VALENCE STATES OF ATOMS AND THEIR CONVERSIONS*

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The algebraic formalism for the description of valence states of atoms and their interconversions is elaborated. It offers a possibility to construct and trace mechanistic paths of chemical reactions, the problem of which is of great importance in computer-assisted organic syntheses. Its systematic application gives exhaustive lists of possible mechanistic paths, and furthermore, very efficient tool to classify chemical reactions and look for their common features.

In construction of an adequate mathematical model of organic chemistry which covers whole its diversity and complexity on microscopic level (*e.g.* the dynamical chemical phenomena are interpreted by the interconversions of valence states of atoms), an indispensable role play those formal tools that are representing the electronic valence states of atoms and their permissible changes. Chemical reactions between educts may be simply described *via* the interconversions of valence states of a few atoms which form the so-called reaction sites unambiguously determined for a given type of chemical process. The purpose of the present communication is to suggest both simple and efficient algebraic approach to formalize the concept of valence states of atoms and their interconversions. We give an exhaustive list of all possible valence states of atoms with nd^4 orbitals; the valence states of atoms of an actual element form only a subset of this list. We say that two valence states are neighbouring if there exists such an elementary "operation" (physically realized by a transfer of an electron) converting a first valence state in another one. Then a distance between two valence states is determined as a number of these elementary steps which converse an initial valence state in a final state. Moreover, we demonstrate that the concept of chemical distance between two molecules (that are mutually related *via* a chemical transformation) is immediately interpreted by the distances of valence states between proper atoms taken from the initial and final molecular

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systems. The present approach allows to formulate simple combinatorial algorithms to enumerate (and simultaneously construct) all the possible products for a given educt (or educts) if we know permissible valence states of atoms from the specified reaction site.

Valence States of Atoms

In chemistry the *valence state* of an arbitrary atom belonging to a molecular system is, in general, described by an ordered 4-tuple composed of non-negative integers[1,2,11] (which is called the *vector of valence state*, VVS),

$$\mathbf{v} = (v_1, v_2, v_3, v_4)\,, \tag{1}$$

where the individual entries have the following simple meaning:

v_1 = number of free (lone or odd) electrons,
v_2 = number of single bonds,
v_3 = number of double bonds,
v_4 = number of triple bonds.

For instance, the valence state of an atom $-\overline{\mathrm{X}}\ll$ is determined by $\mathbf{v} = (2,1,2,0)$. If we restrict ourselves to study only the chemistry of elements with at most nd^4 electrons in valence sphere (*i.e.* inclusive of the so-called over-octet chemistry), the non-negative entries of a VVS should be restricted by

$$v_1 + v_2 + 2v_3 + 3v_4 \leqq 8 \tag{2}$$

which is, roughly speaking, an area of standard chemistry. The relation (*2*) specifies a subset of 4-dimensional space, its elements are composed of non-negative integers restricted by the inequality (*2*). In order to visualize this subset, the entry v_4 (*i.e.* the number of triple bonds) will be substituted by its two permissible values, 0 and 1, respectively. We get

$$v_1 + v_2 + 2v_3 \leqq 8 \quad (\text{for } v_4 = 0)\,, \tag{3a}$$

$$v_1 + v_2 + 2v_3 \leqq 5 \quad (\text{for } v_4 = 1)\,. \tag{3b}$$

The geometric interpretation of both inequalities is presented in Fig. 1 and Fig. 2. Enumerating all possible VVSs that are satisfying the relations (*3a*) and (*3b*) (*i.e.* the possible valence states with none and one triple bond) we arrive at 129 permissible VVSs. We enlarge this set by the following four VVSs: (0,9,0,0), (0,10,0,0), (0,11,0,0) and (0,12,0,0), which correspond to rather scarce valence states known in the chemistry of coordination compounds[3]; thus the total number of VVSs is 133 (Table I). This system is necessarilly open and accessible to new knowledge (over the nd^4 orbitals) and closed for the rule (*2*) with respect to rules (*3a*), (*3b*).

For special bonding situations of some metals (Re, Te, Mo, W, Cr) the dimension of the valence state vector can be extended to 5 – 7 considering the existence of bonds with multiplicity 4 – 6 between their atoms[4]. Operations remain the same as with valence state vectors of the dimension 4.

