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Global Molecular Identification from Graphs. Main-group Triatomic Molecules*

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It is required that molecules with a given graph and with covalent, coordinate-covalent, and ionic bonding contain closed-shell atoms. This requirement results in an equation for each atom, which states that the number of valence electrons pertaining to it before bonding, plus those made available to it in the bonding processes, close its valence shell. Solving the equations results in identifying the atoms and the bond orders of the Lewis diagrams. The algebraic procedure can identify new species. Some of them may be considered impossible (for instance, with high steric strain), or may be transitory, or may be found only under the most unusual conditions. Lists of triatomic molecules, clusters, and resonances found by solving the equations is presented. Closed-shell molecules lie on parallel planes in their chemical spaces, namely those on which isoelectronic molecules are located.

Key words: closed-shell molecules, stoichiometric molecules, octet rule, lewis diagrams, bonding data prediction, data mining, graphs, chemical space, periodic systems of molecules, education.

> *A diatomic molecule has one atom too many.*
> Arthur Shawlow
>
> *A diatomic molecule has one atom too few.*
> Takeshi Oka

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[*] Dedicated to Professor Milan Randić on the occasion on his 70th birthday.

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INTRODUCTION

Tabulated data for molecular properties have been used extensively at this laboratory to make predictions molecules on a global scale; least-squares methods,[1] neural networks,[2] and even Laplace's equation[3] have been used. Attention now turns to furthering the process, but for closed-shell molecules only. This limitation should increase the efficiency of the process for that large segment of chemistry that concerns closed-shell, Lewis structure, molecules. A simple algebraic formulation of closed-shell status has been developed and applied to diatomic molecules. In this paper, the formulation is extended to triatomic species. New aspects of the algebra are presented and the equations compared with the beautiful mathematical model of constitutional chemistry developed by Ugi and his colleagues.[4]

The theory assigns eight valence-shell electrons to each main-group atom, some of them contributed by the atom itself and some by those of the neighboring atom(s) by means of covalent, ionic, and coordinate-covalent bonding. In a parallel development, *s* atoms can be treated as a separate group requiring only two electrons to close the valence shell; this development can lead the way to later determination of *d* elements (including *via* the rule of 18) and *f* elements. The equations lead to the determination of interesting resonances, many of which may have severe steric strain, short lifetimes, or existence only under very unusual conditions. The rate at which unusual molecules are being discovered would suggest that no proposed structure should be discarded without checking with computation or experiment.[5] Geometrical interpretation of the solutions to the equations leads to an understanding of where the subject molecules lie in chemical space (in this case, the triatomic-molecular periodic system).[6,7] Then values of their properties can be plotted in a portion of the space and predictive techniques can be used as before.

THE ALGEBRAIC TREATMENT OF ACYCLIC TRIATOMIC SPECIES

Covalent-bonded Molecules

Let the atoms of the molecule be labeled 1, 2, and 3 from left to right, let C_i be the number of valence electrons of atom i before it became a part of the molecule (or its column number 1 through 8 in older periodic tables), and let v_{ij} be the number of electrons contributed by atom j to a covalent bond with atom i (or, equivalently, the bond order). The equations to solve are

$$C_1 + v_{12} = 8, \tag{1}$$

$$v_{21} + C_2 + v_{23} = 8, \tag{2}$$

$$v_{32} + C_3 = 8, \tag{3}$$

$$v_{ij} = v_{ji} \ . \tag{4}$$

(C_1 includes both bound and free valence-shell electrons.) The equations have solutions F–O–F, F–N=O, O=C=O, and F–C≡N, which are found in the top part (row 1) of Table I. In this part of the table, the first three columns show the numbers of electrons to complete the atoms' shells, and column 5 gives the bond orders. The question of there being no covalent bond between a pair of atoms, as might happen if a rare-gas atom were at one end of the molecule, will be taken up in Section 2.4. Relaxing the restriction to row-2 molecules would allow molecules such as Cl–S–Br and At–O–117. Also, the molecular symbols may be reversed, FNO and ONF are of course the same molecule. These generalizations apply in every subsequent section but will not be restated.

