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Chemical Structural Formulas of Single-Bonded Ions Using the "Even-Odd" Rule Encompassing Lewis's Octet Rule: Application to Position of Single-Charge and Electron-Pairs in Hypo- and Hyper-Valent Ions with Main Group Elements

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Abstract

Lewis developed a 2D-representation of molecules, charged or uncharged, known as structural formula, and stated the criteria to draw it. At the time, the vast majority of known molecules followed the octet-rule, one of Lewis's criteria. The same method was however rapidly applied to represent compounds that do not follow the octet-rule, *i.e.* compounds for which some of the composing atoms have greater or less than eight electrons in their valence shell. In a previous paper, an even-odd rule was proposed and shown to apply to both types of uncharged molecules. In the present paper, the even-odd rule is extended with the objective to encompass all single-bonded ions in one group: Lewis's ions, hypo- and hypervalent ions. The base of the even-odd representation is compatible with Lewis's diagram. Additionally, each atom is subscripted with an even number calculated by adding the valence number, the number of covalent bonds of the element, and its electrical charge. This paper describes how to calculate the latter number and in doing so, how charge and electron-pairs can actually be precisely localized. Using ions known to be compatible with Lewis's rule of eight, the even-odd rule is compared with the former. The even-odd rule is then applied to ions known as hypo- or hypervalent. An interesting side effect of the presented rule is that charge and electron-pairs are unambiguously assigned to one of the atoms composing the single-charged ion. Ions that follow the octet rule and ions that do not, are thus reconciled in one group called "electron-paired ions" due to the absence of unpaired electrons. A future paper will focus on the connection between the even-odd rule and molecules or ions having multiple bonds.

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Keywords

Charge, Molecule, Ion, Even-Odd, Rule, Structural Formula, Octet Rule, Single Bond, Covalent

1. Introduction

A chemical structural formula is a two-dimensional representation of the atom's configuration in a molecule. Lewis's octet rule is currently used to draw structural formulas of molecules mainly in organic chemistry [1]. This rule is not applicable to hyper or hypovalent neutral molecules [2].

An extension of this octet rule has been proposed in an earlier paper as a rule to draw structural formulas of single-covalent-bonded uncharged molecules [3]. This rule, referred to as the even-odd rule, has included hypo- and hypervalent single-covalent-bonded molecules with Lewis's molecules in a single group denoted "electron-paired molecular group" [3].

Unfortunately, both the octet rule and the even-odd rule describe neutral molecules; they however do not give clear instructions in how to draw structural formulas of ions and their internal electrical-charge position.

The aim of this paper is to expand the even-odd rule from neutral molecules [3] to single-charged single-covalent-bonded ions in which the charge position is unambiguous. This adapted rule is first applied to ions following both rules and then to hypo- and hypervalent ions not following the octet rule. Additionally, the drawing of the electron-pairs is detailed for charged atoms in single-covalent-bonded ions. It will be shown that unpaired electrons cannot be included with the ions compatible with the proposed even-odd rule.

2. Expanded Even-Odd Rule for Single-Covalent-Bond between Atoms in Single-Charged Ions

In the even-odd rule, the structure of an ion containing atoms with single-covalent-bonds has the same base that in a Lewis structure.

- In this structure each atom is as follows:
  - Each atom is an element with one or several electron-shells and one outer-shell having an electron number *i.e.* the valence number as defined in the periodic table.
  - Also from the periodic table, the outer-shell of main-group elements contains between one and eight electrons.
  - When an ion or molecule is constituted of only one atom, it has no covalent bond.
  - In an ion or molecule constituted of several atoms, each atom forms a single-covalent-bond with each of its first neighboring atoms. A covalent bond involves two electrons, one from each connected atom.
  - Each covalent-bond is represented by one line between connected atoms.
  - In the 2D structure, each atom is represented by the letters from its element as in the periodic table.
  - Two numbers written on each side of the atoms have to be evaluated.
- The left side number and the effective valence number
  - The left side number, the "valence number", is the number of electrons which can be involved in covalent bonds. It ranges from one for elements like sodium (Na) up to eight for noble gas like Argon (Ar) as in the periodic table.
  - An effective valence number has to be evaluated: For a neutral atom *i.e.* without charge, there is no modification and it is equal to the valence number; for a negatively charged atom *i.e.* that possesses an extra-electron, it is the valence number increased by one; for a positively charged atom, it is the valence number decreased by one.
- The right side number
  - The right-side number, the "Lewis number", is equal to the sum of the effective valence number and the number of covalent bonds of the atom. It can also be expressed as the sum of the number of electrons left in the outer-shell and twice the number of covalent bonds.
  - The Lewis number must be an even number. This is only possible when the number of bonds and the effective valence number are both odd or both even.
  - The lower Lewis number can be equal to zero: the atom has lost electrons from the outer-shell so it is em-