Conversions of Valence States

In the course of a chemical reaction the valence states of some part of atoms (*i.e* reaction sites) are converted. Let us assume that an initial valence state of an atom $\mathbf{v}_i = (v_1^{(i)}, v_2^{(i)}, v_3^{(i)}, v_4^{(i)})$ is converted during the chemical reaction into a final valence state $\mathbf{v}_f = (v_1^{(f)}, v_2^{(f)}, v_3^{(f)}, v_4^{(f)})$. The conversion of $\mathbf{v}_i$ into $\mathbf{v}_f$ is unambiguously determined by the so-called *vector of conversion* (VC) denoted by $\Delta\mathbf{v}_{i\to f}$,

$$\mathbf{v}_i + \Delta\mathbf{v}_{i\to f} = \mathbf{v}_f\,, \qquad (4a)$$

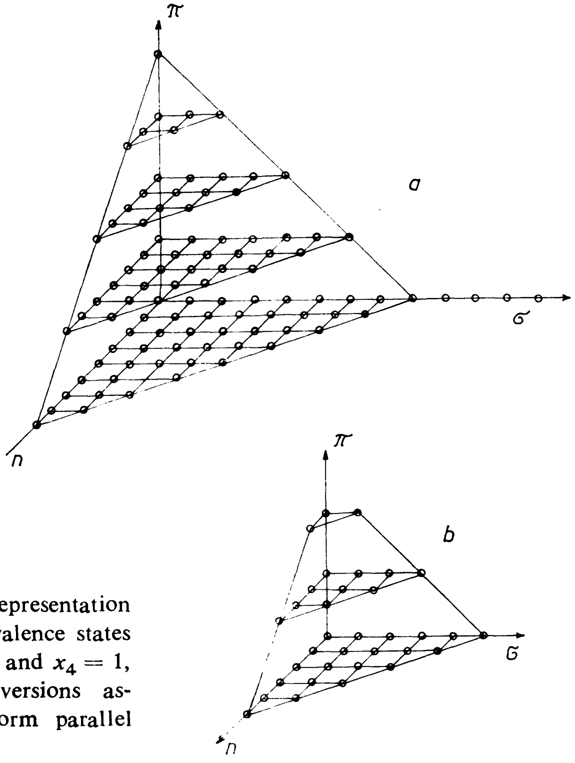


FIG. 1

Geometric three-dimensional representation of elementary conversions of valence states of atoms for two cases: $x_4 = 0$ and $x_4 = 1$, respectively. Elementary conversions assigned to the same VECs form parallel lines; *a* $x_4 = 0$; *b* $x_4 = 1$

or

$$\Delta \mathbf{v}_{i\to f} = \mathbf{v}_f - \mathbf{v}_i = \left(\Delta v_1, \Delta v_2, \Delta v_3, \Delta v_4\right), \tag{4b}$$

where $\Delta v_j = v_j^{(f)} - v_j^{(i)}$, for $j = 1, 2, 3, 4$. The individual entries of $\Delta v_{i\to f}$ have the following meaning:

Δv_1 = number of gained $(\Delta v_1 > 0)$ or lost $(\Delta v_1 < 0)$ free electrons,
Δv_2 = number of formed $(\Delta v_2 > 0)$ or broken $(\Delta v_2 < 0)$ single bonds,
Δv_3 = number of formed $(\Delta v_3 > 0)$ or broken $(\Delta v_3 < 0)$ double bonds,
Δv_4 = number of formed $(\Delta v_4 > 0)$ or broken $(\Delta v_4 < 0)$ triple bonds.

Most part of conversions of valence states is realized through the so-called *elementary conversions of valence states*, ECVS (ref.[5]). For instance, the conversion of atom $|\underline{X}-$ → $>X<$ should be interpreted as a successive step-by-step change of n and π electrons from reaction partner and partially at the cost of proper n-electrons, through different oxidation states of atom X (for example by a path $|\underline{X}-$ → $-\underline{X}-$ → $-\underline{X}=$ → $=X=$ → $>X=$ → $>X<$ → $>X<$). This is in a close analogy with the work of Ugi and coworkers[6], who have introduced basis reaction matrices to describe the most elementary mechanistic steps in an arbitrary chemical reaction.