TABLE I

All $N = 2$, acyclic $N = 3$, and a sample of $N = 4$ linear/bent molecules

Atoms			Bonds		Molecules after all bonds have been formed
1	2	3	Other bonds	Covalent bonds	
8	8	8		11,12,22,13	F–O–F, F–N=O, O=C=O, F–C≡N
2	8	8	Ionic, q_{12}=1	1, 2, 3	$[\mathrm{Li}]^{+}[\mathrm{O}]^{-}$–F, $[\mathrm{Li}]^{+}[\mathrm{N}]^{-}$=O, $[\mathrm{Li}]^{+}[\mathrm{C}]^{-}$≡N
			Ionic, q_{12}=2	1, 2, 3	$[\mathrm{Be}]^{2+}[\mathrm{N}]^{2-}$–F, $[\mathrm{Be}]^{2+}[\mathrm{C}]^{2-}$=O, $[\mathrm{Be}]^{2+}[\mathrm{B}]^{2-}$≡N
2	8	2	q_{12}=1, q_{23}=1		$[\mathrm{Li}]^{+}[\mathrm{O}]^{2-}[\mathrm{Li}]^{+}$
			q_{12}=1, q_{23}=2		$[\mathrm{Li}]^{+}[\mathrm{N}]^{3-}[\mathrm{Be}]^{2+}$
			q_{12}=2, q_{23}=3		$[\mathrm{Be}]^{2+}[\mathrm{C}]^{4-}[\mathrm{Be}]^{2+}$
			q_{12}=2, q_{23}=2		$[\mathrm{Be}]^{2+}[\mathrm{B}]^{5-}[\mathrm{B}]^{3+}$
			q_{12}=3, q_{23}=3		$[\mathrm{B}]^{3+}[\mathrm{Be}]^{6-}[\mathrm{B}]^{3+}$
8'	.8	8	Dative	01, 02, 03	Ne–N–F, Ne–C=O, Ne–B≡N
				11, 12, 21	F=C–F, F=B=O, O≡B–F
8''	..8	8	Dative	01, 02	Ne=B–F, Ne=Be=O
					F≡Be–F
8'''	…8	8	Dative	01	Ne≡Li–F

TABLE I (cont.)

Atoms			Bonds		Molecules after all bonds have been formed
1	2	3	Other bonds	Covalent bonds	
.8	8'	8	Dative	01, 02, 03	O–F–F, O–O=O, O–N≡N
				11, 12, 21	N=O–F, N=N=O, C≡N–F
..8	8''	8	Dative	01, 02	C=F–F, C=O=O
				11	B≡O–F
…8	8'''	8	Dative	01	Be≡F–F
.8	8''	.8	Dative	00	O–Ne–O
				01, 02	O–F=N, O–O≡C
				11	N=O=N
..8	8'''	.8	Dative	00	C=Ne–O
				01	C=F=N
				10	B≡F–O
..8	8''''	..8	Dative	00	C=Ne=C
…8	8''''	.8	Dative	00	Be≡Ne–O
8'	..8	8'	Dative	00	Ne–C–Ne
				01, 02	Ne–B=F, Ne–Be≡O
				11	F=Be=F
8''	…8	8'	Dative	00	Ne=Be–Ne
				01	Ne=Li=F
				10	F≡Li–Ne
8''	….8	8''	Dative	00	Ne=He=Ne
8'''	….8	8'	Dative	00	Ne≡He–Ne
8'	.8'	.8	Dative	00	Ne–O–O
				01, 02	Ne–N=N, Ne–C≡C
				10, 20	F=N–O, O≡C–O
				11	F=C=N
8''	..8'	.8	Dative	00	Ne=C–O
				01	Ne=B=N
				10	F≡B–O
8'	.8''	..8	Dative	00	Ne–O=C
				01	Ne–N≡B
				10	F=N=C
8'	8'''	8	Dative	00	Ne–O≡Be
8''	..8''	..8	Dative	00	Ne=C=C

Ugi and his colleagues[4] approached the same goal by defining symmetric »bond and electron matrices« ***B***, where the *i*-th row and column pertain to atom i, the off-diagonal entries b_{ij} in the row or column are the bond orders of the covalent bond between atoms i and j, and the diagonal entry b_{ii} is the number of free (non-bonded) electrons in the valence shell. Their example for HCN illustrates the concept very well:

$$\boldsymbol{B} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 3 \\ 0 & 3 & 2 \end{pmatrix}. \tag{5}$$

Row or column three (corresponding to N) records that there is no bond to H, that there is a triple bond to C, and that there is a non-bonded lone pair on N. The number of valence-shell electrons in the isolated atom in indicated by the sum of the row or column (5 for nitrogen); it is this sum that corresponds to C_i in this paper. In fact, the $\boldsymbol{B}$ matrix can be recast in terms of the variables in this paper, with the help of Eq. (4), as follows:

$$\boldsymbol{B} = \begin{pmatrix} C_1 - (v_{12} + v_{23}) & v_{12} & v_{13} \\ v_{12} & C_2 - (v_{12} + v_{23}) & v_{23} \\ v_{13} & v_{23} & C_3 - (v_{13} + v_{23}) \end{pmatrix}. \tag{6}$$

Conversely, Eqs. (1) to (3) can be rewritten in terms of the matrix elements as

$$b_{11} + 2b_{12} + 0 = 8, \tag{7}$$

$$2b_{12} + b_{22} + 2b_{23} = 8, \tag{8}$$

$$0 + 2b_{23} + b_{33} = 8, \tag{9}$$

where Eq. (4) has again been used. These equations could be used for predictive purposes just as could Eqs. (1) to (3), however an added step (summing b_{ij} over j) would be necessary for each equation in order to identify the atoms.

In the Section »Distribution of Closed-shell Linear Molecules in Chemical Space« there will be need for the sum Eqs. (1) to (3),

$$C_1 + C_2 + C_3 + 2v_{12} + 2v_{23} = 24, \tag{10}$$

and for the sum but with Eq. (2) multiplied by –1,

$$C_1 - C_2 + C_3 = 8. \tag{11}$$

The bond orders are completely eliminated in Eq. (11).