pty and with no bonds.
- The Lewis number can range up to twice the effective valence number: this is twice the maximum number of covalent bonds for this element. This number is charge dependent through the effective valence number.
- If all atoms of an ion have their Lewis numbers equal to eight, the ion is compatible with the octet rule.

- Electron pairs in the outer-shell of a connected element
  - The number of electrons in the outer-shell is calculated by subtracting the effective valence-number and the number of covalent bonds. It is an even number.
  - As a consequence, the outer-shell contains electron-pairs not involved in any covalent bond.
  - This electron-pair number ranges from 0 to 4 whatever the charge of the element.
  - When this electron-pair number is 0, no additional covalent bond can be formed by the element.

Globally in this rule, it seems possible that all single-bonded ions following Lewis's octet rule named "octet ions" are included in the group of single-covalent-bonded ions following the even-odd rule. Ions in this group will be named "Electron-paired ions".

3. Application to Single-Charged Single-Covalent-Bonded Ions

In the following, the validity of the even-odd rule is tested using well-known charged ions with single-covalent-bonds. As there are a large number of these ions, this test is limited to ions having elements from the main group of the periodic table and with one covalent bond between each of their first-neighbor atoms.

Tables 1-3 list structural formulas of single-charged ions having single-covalent bonds. Both first tables bring together ions following both rules: Lewis's octet rule and the even-odd rule. The right side number, the Lewis number, of all elements composing these ions is equal to 8. **Table 3** brings together ions following only the even-odd rule: one of the composing atoms has a Lewis number greater or less than 8.

In **Table 1**, the first ion Cl(−) is composed of only one element and no chemical bond. The valence number is 7 from the periodic table and the effective valence number is 8 (7 + 1 negative charge). Since there is no bond in this ion, the right-side number is equal to 8 (8 + 0 bond). This ion follows the octet rule. The difference between the effective valence number (8) and the number of covalent-bonds (0) indicates that the outer shell has 4 electron-pairs confirming a saturated outer shell.

The second ion is hydrogen H(−): one valence electron and one negative charge. The effective valence number is 2. The right-side number is also 2 (2 + 0 covalent bond) in agreement with the Lewis rule for hydrogen. As there is no covalent bond, there is only one electron-pair in this element's outer-shell.

The third ion OH(−) contains one oxygen atom with 6 valence electrons. The negative charge gives an effective valence number of 7. The right-side number is equal to 8 (7 + 1 covalent bond). This ion follows the octet rule. The number of electrons in the outer shell is 6 (7 − 1 covalent bond): 3 electron-pairs.

Table 1. Single-charged ions compatible with Lewis-octet rule and the even-odd rule. Chemical structural formulas of single-charged ions composed of the main group elements in the periodic table. In these ions, two neighbors are interconnected by only one covalent bond. Classical structure representations are surrounded by square brackets. Ions in agreement with the even-odd rule have two numbers associated to each element and the charge is assigned to one element in the ion.