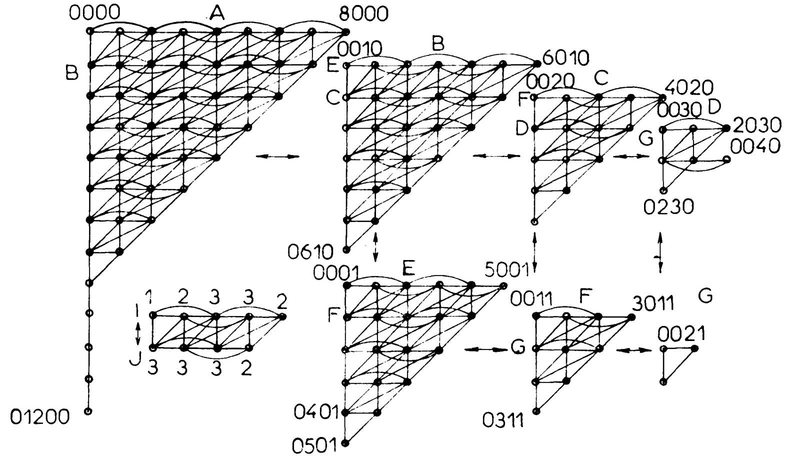
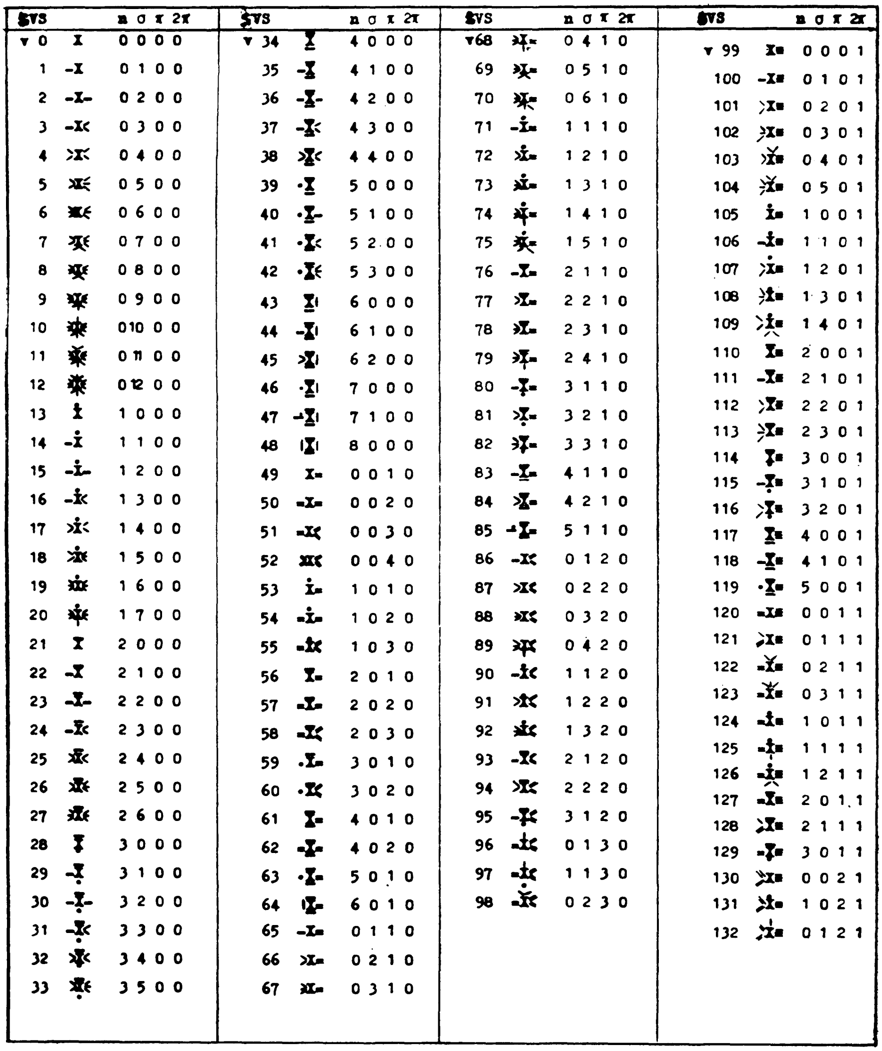


FIG. 2

Graph representation of the adjacency matrix of elementary conversions of valence states of atoms. Its 133 vertices form in four-dimensional space a grid composed of two blocs that are assigned to $x_4 = 0$ and $x_4 = 1$. The blocks are divided into planes A, B, C, D, and E, F, G, respectively. Transitions between valence states are expressed by edges. Schematically, for better illustration, the transitions between planes A—B—C—D and E—F—G are figured separately. The transitions between planes B—E, C—F, D—G are possible, too

TABLE I

List of vectors of valence states of atoms (VS = sign of VC)



