal deviations from the Huckel rule in the polycyclic systems, for instance, the acenaphthylene contains 12  $\pi$ -electrons, and pyrene possesses 16  $\pi$ -electrons, although both are aromatic. However it means only that the Hückel rule should be applied only to the peripheral  $\pi$ -electrons involved in the ring current in the cycle.

The case of the Hirsch rule  $2(n + 1)^2$  is more complex. Here it seems practical to separate two types of the three-dimensional aromaticity. The first one, "spherical" as named by Hirsch, has been successfully applied to fullerenes and heterofullerenes [2, 3, 6–8], but it is difficult not to agree with Sidorov et al. [9, p. 105], when they regard as senseless the discussion of forms  $C_{60}^{10+}$  and  $C_{60}^{12-}$  that are aromatic in keeping with the rule  $2(n + 1)^2$ . The electronic structure of the spherically symmetric structures was related in [7] to the electronic structure of the filled electron shell of the inert gas with the help of a Gedankenexperiment by extending the size of an atom from a point to a hollow sphere with a uniform distribution of the positive charge on its surface and further to the size of the corresponding polyhedron with distorted uniform distribution of the charge and its localization on the vertices of the polyhedron. Interestingly, with the growing radius of the sphere (pseudoatom) the sequence of energy levels changes from the usual ( $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, \dots$ ) to "inverted" ( $1s, 2p, 3d, 2s, 3p, 3s, 4p, 4s, \dots$ ) because the remoteness from the nucleus results in stronger destabilization of the  $s$ -levels initially most strongly bound to it. Johansson et al. [7] discuss beside the limits of application of the rule  $2(n + 1)^2$  caused by the fact that with the growing size of the spherical system the orbital energy levels approach each other, and the corresponding states mix.

The three-dimensional aromaticity of the second type occurring in various cage-like structures (see examples in [10–17] and references therein) may be called "spatial". We believe that the fundamental difference between the "spherical" and "spatial" aromaticity consists in the partial conservation of the "spherical" aromaticity when, for example, fullerene is "rolled" into a planar structure (as a globe into a map); the planar system remains aromatic. On the contrary, the broken bond in the three-dimensional cage-like structure and its

conversion into monocyclic or linear molecule results in complete loss of the aromaticity. Thus it may be concluded that with respect to three-dimensional aromatic systems the Hirsch rule concerns first of all the systems of "spherical" aromaticity (like fullerenes [2, 3, 6]), and the Huckel rule is valid for the systems of "spatial" aromaticity (like adamantane derivatives [10–13], *closo*-carboranes [14] and -azaboranes [15], dilithium salt of the tetrasilylcyclobutadienyl dianion [16], germanyl clusters [17] etc.).

It should be stressed in conclusion that both the planar and three-dimensional aromaticity same as the corresponding rules for counting electrons have a common origin. It is related, on the one hand, to the formal consideration of an arbitrary  $n$ -dimensional space of states, and on the other hand, to the fact that all elementary particles in chemistry (electrons, protons, and neutrons) as the objects in this space are fermions, obeying the Fermi–Dirac statistics and consequently the Pauli principle.

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