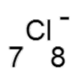
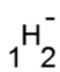
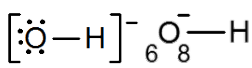
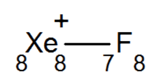
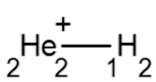
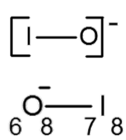
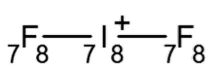
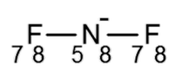
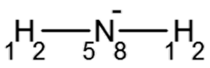
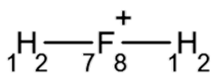
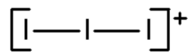
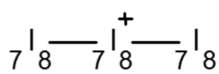
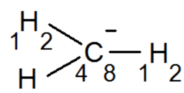
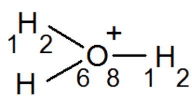
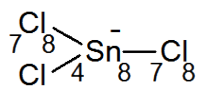
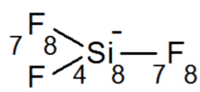
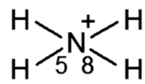
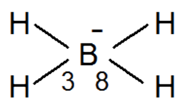
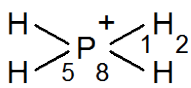
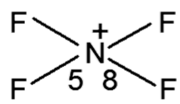
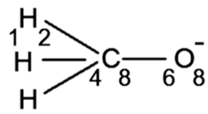
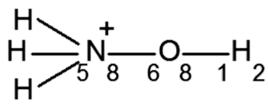
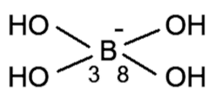
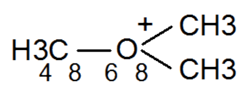
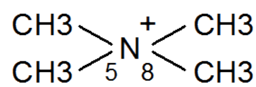
Cl(−) Chloride anion In solution [4]  [5]-[7]	H(−) [4]-[6] Hydrogen anion  [5]-[7]	OH(−) [5] [7] Hydroxide anion  [7] [6]	XeF(+) [4] [7] Fluoroxenonium 
HeH(+) [7] Helium hydride ion 	IO(−) Hypoiodite anion From hypoiodous acid  [5]-[7]	IF2(+) Difluoroiodonium  [5]	NF2(−) [7] Difluoroamino ion  [5] [6]

Table 2. Single-charged ions compatible with Lewis-octet rule and the even-odd rule. Chemical structural formulas of single-charged ions composed of the main group elements in the periodic table. In these ions, two neighbors are interconnected by only one covalent bond. Classical structure representations are surrounded by square brackets. Ions in agreement with the even-odd rule have two numbers associated to each element and the charge is assigned to one element in the ion.

NH2(−) [4] [5] [7] Amide anion  [6]	H2F(+) [4] [5] [7] Fluoronium cation  [6]	I3(+) [4] [5] [7] Triiodide cation  [4]  [6]	CH3(−) [4] [5] [7] Methyl anion  [6]
H3O(+) [4] [5] [7] Hydronium Cation  [6]	SnCl3(−) Tin trichloride ion Trichloro stannate  [5] [6]	SiF3(−) [7] Trifluorosilyl  [5] [6]	NH4(+) [4] [7] Ammonium  [5] [6]
BH4(−) [5] [7] Borohydride anion  [6]	PH4(+) [4] [5] [7] Phosphonium ion  [6]	NF4(+) [5]-[7] Tetrafluoroamonium  [7]	CH3O(−) [7] Methoxide ion  [5] [6]
NH3OH(+) [4] Hydroxyammonium ion  [5] [6]	B(OH)4(−) [7] Tetrahydroxyborate  [5] [6]	O(CH3)3(+) Trimethyloxonium  [5]-[7]	N(CH3)4(+) Tetramethylammonium  [5]-[7]

The same calculation procedure has been applied to all ions in **Table 2**. For all of them, the right-side number, calculated with the even-odd rule, is equal to 8, and all of them follow the octet rule. The number of electron pairs in the outer shell, calculated by difference for each ion, ranges from 0 to 4.

In **Table 1**, one ion is noticeable: XeF(+).

Applied on XeF(+) ion, including a rare gas element, the even-odd rule assigns a positive charge to the Xenon atom and not to the fluorine atom. Xe(+) effective valence number is 7 as for the Fluorine element. Each gives one electron to a covalent bond and are left with 3 electron-pairs in their outer-shell. Both atoms follow the octet rule.