#VS	n	σ	π	2π
▼ 0	0	0	0	0
1	0	1	0	0
2	0	2	0	0
3	0	3	0	0
4	0	4	0	0
5	0	5	0	0
6	0	6	0	0
7	0	7	0	0
8	0	8	0	0
9	0	9	0	0
10	0	10	0	0
11	0	11	0	0
12	0	12	0	0
13	1	0	0	0
14	1	1	0	0
15	1	2	0	0
16	1	3	0	0
17	1	4	0	0
18	1	5	0	0
19	1	6	0	0
20	1	7	0	0
21	2	0	0	0
22	2	1	0	0
23	2	2	0	0
24	2	3	0	0
25	2	4	0	0
26	2	5	0	0
27	2	6	0	0
28	3	0	0	0
29	3	1	0	0
30	3	2	0	0
31	3	3	0	0
32	3	4	0	0
33	3	5	0	0
▼ 34	4	0	0	0
35	4	1	0	0
36	4	2	0	0
37	4	3	0	0
38	4	4	0	0
39	5	0	0	0
40	5	1	0	0
41	5	2	0	0
42	5	3	0	0
43	6	0	0	0
44	6	1	0	0
45	6	2	0	0
46	7	0	0	0
47	7	1	0	0
48	8	0	0	0
49	0	0	1	0
50	0	0	2	0
51	0	0	3	0
52	0	0	4	0
53	1	0	1	0
54	1	0	2	0
55	1	0	3	0
56	2	0	1	0
57	2	0	2	0
58	2	0	3	0
59	3	0	1	0
60	3	0	2	0
61	4	0	1	0
62	4	0	2	0
63	5	0	1	0
64	6	0	1	0
65	0	1	1	0
66	0	2	1	0
67	0	3	1	0
▼68	0	4	1	0
69	0	5	1	0
70	0	6	1	0
71	1	1	1	0
72	1	2	1	0
73	1	3	1	0
74	1	4	1	0
75	1	5	1	0
76	2	1	1	0
77	2	2	1	0
78	2	3	1	0
79	2	4	1	0
80	3	1	1	0
81	3	2	1	0
82	3	3	1	0
83	4	1	1	0
84	4	2	1	0
85	5	1	1	0
86	0	1	2	0
87	0	2	2	0
88	0	3	2	0
89	0	4	2	0
90	1	1	2	0
91	1	2	2	0
92	1	3	2	0
93	2	1	2	0
94	2	2	2	0
95	3	1	2	0
96	0	1	3	0
97	1	1	3	0
98	0	2	3	0
▼ 99	0	0	0	1
100	0	1	0	1
101	0	2	0	1
102	0	3	0	1
103	0	4	0	1
104	0	5	0	1
105	1	0	0	1
106	1	1	0	1
107	1	2	0	1
108	1	3	0	1
109	1	4	0	1
110	2	0	0	1
111	2	1	0	1
112	2	2	0	1
113	2	3	0	1
114	3	0	0	1
115	3	1	0	1
116	3	2	0	1
117	4	0	0	1
118	4	1	0	1
119	5	0	0	1
120	0	0	1	1
121	0	1	1	1
122	0	2	1	1
123	0	3	1	1
124	1	0	1	1
125	1	1	1	1
126	1	2	1	1
127	2	0	1	1
128	2	1	1	1
129	3	0	1	1
130	0	0	2	1
131	1	0	2	1
132	0	1	2	1

Valence state vectors of atoms describe bonding situations of atoms in molecules of educts and products as well as bonding situations (sometimes formalized) of transition states and intermediates. (*E.g.*, for a S_{N2} mechanism at a saturated carbon atom formalization assumes a step *via* a trigonally bipyramidal (D_{3h}) pentacoordinated state[7]).

In order to construct the *vectors of elementary conversions* (VEC) we shall assume that the elementary conversions of valence states correspond to *1*) a transfer of one and two electrons, respectively, and/or *2*) a formation/breaking of one bond.
In Table II we have summarized all possible 22 VEC corresponding to elementary heterolytic, homolytic, and redox chemical reactions[2]. The notation used is interpreted as follows:

The term $nD_X(nA_X)$ denotes a break = dissociation (forming = association) process (of course, with respect to the reference I atom) of n-tuple bond, and

the subscript X = N, E, R characterizes the nature of the second atom J, *i.e.* whether it is a nucleophil (N), electrophil (E) or radical (R). A similar notation was also used for the classification of redox reactions,

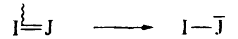
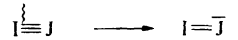
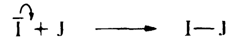
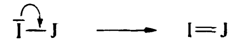
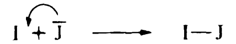
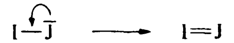
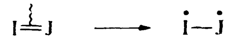
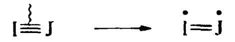
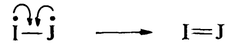
the term $nD_0(nA_r)$ denotes an n-electron oxidation (reduction) of the reference I atom. It is easy to see that VECs are not linearly independent; there may be obtained many interrelationships among the elements listed in Table II. But nevertheless, we can simply choose a set composed of four linearly independent VECs which forms a basis set for all 22 VECs. An application of VECs to VVSs may be geometrically visualized. For better contact with usual chemical thinking we have constructed an graph which represents in a telling way the conversions of VVSs by application of VECs listed in Table II. Its vertices/edges correspond to VVSs/VECs: in particular, the elementary conversion (*4a* – *b*) is graphically realized by an line starting (ending) at the vertex corresponding to $\mathbf{v}_i(\mathbf{v}_f)$. Theoretically speaking, each vertex is incident with at most 22 incoming and 22 outgoing edges, respectively. These values are, of course, only upper bounds for the number of edges that are attached to a vertex. Here, the following two restrictions are used:

1) Let us have a pair of VVS and VEC denoted by $\mathbf{v} = (v_1, v_2, v_3, v_4)$ and $\Delta\mathbf{v} = (\Delta v_1, \Delta v_2, \Delta v_3, \Delta v_4)$. The first restriction is that an VEC $\Delta\mathbf{v}$ is applicable to the VVS $\mathbf{v}$ only if the resulting VVS $\mathbf{v}' = \Delta\mathbf{v} + \mathbf{v}$ has all the entries nonnegative, *i.e* $v_i + \Delta v_i \geqq 0$, for $i = 1, 2, 3, 4$. For instance, we try to apply the VEC corresponding to elementary conversion $1D_E$, $\Delta\mathbf{v} = (2, -1, 0, 0)$ (Table II), to the VVS $\mathbf{v} = (4, 0, 1, 0)$ assigned to an atom $\underline{\overline{X}}=$. The resulting VVS $\mathbf{v}' = (6, -1, 1, 0)$ has the second entry negative; hence the $1D_E$ VEC is inapplicable to the VVS of $\underline{\overline{X}}=$. This is obvious, since $1D_E$ simultaneously breaks a single bond and gains two free electrons, but the VVS $\underline{\overline{X}}=$ has no a single bond.