Covalent-bonded Molecules Requiring the Rule of 2

Some atoms (principally *s* atoms) may be considered as belonging to a separate group requiring two electrons to close the valence shell (a »rule of two«). The closed-shell row-2 atom in this group is then Be.[8]

If atom 1 is an *s* atom, then Eq. (1) has 2 instead of 8 at right. The solutions lead to the row-2 molecules Li–O–F, Li–N=O, and Li-C≡N. If there are two *s* atoms in the molecule, with a *p* atom necessarily in the center, then Eqs. (1) and (3) both have 2 instead of 8 at right. The solution leads to the molecule Li–O–Li. The same molecules are obtained by using equations for ionic bonding, as will be demonstrated in the next section.

For the *spp* molecules discussed above, Eqs. (10) and (11) have 18 and 2 on the right; for the *sps* molecules, they have 12 and –4 at the right.

Molecules with Ionic and Covalent Bonds

If atom 1 is a rule-of-2 atom participating in an ionic bond with atom 2, and if atoms 2 and 3 are covalent-bonded *p* atoms, then the equations become

$$(C_1 - q_{12}) = 0, \tag{12}$$

$$(C_2 + q_{12}) + v_{23} = 8, \tag{13}$$

$$v_{23} + C_3 = 8\ , \tag{14}$$

where q_{12} is the number of electrons transferred (assumed equal to the number of valence electrons of atom 1). If $q_{12} = 1$, the row-2 molecules are $[Li]^+[O]^-$–F, $[Li]^+[N]^-$=O, and $[Li]^+[C]^-$≡N; these very same molecules were obtained, using the equations for covalent bonding, in the previous section. If $q_{12} = 2$, they are $[Be]^{2+}[N]^{2-}$–F, $[Be]^{2+}[C]^{2-}$=O, and $[Be]^{2+}[B]^{2-}$≡N. q_{12} cannot be 3 because then atom 1 would no longer be an *s* atom, as in $[B]^{3+}[C]^{3-}$–F. The second triad of molecules cannot be obtained from Eqs. (1) to (3) because doing so would require a double bond to Be, which fails to give it an octet of electrons. Both triads contain species with 14, 12, and 10 valence electrons.

These species are all shown in the second part of Table I. In this part of the table, q_{ij} is indicated in column 4. In column 5, there is an entry for the covalent bond only; thus, »1« means that there is one covalent single bond in the triatomic molecule and that the other bond is ionic. Note how the ionically-bonded species mimic the covalent species with the substitution of Li for F.

The sum of Eqs. (12) to (14) is

$$C_1 + C_2 + C_3 + 2v_{23} = 16 \tag{15}$$

independent of q_{12}. The sum of the equations, with Eq. (13) multiplied by –1, again has the covalent bond symbol missing as does Eq. (11):

$$C_1 - C_2 + C_3 - 2q_{12} = 0. \tag{16}$$

If atoms 1 and 3 are rule-of-2 atoms participating in ionic bonds with atom 2, and if again the rule-of-2 atoms transfer all of their valence electrons to the central *p* atom, then the equations become

$$C_1 - q_{12} = 0, \tag{17}$$

$$q_{12} + C_2 + q_{23} = 8, \tag{18}$$

$$C_3 - q_{23} = 0. \tag{19}$$

The solutions yield $[Li]^+[O]^{2-}[Li]^+$ and some improbable 8-electron species like $[Li]^+[N]^{3-}[Be]^{2+}$, $[Be]^{2+}[C]^{4-}[Be]^{2+}$, $[Be]^{2+}[B]^{5-}[B]^{3+}$, and $[B]^{3+}[Be]^{6-}[B]^{3+}$. These molecules are in the third part of Table I. Note how an *s* atom (Be in the last molecule) may, in this theory, serve as a rule-of-8 atom and how a *p* atom (B) may serve as a rule-of-2 atom.

The sum of Eqs. (17) to (19) is

$$C_1 + C_2 + C_3 = 8 \tag{20}$$

and the sum of the equations with Eq. (18) multiplied by –1 is

$$C_1 - C_2 + C_3 - 2q_{12} - 2q_{23} = -8. \tag{21}$$

Molecules with Covalent and Coordinate-covalent Bonds

The molecules treated in this section are formed only of *p* atoms. In principle, it would be possible to have an ionic bond between *s* atom 1 and *p* atom 2, and a coordinate-covalent bond between *p* atoms 2 and 3. However, this arrangement seems so unlikely to occur that it is not considered.

If the atom 1 delegates lone pairs to form additional bonds to atom 2, then the outer-shell electron inventory of atom 1 remains unchanged but that of atom 2 is increased by twice the number of delegated lone pairs. The equations for this particular case are

$$(C_1 - 2p_{12}) + (v_{12} + 2p_{12}) = C_1 + v_{12} = 8, \tag{22}$$

$$(v_{12} + 2p_{12}) + C_2 + v_{23} = 8, \tag{23}$$

$$v_{23} + C_3 = 8\ . \tag{24}$$

In the spirit, if not the letter, of Ref. 4, it is possible to add an asymmetric matrix to the adjacency matrix of the molecule »before« (so to speak) the dative bond is formed to obtain an asymmetric adjacency matrix for the molecule »after« that bond is formed. The asymmetric matrix ***R*** is such because it contains information about the direction of the dative bond. In the case at hand

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 2 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \tag{25}$$

showing that the dative bond is added by atom 1 to the bond v_{12}.