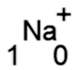
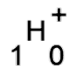
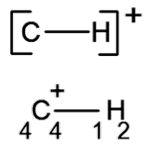
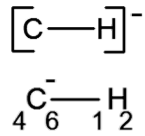
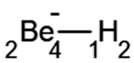
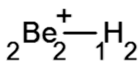
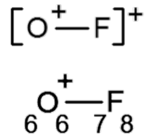
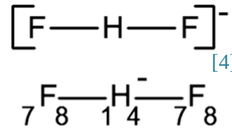
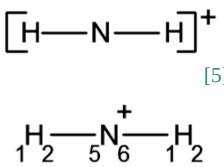
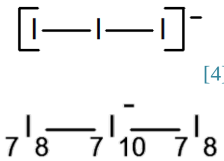
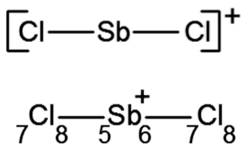
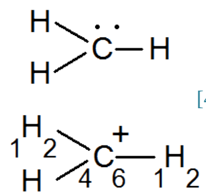
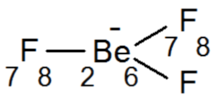
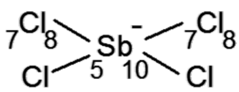
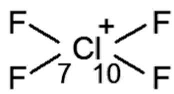
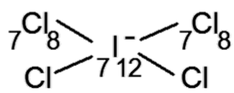
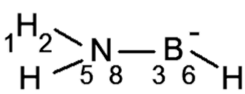
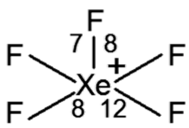
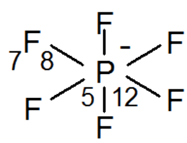
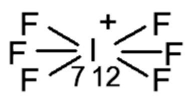
In **Table 2**, BH4(−) is noticeable. The Boron element builds 4 single-covalent bonds with its hydrogen neighbors. In order to have an even right-side number, the element must take one extra electron and thus ends up with an empty outer-shell.

Globally in **Table 1** and **Table 2**, elements from column 1 and 2 in the periodic table are not present due to the too small valence number of these elements to follow the octet rule.

In **Table 3**, all ions are represented as in **Table 1**. Both valence and Lewis numbers *i.e.* left side and right side numbers are calculated with the same procedure. In all these ions nevertheless, one atom at least has a right-side number not equal to 8. As a consequence, these ions are only in agreement with the proposed even-odd rule.

The first ion is sodium cation Na(+) with one positive charge. The effective valence number in this atom is 0 and this atom has an empty outer-shell. The right-side number is zero showing that this ion has a noble gas electronic structure, the saturated inner-shell is available. The second ion is a proton H(+) that has no valence electron. Its outer-shell is empty and therefore does not follow the Lewis rule.

Table 3. Single-charged ions only following the even-odd rule. Chemical structural formulas, for single-charged ions with elements of the main group in the periodic table and with its first neighbors related by only one covalent bond represented by a line. A classical structure is surrounded by square brackets. An ion designed in agreement with the even-odd rule, has elements associated with two numbers. With this second case, the charge position is always in one element.

Na(+) Sodium Cation  [5] [6]	H(+) Proton Hydrogen cation  [5]-[7]	CH(+) Carbyne cation  [4]	CH(−) Carbyne anion  [4]
BeH(−) [5] Beryllium hydride 	BeH(+) [5] Beryllium hydride 	FO(+) Fluorine oxide  [5]	HF2(−) [4] [7] Hydrogen difluoride ion  [4] [7]
NH2(+) [5] [7] Nitrenium ion  [5] [7] [6]	I3(−) Triiodide ion  [4] [7] [5]	SbCl2(+) Dichloroantimonium [7] Dichlorostibinyl [5]  [5]	CH3(+/−) [4] [5] [7] Carbonium ion +/−  [4] [7] [5] [6]
BeF3(−) [4]-[6] Beryllium trifluoride  [5]	SbCl4(−) [5] [7] Tetrachloroantimonate  [5]	ClF4(+) [4] [5] Halogen cation  [4] [5]	Cl4I(−) [5] Iodine tetrachloride  [5]
H3NB(−) [5] Amino borate  [5]	XeF5(+) [4] Xenon fluoride  [8]	PF6(−) [5]-[7] Hexafluorophosphate Anion  [4] [5]	IF6(+) [4] [5] [7] Halogen cation  [4]

The fifth ion is Beryllium hydride BeH(−). The negative charge cannot be on the hydrogen which has a right-side number equal to 2 with one covalent bond. For the Beryllium element, with a valence number of 2, the negative charge gives an effective valence number of 3. With one covalent bond, the calculation gives a right-side number of 4, which contradicts Lewis's rule. The number of electrons in the outer-shell is calculated as above and gives one electron-pair in the outer-shell of the Beryllium element. This ion can be included in the electron-pair ion's group.