2) Let the VEC $\Delta\mathbf{v}$ be applicable to the VVS $\mathbf{v}$ from the standpoint of above first restriction. The second restriction is that the resulting VVS $\mathbf{v}' = \Delta\mathbf{v} + \mathbf{v}$ should

TABLE II

List of vectors of elementary conversions (VEC)

No	Notation	Reaction scheme	VEC for reference I atom
		Heterolytic reactions	
1	$1D_E$		(2, −1, 0, 0)
2	$2D_E$		(2, 1, −1, 0)
3	$3D_E$		(2, 0, 1, −1)
4	$1D_N$		(0, −1, 0, 0)
5	$2D_N$		(0, 1, −1, 0)
6	$3D_N$		(0, 0, 1, −1)
7	$1A_E$		(−2, 1, 0, 0)
8	$2A_E$		(−2, −1, 1, 0)
9	$3A_E$		(−2, 0, −1, 1)
10	$1A_N$		(0, 1, 0, 0)
11	$2A_N$		(0, −1, 1, 0)
12	$3A_N$		(0, 0, −1, 1)
		Homolytic reactions	
13	$1D_R$		(1, −1, 0, 0)
14	$2D_R$		(1, 1, −1, 0)
15	$3D_R$		(1, 0, 1, −1)
16	$1A_R$		(−1, 1, 0, 0)
17	$2A_R$		(−1, −1, 1, 0)
18	$3A_R$		(−1, 0, −1, 1)
		Redox reactions	
19	$1D_0$		(−1, 0, 0, 0)
20	$2D_0$		(−2, 0, 0, 0)
21	$1A_r$		(1, 0, 0, 0)
22	$2A_r$		(2, 0, 0, 0)

be listed in Table II. This means nothing else than a "closure" of the proposed set of VVSs listed in Table I under the application of permissible VECs listed in Table II. In Fig. 3 we present, for better perception, an subgraph only for heterolytic conversions of VS.

Distance between Vectors of Valence States

First, before the formulation of this concept, we formally summarize our considerations from the previous section. Let 𝔊 be an oriented graph of elementary conversions, its vertices are VVSs listed in Table I and they are linked by edges corresponding to permissible VECs from Table II. The graph 𝔊 is connected, and furthermore, each pair of its vertices can be traversed, at least, by one path composed of edges belonging to 𝔊. Now we are ready to defined the distance $d(\mathbf{v}_1, \mathbf{v}_2)$ between two

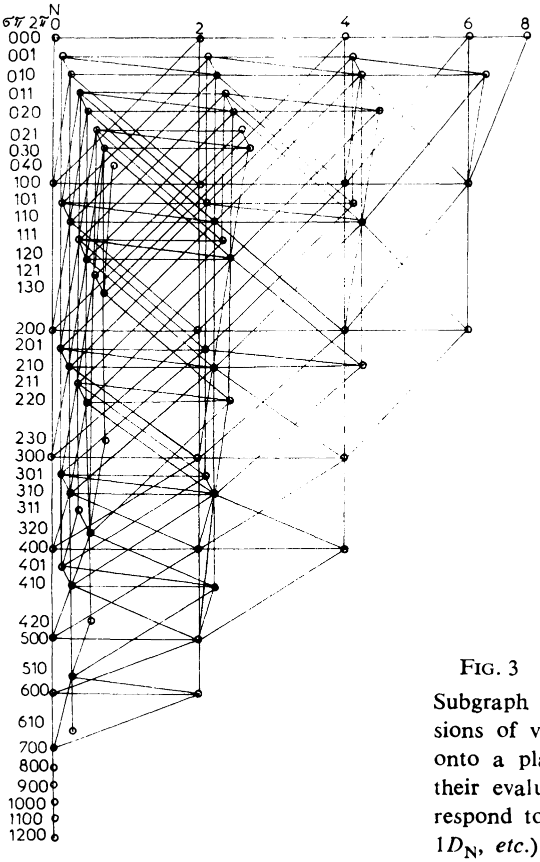


FIG. 3

Subgraph of heterolytic elementary conversions of valence states of atoms projected onto a plane. Directions of edges express their evaluation (*e.g.* horizontal lines correspond to D_0 and A_r, vertical to $1A_N$ and $1D_N$, *etc.*)