The sum of Eqs. (22) to (24) becomes

$$C_1 + C_2 + C_3 + 2v_{12} + 2v_{23} + 2p_{12} = 24, \tag{26}$$

and the alternate-sign sum is

$$C_1 - C_2 + C_3 + 2p_{12} = 8 \ . \tag{27}$$

The sum of the three terms in Eq. (26) that follow C_3 is twice the total number of bonds, or equivalently is equal to the total number of electrons in the bonds. The same can be seen to have been true in Eqs. (10) and (15).

The covalent bond v_{12} that existed »before« atom 1 delegated a lone pair to form the dative bond p_{12} could be a null bond, possibly a van der Waals bond. Thus, coordinate-covalent bonding allows molecules containing an inert-gas atom to satisfy the requirement of having bonded closed-shell atoms. It should be kept in mind that molecules with rare-gas atoms are very familiar to investigators of clusters and of radio-frequency and arc plasmas; hence they should be included as legitimate entities in this study. They appear frequently in property databases.[9–11]

There are several other scenarios than to have atom 1 delegating one or more lone pairs to form additional bonds to atom 2. The molecules with all the scenarios occupy the remaining part of Table I. A special notation applies to the rule of 8 values in columns 1 through 3: an atom that donates one or more lone pairs is indicated by one or more primes after the value; an atom that senses the additional bond(s) is indicated by one or more dots in front of the value. The bond orders in column 7 refer to the situation that obtains before the lone pair moves over to add a bond; the situation after the move is indicated in the molecular formula in the last column. All of the entries in the last column have reversed versions (with the atoms reflected through the central atom) which can be obtained algebraically by reversing the entries in columns 1 to 3 and column 5. Note how helium may be considered the row-2 atom with zero valence-electron count.[12]

Solving Eqs. (22) to (24) by randomly entering v_{ij} and p_{ij} values (even using the correctly limited values $v_{ij} = 0$ to 3 and $p_{ij} = 1$ to 3) can give spurious results, for instance molecules with a quadruple bond or atoms in a molecule having more than an octet of electrons. These results can be found and eliminated by checking each molecule against the octet rule after the equations are solved. Another way to spot spurious is to note that the effect of a new dative bond from atom 1 is to reduce the value of C_2 by 2. As examples, compare the »11« and »12« molecules FOF and FNO (top part of Table I) with FCF and FBO (among the »8'.8 8« entries in the last part of the Table). It is possible to avoid spurious results by using the rule of thumb

$$\sum_{\text{bonds}} (v_{ij} + p_{ij} + p_{ji}) < 5 \ . \tag{28}$$

Comparison with Eq. (26) shows that $C_1 + C_2 + C_3 \geq 14$, consistent with the results shown in Table I and in Figure 1. Of course, paper-and-pencil solution to the equations is tedious and prone to errors, so a Java™ computer program was developed. The code for this program is still under development.

In the fourth part of Table I, it is seen that the more electronegative atom delegates electron pairs to serve as dative bonds (*e.g.* in F=C–F). This happens throughout the table except where a dative bond is formed between equally electronegative atoms, for example OOO and ONN (in the fifth part). However, it should be noted that the more (or equally) electronegative atoms do not actually lose valence electrons but merely reposition them. (Pauling electronegativities are used.)

Distribution of Closed-shell Linear Molecules in Chemical Space

Figure 1 shows the space with C_1, C_2, C_3 axes and all acyclic, neutral, diatomic molecules with covalent and coordinate-covalent bonds. A series of parallel planes, perpendicular to the line forming equal angles with the axes and containing homonuclear species, passes through most of them (those with all p atoms). These parallel planes contain series of isoelectronic molecules and are given by Eqs. (10) and (26) as

$$C_1 + C_2 + C_3 = n_e \ , \tag{29}$$

n_e being the number of valence-shell electrons (bound and free) equal to 16, 18, and 20. The molecules in each plane lie in a triangle with purely covalently-bonded molecules toward their centers and with some rare-gas mole-