The same calculation procedure has been applied to all other ions that have at least one atom not following Lewis's octet rule. For each of them, the right-side number is always an even number but not equal to 8. The calculated number of electrons in their outer-shell is always even, which can be expressed differently: electrons in the outer-shell come in pairs.

The last two ions in Table 3 are noticeable. The covalent-bond number gives to their central atoms a right-side number far above 8. They are classified as hypervalent ions.

Globally in Table 3, all ions are compatible with the proposed even-odd rule. They are classically classified as either hypovalent or hypervalent ions but with the even-odd rule, they belong to the "electron-paired ion" group.

In **Table 3** appear also elements from column 2 of the periodic table. This shows that the field of application of the even-odd rule presented here is indeed wider than that of the octet rule. This shows that the "electron-paired ions" group encompassed a higher number of ions than the "octet ion" group.

Only in both tables, the charge position is mainly in the ion's center. This position is therefore the same in all ions whatever the rule is.

4. Discussion

All ions presented in this paper are well known and their structural formulas have been constructed using always the same procedure in agreement with the even-odd rule. **Table 1** and **Table 2** bring together ions following both rules whereas **Table 3** lists hypo- and hypervalent ions. This confirms the applicability of the proposed even-odd rule. The objective of this paper is successfully reached. It shows that both octet ions and non-octet ions follow the proposed rule. Moreover, ions following Lewis's octet rule are in a group completely encompassed in the group of ions following the even-odd rule. The Lewis group can be named "octet ions" and the even-odd group can be named "Electron-paired ions".

In each table, the charge-position is given in the even-odd rule by calculating the effective valence number. Hypovalent ions as BeF3(−) and CH3(+) or hypervalent ions as ClF4(+) and PF6(−) are also addressed. This seems to be an advantage of the proposed rule over the classical one.

As a side effect, the number of electron-pairs in the outer-shell of a charged atom in an ion can be evaluated. This number ranges from 0 to 4: Ions like HeH(+), Na(+), BeH(+), BeF3(−) and PF6(−) have an empty outer-shell; one pair in H3O(+), two in FH2(+), three in IO(−) and four in Cl(−). It seems that this electron-pair number does not have any relation with the Lewis octet rule.

5. Conclusions

In a previous paper, the even-odd rule has been applied to neutral single-bonded molecules. This rule is expanded here to incorporate a single charge, positive or negative, in structural formulas. This expanded rule is applied to ions following Lewis's octet rule and to hypo- or hypervalent ions. For each atom of the ion, the rule uses its valence number, the charge and the number of covalent bonds to calculate two numbers: the Lewis number and the number of electrons in the outer-shell of the atom. For several ions, the Lewis number is equal to 8 and they are following the octet rule. These ions are "octet ions". Several other ions are not following this rule. They mainly are composed of atoms that possess between 0 and 4 electron-pairs in their outer-shell. These ions are "electron-paired ions". This last group encompasses octet ions.

The even-odd rule brings strong constraints on values associated to atoms composing ions. An interesting side-effect of these constraints is that they lead each time to a unique possible position for the charge. The assignation of the charge to one specific atoms in ions is thus strongly linked to the ion's structural formula.

In the near feature, the even-odd procedure will be evaluated with classical structural formulas presenting multi-bonded chemical connections.

References

[1] Zumdahl, S. (2005) Chemical Principles. 5th Edition, Mifflin, Houghton.

[2] Gillespie, R.J. and Popelier, P.L.A. (2001) Chemical Bonding and Molecular Geometry. Oxford University Press, Oxford.

[3] Auvert, G. (2014) Improvement of the Lewis-Abegg-Octet Rule Using an "Even-Odd" Rule in Chemical Structural Formulas: Application to Hypo and Hypervalences of Stable Uncharged Gaseous Single-Bonded Molecules with Main Group Elements. *Open Journal of Physical Chemistry*, **4**, 2.

[4] Greenwood, N.N. and Earnshaw, A. (1998) Chemistry of the Elements. 2nd Edition, Butterworth-Heinemann.

[5] http://www.chemspider.com/

[6] http://www.ncbi.nlm.nih.gov/

[7] http://en.wikipedia.org/

[8] http://bioportal.weizmann.ac.il/course/structbioinfo/databases/CCDC_teaching_egs/teaching_examples.3.27.html