vertices assigned to VVSs $\mathbf{v}_1$ and $\mathbf{v}_2$. respectively. The distance $d(\mathbf{v}_1, \mathbf{v}_2)$ is determined as the length of a shortest path between the vertices corresponding to $\mathbf{v}_1$ and $\mathbf{v}_2$. Obviously, the distance satisfies $d(\mathbf{v}_1, \mathbf{v}_2) \geqq 0$ $(= 0$ only for $\mathbf{v}_1 = \mathbf{v}_2)$, $d(\mathbf{v}_1, \mathbf{v}_2) = d(\mathbf{v}_2, \mathbf{v}_1)$, and the "triangular inequality" $d(\mathbf{v}_1, \mathbf{v}_3) \leqq d(\mathbf{v}_1, \mathbf{v}_2) + d(\mathbf{v}_2, \mathbf{v}_3)$. Hence the concept „distance" forms a metrics for the set of VVS listed in Table I.

The main purpose of this section is to formulate an algebraic approach to calculate directly (without a relation to the graph $\mathfrak{G}$) the distance between two VVSs. Let us introduce the following basis set $\mathfrak{A} = \{\Delta\mathbf{v}_{1\mathrm{D_0}}, \Delta\mathbf{v}_{1\mathrm{D_N}}, \Delta\mathbf{v}_{2\mathrm{D_N}}, \Delta\mathbf{v}_{3\mathrm{D_N}}\}$ of VECs. An arbitrary $\Delta\mathbf{v}$ can be expressed as a linear combination of the above four VECs. We shall study the conversion between two VVS $\mathbf{v}_i$ and $\mathbf{v}_f$; they are mutually related by *(4a – b)*. Hence, the vector of conversion $\Delta\mathbf{v}_{i\to f}$ is expressed by

$$\Delta\mathbf{v}_{i\to f} = x_1\,\Delta\mathbf{v}_{1\mathrm{D_0}} + x_2\,\Delta\mathbf{v}_{1\mathrm{D_N}} + x_3\,\Delta\mathbf{v}_{2\mathrm{D_N}} + x_4\,\Delta\mathbf{v}_{3\mathrm{D_N}}\,, \tag{5}$$

it produces a system of four linear equations. Solving this system we get

$$\begin{aligned} x_1 &= -\Delta v_1\,,\\ x_2 &= -\Delta v_2 - \Delta v_3 - \Delta v_4\,,\\ x_3 &= -\Delta v_3 - \Delta v_4\,,\\ x_4 &= -\Delta v_4\,. \end{aligned} \tag{6}$$

In order to calculate the distance between $\mathbf{v}_i$ and $\mathbf{v}_f$ we have used the following simple reasoning: The distance is the smallest number of elementary conversions, their successive application converts the initial VVS $\mathbf{v}_i$ into the final VVS $\mathbf{v}_f$. In the course of each elementary conversion a bond is either broken or formed, and/or free electrons are transferred. The number of broken/formed bonds is determined by the coordinates x_2, x_3, x_4. This number should be modified by a number of free electrons transferred due to the possible redox processes. After simple but slightly tedious algebra we arrive at

$$d(\mathbf{v}_i, \mathbf{v}_f) = B + F(|x_1| - 2B) \div 2 + G(|x_1| - 2B)\,\mathrm{mod}_2\,(|x_1|)\,, \tag{7}$$

where

$$B = |x_2| + |x_3| + |x_4|\,, \tag{8a}$$

$$F(x) = \begin{cases} x & (\text{for } x > 0)\,,\\ 0 & (\text{for } x \leqq 0)\,, \end{cases} \tag{8b}$$

$$G(x) = \begin{cases} 1 & (\text{for } x > 0), \\ 0 & (\text{for } x \leqq 0), \end{cases} \qquad (8c)$$

and $\div$ denotes the integer divide, and mod_2 ( ) is the modulo- two function. The first term in (7) expresses a number of broken/formed bonds. The second and third terms correspond to the elementary redox conversions $2D_0$, $2A_r$ and $1D_0$, $1A_r$. Introducing (6) into (7) and (8a) we get the alternative formula for $d(\mathbf{v}_i, \mathbf{v}_f)$,

$$d(\mathbf{v}_i, \mathbf{v}_f) = B + F(|\Delta v_1| - 2B) \div 2 + G(|\Delta v_1| - 2B) \,\text{mod}_2\, (|\Delta v_1|), \qquad (9)$$

where $B = |\Delta v_2 + \Delta v_3 + \Delta v_4| + |\Delta v_3 + \Delta v_4| + |\Delta v_4|$.

Example 1: Let us have $\mathbf{v}_i = (6, 1, 0, 0)$ and $\mathbf{v}_f = (0, 1, 3, 0)$, then $\Delta\mathbf{v}_{i\to f} = (-6, 0, 3, 0)$. Using relation (9) we get $d(\mathbf{v}_i, \mathbf{v}_f) = 6 + 0 + 0$, this result can be simply checked on the graph.