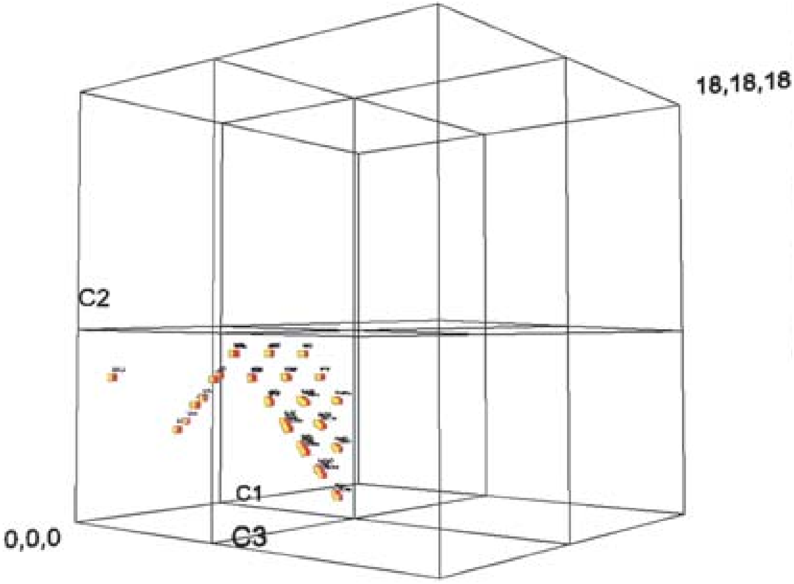

Figure 1. The chemical space of triatomic molecules whose atoms obey the rules of 8 and 18. The three axes are C_1 (toward right rear), C_2 (up), and C_3 (toward front right). The inner volume extends from (0,0,0) to (8,8,8) and contains sites for the triatomic molecules with *s* and *p* atoms. The molecules shown are closed-shell linear species comprised of period-2 atoms having covalent and dative bonds; their formulae will be resolved in subsequent figures. Most of these molecules lie on three distinct planes, with n_e = 16, 18, and 20, going from the central area toward the upper right corner of the inner volume. The remaining seven molecules contain atoms obeying the »rule of 2.« Six of them appear to lie on a plane given by Eq. (29) but additional data show that it is better to consider them as lying in planes n_e = 10, 12, and 14.

cules on the edges. There are interesting symmetries in the distribution of molecules in the triangles.[13,14]

Preliminary plotting of data on these planes indicates that the maximum stability (as measured by entropy, heat of formation, and boiling points) lies close to OCO on n_e = 16 and decreases from there such that contours of equal values are somewhat hemispherical around the point where OCO lies. The few molecules below and to the left of the three main planes are molecules containing »rule of 2« atoms. These species can be imagined to lie, albeit sparsely, on parallel planes with n_e equal to 8 (Eq. (20)), and equal to 10, 12, and 14 (Eq. (15)).

Figure 2 shows the very few *p*-atom molecules that exist when only covalent bonding is allowed. These molecules lie on a plane described by

$$C_2 = C_1 + C_3 + h, \tag{30}$$

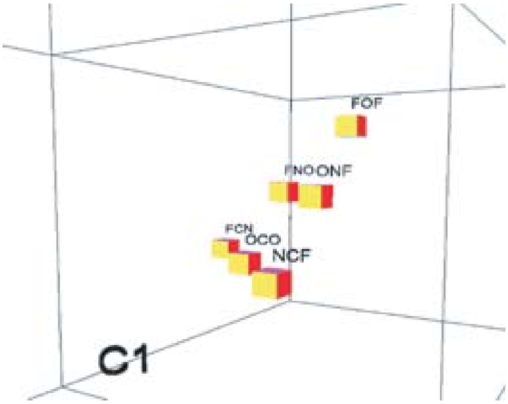

Figure 2. Close-up in the space of Figure 1, but showing only those few closed-shell linear species comprised of period-2 atoms having covalent bonds. They appear to lie on a plane given by Eq. (29) but additional data show that it is better to consider them as lying in planes n_e = 16, 18, and 20.

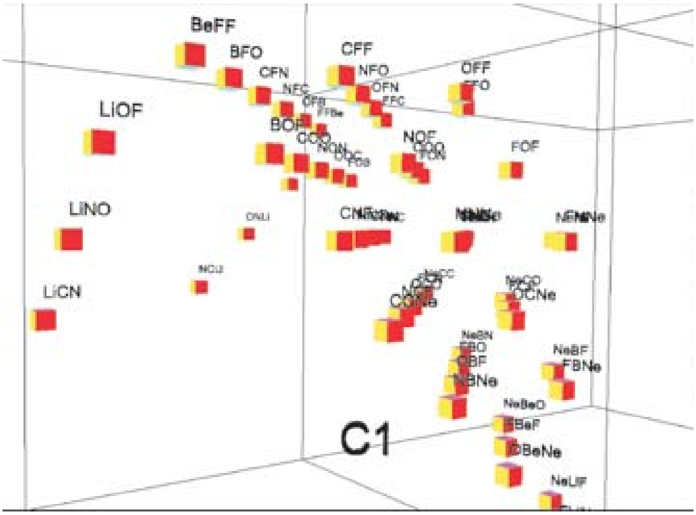

Figure 3. Close-up of Figure 1, showing all the molecules except LiOLi, which is above and to the left of the figure. The line of sight is contained both in the plane of n_e = 18 (*e.g.,* CFF) and a horizontal plane between the planes with molecules having central atoms nitrogen and oxygen. This orientation is such as to show most of the formulae for molecules with central atoms F, O, and C, and the ionically-bonded species LiCN, LiNO, and LiOF. Molecules with Ne as the left-hand atom are on the back wall of the inner volume (from just left of center to almost the right edge of the figure; those with Ne as the right-hand atom are on the wall through which the inner volume is viewed). All molecules are comprised of period-2 atoms, but similar figures containing isovalent species could be presented.