Example 2: For $\mathbf{v}_i = (0, 1, 0, 0)$ and $\mathbf{v}_f = (6, 1, 0, 0)$ the corresponding VEC is $\Delta\mathbf{v}_{i\to f} = (6, 0, 0, 0)$, we get $d(\mathbf{v}_i, \mathbf{v}_f) = 0 + 3 + 0 = 3$. Hence, the shortest path between $\mathbf{v}_i$ and $\mathbf{v}_f$ is composed of three 2-electron reductions.

Chemical Distance and Conversion of Valence States of Atoms

The chemical distance between two molecular systems M and M′ of one EM is determined as a metric between corresponding bond-electron (BE) matrices or adjacency matrices[1,8], both this alternative definitions are simply related, the later entity should be multiplied by factor 2 and then we get the former one. In general, the chemical distance expresses a number of electrons that must be rearranged in the course of reaction M → M′. The purpose of this section is to demonstrate that the chemical distance between an educt M and product M′ molecular system is an additive function of chemical distances between pairs of atoms (A_i, A'_i), where $A_i \in M$ and $A'_i \in M'$. From this formulation of our task we see that the chemical distance implicitly depends on the indexing of atoms in M and M′, respectively. Let us have an arbitrary pair of atoms (A, A′), where A ∈ M, A′ ∈ M′, and the atoms A and A′ are labeled in both molecular systems by the same index. The VVSs of A and A′ will be denoted by $\mathbf{v}$ and $\mathbf{v}'$, respectively, and let the VEC $\Delta\mathbf{v}$ be determined by $\mathbf{v} + \Delta\mathbf{v} = \mathbf{v}'$. The total number of free electrons, N, rearranged by the reaction M → M′ is

$$N = |\Delta v_1| \, . \qquad (10)$$

In similar way, a number of electrons shifted in the course of change of the valence state is determined by the entity B, see (8a) and comment below (9). The value of B

should be included twice, since during one elementary conversion, at least, none or two electrons are shifted. This fact is counterbalanced by the observation that each change of a valence state is running for two atoms. Hence, the total contribution of the studied pair of atoms is

$$N' = B\,. \tag{11}$$

Finally, we have to determine the number of electrons that were shifted by a change of bonding conditions between atoms A and A'.

Let $\mathfrak{A}(\mathfrak{A}')$ be a set of such indices i that the atom $A_i(A'_i)$ is bounded with the atom A(A'). Next, let $\mathfrak{B}$ be a set of those indices i that the atoms A and A' are bounded with the atoms A_i and A'_i, respectively, and the order of these bonds is the same. Using these sets we define the following set $\mathfrak{C} = \mathfrak{A} \cup \mathfrak{A}' - \mathfrak{B}$, then a number of changed neighbours of A and A' is simply determined by $c = |\mathfrak{C}|$, where $|\mathfrak{C}|$ denotes the number of elements (cardinality) of the set $\mathfrak{C}$. Since the evaluated entity c was already partially taken into account by the above entity B, the resulting contribution is expressed by

$$N'' = F(c - B)\,, \tag{12}$$

where F is the function (*8b*). This simple considerations can be repeated for all pairs (A, A') of atoms mutually assigned by the indexing, the chemical distance of a pair of atoms A, A' is determined by a relation

$$D(\mathrm{A}, \mathrm{A}') = N + N' + N''\,. \tag{13a}$$

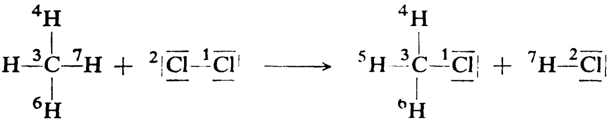
The chemical distance $D(\mathrm{M}, \mathrm{M}')$ between molecular systems M and M' is determined as the sum of all contributions (*10*), (*11*), and (*12*), we get

$$D(\mathrm{M}, \mathrm{M}') = N_{\mathrm{tot}} + N'_{\mathrm{tot}} + N''_{\mathrm{tot}}\,, \tag{13b}$$

$$N_{\mathrm{tot}} = \sum_{i=1}^{n} N_i\,, \quad N'_{\mathrm{tot}} = \sum_{i=1}^{n} N'_i\,. \quad N''_{\mathrm{tot}} = \sum_{i=1}^{n} N''_i\,, \tag{13c}$$

where the terms N_i, N'_i, and N''_i are determined by (*10*), (*11*) and (*12*), respectively, for actual atoms A_i, A'_i. The individual terms from the right-hand side of (*13*) are of the following simple chemical meaning: *1*) The term N_{tot} immediately corresponds to changes of oxidation states of atoms. *2*) The term N'_{tot} expresses conversions of valence states of atoms in the course of reaction M → M' (*e.g.* its non-zero value indicates an addition and/or elimination resp. rearrangement type of reaction). (*3*) The term N''_{tot} manifests a chemical change without the conversion of valence states of some atoms (*e.g.* substitution reaction).

Example 1: Substitution reaction



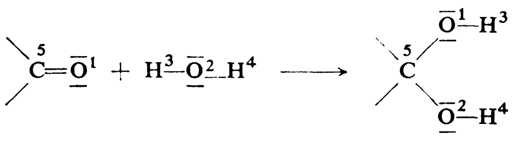
The evaluation of $D(\mathrm{M}, \mathrm{M}')$ can be summarized as follows:

Atom	N	N'	N''	$\sum$
^{1}Cl	0	0	2	2
^{2}Cl	0	0	2	2
^{3}C	0	0	2	2
^{4}H	0	0	0	0
^{5}H	0	0	0	0
^{6}H	0	0	0	0
^{7}H	0	0	2	2
$\sum$	0	0	8	$8 = D(\mathrm{M}, \mathrm{M}')$

The resulting chemical distance is $D(\mathrm{M}, \mathrm{M}') = 8$, the non-zero value of N''_{tot} indicates that the studied reaction is of a substitution type.

Note: For a S_N2 mechanism the distance $D(\mathrm{M}, \mathrm{M}')$ is non-zero also because N''_{tot} n equation (*13b*) has a non-zero value.

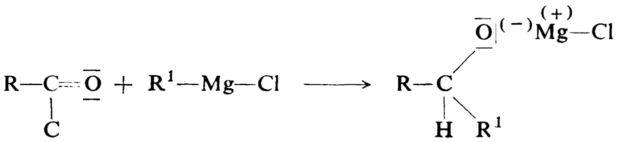
Example 2: Addition reaction



Atom	N	N'	N''	$\sum$
^{1}O	0	2	0	2
^{2}O	0	0	2	2
^{5}C	0	2	0	2
^{3}H	0	0	2	2
^{4}H	0	0	0	0
$\sum$	0	4	4	$8 = D(\mathrm{M}, \mathrm{M}')$

The non-zero value of N' indicates the conversion of valence states of atoms, the non-zero value of N'' demonstrates that the given substitution can be interpreted from the standpoint of some atoms, as a substitution reaction.

Example 3: Addition of Grignard reagents to carbonyl group



Atom (group)	N	N'	N''	Σ
C	0	2	0	2
O	2	1	0	3
H	0	0	0	0
Mg	0	1	0	1
Cl	0	0	0	0
R	0	0	0	0
R^1	0	0	2	2
Σ	2	4	2	$8 = D(M, M')$

This reaction was presented mainly as an illustrative example with high complexity of evaluation.

DISCUSSION AND CONCLUSION

We have demonstrated that the suggested formalism of valence states of atoms and their interconversions represents simple and efficient algebraic tools to analyze known as well as predictable reactions. Of course, it offers only an onesided view on the chemical processes, the energy conditions whether a considered reaction may run or not are strongly suppressed. By using the formalism we are able to construct an exhaustive list of possible reaction paths going through the permissible valence states of atoms that are listed separately for all types of contributing atoms. In order to extract from these formally possible reaction paths those ones that are physically and chemically relevant, a screening procedure through a "sieve" of chemical-reaction theories (formulated on different levels of sophistication) should be used.

The main results of the present algebraic theory of valence states of atoms (from the standpoint of our mathematical model of organic chemistry) are summarized as follows:

1) For a given type of atom the graph of conversions of valence states (GCVS) is *a-priori* connected, *i.e.* an arbitrary valence state should be reached starting from another possible valence state. In some special cases we have observed that the constructed GCVS does not satisfy the above mentioned condition of connectivity. This immediately implies that the known valence states of a given atom described in literature should be enlarged by additional valence states and their interconversions with former and/or added valence states. Hence, we believe, a systematic analysis based on suggested algebraic approach is highly inspiring in looking for new valence states of atoms and their interconversions.

2) GCVSs offer very serious and fruitful ideas in modelling the reaction mechanism paths of new or rather complex chemical reactions (*e.g.* inorganic systems).

3) For computer-assisted organic syntheses working in retrosynthetic and synthetic mode, respectively, for a given strategic reaction site the GCVS gives a complete set of permissible precursors. In other words, the present approach combined with GCVSs may be used by chemists for construction of multi-step organic syntheses[9].

4) In order to visualize our considerations with GCVSs assigned to different atoms, we have coloured their vertices and edges by the following way (this is fully equivalent with their evaluation by proper symbols or numbers): The vertices are coloured by four different colours in dependence of their character – donor, acceptor, radical and neutral "insipid", respectively. In similar way, the four different colours are used for the colouring of edges that are corresponding to elementary conversions of valence states D_NA_N, D_EA_E, D_RA_R, and D_0A_r, respectively. Then, using these coloured GCVSs we can immediately deduce the character of changes of reaction sites in substrates and the type of assigned reagents (*e.g.* Nu, E, R′, *hν*, *etc.*) that are necessary for a realization of deduced conversions in substrates. Moreover, the character of the first step in elementary conversions of valence states determines, in general, the type of reaction mechanism.

The present algebraic approach is implemented in FORTRAN for ADT 4300 computer[10]. In particular, it was used for the construction of complete list of conversions of valence states in form of an adjacency matrix.

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