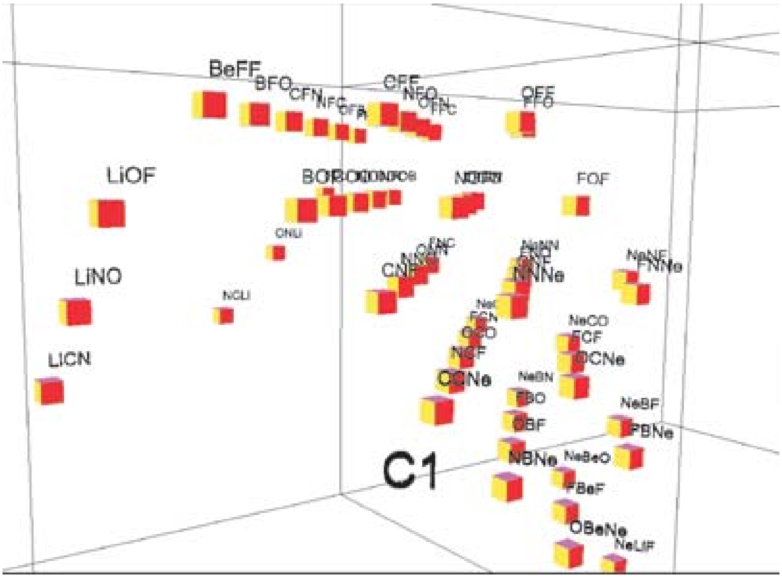

Figure 4. Same as Figure 3 except that the line of sight is contained both in the plane of $n_e = 20$ (*e.g.,* OFF) and a horizontal plane between the planes with molecules having central atoms oxygen and fluorine.

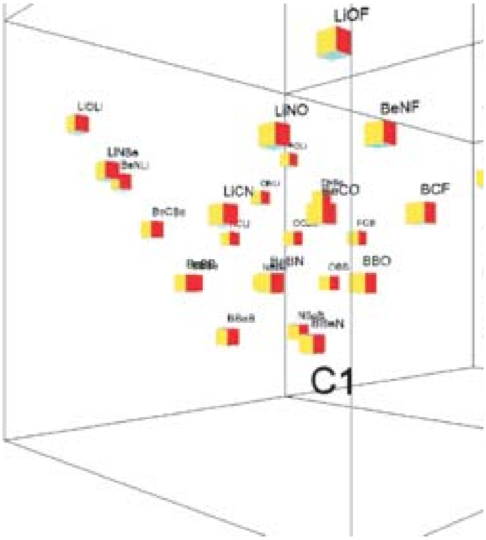

Figure 5. All of the molecules obtained from solving the equations for ionic bonding. The ionically-bonded species shown in Figures 1 and 3, and that can be identified also with the equations for covalent bonding, appear at the top. Planes containing LiOLi to BBeB ($n_e = 8$) and LiCN to BBeN ($n_e = 10$) are visible in this view.

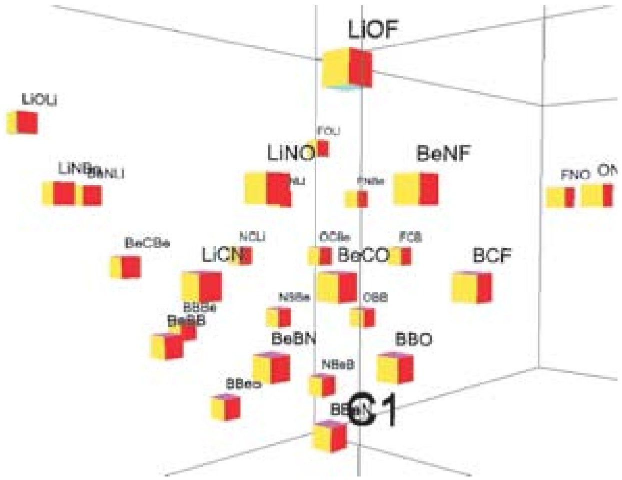

Figure 6. Same as Figure 5 except that the line of sight lies in the plane of the resonances with n_e = 12 (LiNO to BBO). Molecules in the 14-electron series are visible above and to the right.

where h is the intercept on the C_2 axis. Eqs. (11) and (27) are of this same form. The six molecules with two p atoms and one s atom, determined from the equations in Section »Covalent-bonded Molecules Requiring the Rule of 2« and also from those in Section »Molecules with Ionic and Covalent Bonds«, seem in Figure 1 to lie on a plane parallel to that for the purely covalently-bonded molecules with p atoms. The question arises, »Are these planes more appropriate loci for the molecules than are those described in the previous paragraph?« The answer to that question for molecules with covalent and dative bonds is seen in Figures 1, 3, and 4. The answer to that same question for ionically-bonded molecules appears in Figures 5 and 6.

The space with C_1, C_2, C_3 is only part of the six-dimensional chemical space constituting the periodic system of triatomic molecules,[8,9] so acyclic closed-shell triatomic molecules containing atoms from all periods of the chart of the elements lie on parallel hyperplanes in that system.

THE ALGEBRAIC TREATMENT OF CYCLIC TRIATOMIC MOLECULES, CLUSTERS, AND RESONANCES

Species with Covalent and Coordinate-covalent Bonds

All three of the equations for covalent bonding and coordinate-covalent bonding among these Lewis structures have two v_{ij} terms. For the special case described by Eqs. (22) to (24), those equations become

TABLE II

Cyclic triatomic molecules with covalent and coordinate-covalent bonds

BBNe	BBO	BBeF	BCF	BCN
BFBe	BFC	BFO	BLiNe	BNC
BNNe	BNO	BNeB	BNeLi	BNeN
BOB	BOF	BON	BeBF	BeBeNe
BeCNe	BeCO	BeFB	BeFF	BeFN
BeNF	BeNN	BeNeBe	BeNeC	BeNeO
BeOC	BeONe	BeOO	CBF	CBN
CBeNe	CBeO	CCC	CCNe	CCO
CFB	CFF	CFLi	CFN	CHeNe
CLiF	CNB	CNF	CNN	CNeBe
CNeC	CNeHe	CNeO	COBe	COC
CONe	COO	FBBe	FBC	FBO
FBeB	FBeF	FBeN	FCB	FCF
FCLi	FCN	FFBe	FFC	FFHe
FHeF	FHeN	FLiC	FLiO	FNBe
FNC	FNHe	FNO	FOB	FOLi
FON	HeCNe	HeFF	HeFN	HeNF
HeNeC	HeNeO	HeONe	HeOO	LiBNe
LiCF	LiFC	LiFO	LiNNe	LiNO
LiNeB	LiNeN	LiOF	LiON	NBC
NBNe	NBO	NBeF	NBeN	NCB
NCF	NCN	NFBe	NFC	NFHe
NFO	NHeF	NLiNe	NLiO	NNBe
NNC	NNNe	NNO	NNeB	NNeLi
NNeN	NOB	NOF	NOLi	NON
NeBB	NeBLi	NeBN	NeBeBe	NeBeC
NeBeO	NeCBe	NeCC	NeCHe	NeCO
NeHeC	NeHeO	NeLiB	NeLiN	NeNB
NeNLi	NeNN	NeOBe	NeOC	NeOHe
OBB	OBF	OBN	OBeC	OBeNe
OBeO	OCBe	OCC	OCNe	OCO
OFB	OFLi	OFN	OHeNe	OHeO
OLiF	OLiN	ONB	ONF	ONLi
ONN	ONeBe	ONeC	ONeHe	OOBe
OOC	OOHe	OOO		

$$v_{12} + C_1 + v_{13} = 8, \tag{31}$$

$$(v_{12} + 2p_{12}) + C_2 + v_{23} = 8, \tag{32}$$

$$v_{13} + C_3 + v_{23} = 8. \tag{33}$$

The sum of Eqs. (31) to (33) becomes

$$C_1 + C_2 + C_3 + 2v_{12} + 2v_{13} + 2v_{23} + 2p_{12} = 24. \tag{34}$$

It has the same form as Eq. (24). The alternate-sign sum is

$$C_1 - C_2 + C_3 + 2v_{13} - 2p_{12} = 8. \tag{35}$$

In contradistinction to Eqs. (11), (16), and (27), and to the equations for diatomic molecules,[15] a bond term v_{ij} appears in this equation for cyclic triatomic species. The same is true for larger cyclic species with odd numbers of atoms.[14]

The five equations in this section are for one special case of dative bonding only (atom 1 delegates a lone pair to form a bond to atom 2); there are many other scenarios. The rule of thumb for hand computation of possible structures (Eq. (28)) fails for some of these cyclic forms; in fact it would have been impossible to complete the exploration of all the forms without the computer program. The structures associated with the solutions to all the possible cases are shown in Table II. The numbers and directions of the covalent and dative bonds (of which there may be several for three given atoms) are not shown in the table.

Distribution of Closed-shell Cyclic Species in Chemical Space

The distribution of cyclic row-2 species with purely covalent bonding appears in Figure 7. This distribution is best interpreted as lying on parallel

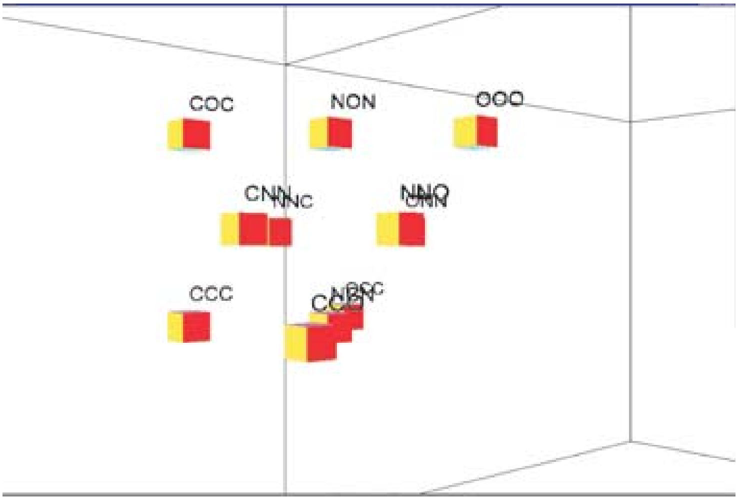

Figure 7. Close-up in the space of Figure 1, but showing only those few closed-shell cyclic species comprised of period-2 atoms having only covalent bonds.

planes pertaining to series with 12, 14, 16, and 18 valence-shell electrons (Eq. (29)) because of the behavior of the totality of cyclic row-2 species. If all the cyclic structures listed in Table II were plotted in the coordinates space of Figure 1, they would largely fill a slab bounded by the planes $n_e = 12$ and 18. Many of the locations that are occupied by the cyclic structures with n_e = 16 and 18 are also the locations of linear molecules; in fact only nine linear molecules do not have the same coordinates as some cyclic structure. Among the few locations in the slab not occupied by a cyclic structure are all the ionically-bonded molecules of Section »Molecules with Covalent and Coordinate-covalent Bonds« (some of which were also obtained in Section »Covalent-bonded Molecules Requiring the Rule of 2«).

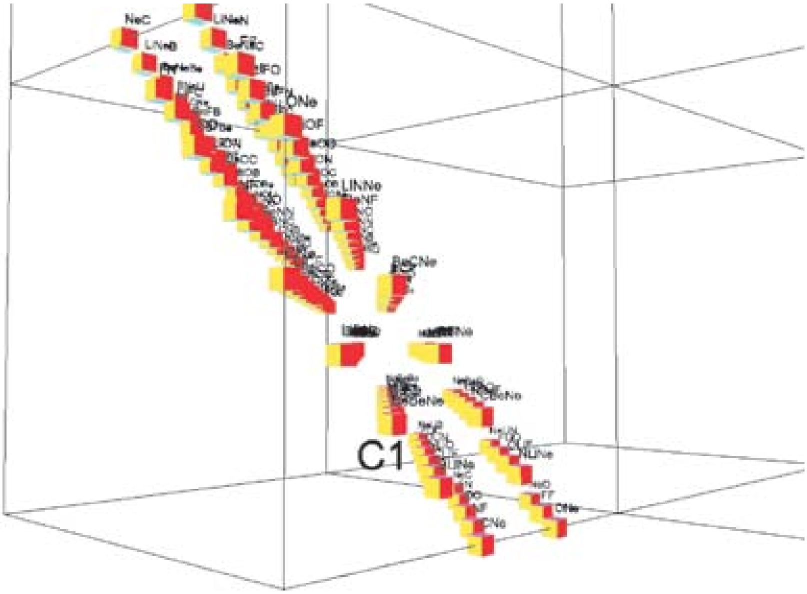

Figure 8. Cyclic Lewis structures n_e = 12 and 14. If this figure and Figures 5 and 6 were superposed onto Figures 1 or 3 or 4, the totality of all cyclic structures with the three bond types would be shown.

The cyclic triatomics ABC that have no associated linear molecule ABC, ACB,... or CBA all have 12 or 14 valence-shell electrons; they are shown in Figure 8. As mentioned just above Eq. (28), each dative bond v_{ij} reduces the value of C_j by 2; so it follows that the structures in Figure 8 are those with the greater number of dative bonds.

DISCUSSION

An algebraic formalism has been presented that allows the determination of all species with a given graph and with given dative bonds. The formalism thus makes it possible to identify all molecules with a given number of atoms. Since in organic chemistry these are the molecules most studied, their identification should facilitate the study of how molecular properties are distributed the *N*-atom periodic system of molecules.

The process of solving the equations for some larger molecules has brought to light that the sum or difference equation for at least a few structures (*e.g.*, linear or cyclic) can be generalized to any number of atoms. Finally, the inferences made in this study have suggest that the time may have come for an axiomatic exposition of this limited area of structural chemistry (*i.e.*, closed-shell Lewis structures).

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SAŽETAK

Globalna identifikacija molekulâ iz grafova. Molekule od triju atoma glavnih skupina

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Poželjno je da molekule s danim grafom i s kovalentnom, koordinativno-kovalentnom i ionskom vezom sadržavaju atome sa zatvorenom ljuskom. Taj zahtjev rezultira po jednom jednadžbom za svaki atom, koja kaže da zbroj broja valentnih elektrona koji pripada atomu prije vezivanja i broja valentnih elektrona dostupnih u procesu vezivanja, čini njegovu valentnu ljusku. Rješavanje jednadžbi rezultira identifikacijom atomâ i redoslijeda vezâ u Lewis-ovim diagramima. Algebarskom procedurom mogu se identificirati nove vrste. Neke od njih mogu se smatrati nemogućima (npr. s visokim steričkim napetostima), ili mogu biti kratkoživuće, ili se mogu naći samo pod vrlo neobičnim uvjetima. Prikazane su liste troatomnih molekula, molekulskih grozdova i rezonancijâ nađenih rješavanjem predloženih jednadžbi. Molekule zatvorenih ljuski leže na paralelnim ravninama u njihovim kemijskim prostorima, naime u onima u kojima se nalaze izoelektronske molekule.