

Picometer Toroidal Structures Found in the Covalent Bond

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The same topology observed for the atom's nuclei is identified in the covalent chemical bond. A linear correlation is found between the normalized bond longitudinal cross section area and its correspondent bond energy. The normalization number is a whole number. This number is interpreted as the Lewis electron pair. A new electron distribution for different diatomic molecules follows. Same number of electrons present different bond energies, occupying different areas. Therefore, it is inferred that the chemical energy is a consequence of the mass defect or gain due to the mass fusion of valence electrons participating in the bond.

1 Introduction

The topological analysis of the electron density has provided useful information about the bonding in a molecule. However, not much progress has been made to reveal the fundamental features of chemical bonding postulated by Lewis, i.e. the electron pair. According to Lewis structures there are bonding electron pairs in the valence shell of an atom in a molecule, and there are also nonbonding pairs or lone pairs in the valence shell of many of the atoms in a molecule. So far, it has not been seen any evidence of electron pairing in the topological analysis of the electron density. An increased concentration of electron density is observed between the two bonded atoms, which could be interpreted as the electron density equivalent of a Lewis bonding pair [1]. Nevertheless, there is no way to be sure about it. The same occurs about the existence of lone pairs. This same reference arrives to the conclusion that electron pairs are not always present in molecules, and even when they are, they are not as localized as the approximate models may suggest [2].

Therefore, a method to measure the number of electrons that participate in the bond will definitely probe or not the existence of Lewis electron pairs.

In 1996 the shapes of the deuteron at the femtometer scale were reported. The deuteron presents three different shapes: a torus, a sphere inside another sphere and two separated spheres [3]. These are the same shapes observed in every single molecule's Laplacian of the electron density but at the picometer scale. It is inferred that those are the shapes of the electron while it is participating in the chemical bond. Lack of identifying these shapes with the electron misleads the molecule's topological analysis.

This paper uses this new shapes in the analysis of different diatomic molecules and CO₂. Thanks to this, the topology of the chemical bond is properly identified. The longitudinal cross section area of the bond is correlated with its bond energy. Only when this area is divided by a whole number, a linear correlation between this bond area and its energy occurs. This whole number is most of the time an even number and thus, it is interpreted as the electron pair. Conse-

quently, an electron distribution in the molecule is possible. First time model independent evidence of the Lewis electron pair is found.

1.1 Electron pair topology

Covalent bonds or lone pairs will be detected by using the structures observed in Fig. 1, namely: the two separated spheres (*ts*), the torus (*t*) and the sphere in a sphere (*ss*). Valence electrons participating in the σ bond (two electrons involved) occur by adopting the two separated sphere structure, *ts*. Double (four electrons involved) and quadruple bonds (eight electrons involved) also use this structure. A lone pair occurs as a torus shape around quadruple bonds or as a *ss* structure around more electronegative atoms. As the electronegativity of the nucleus increases, non-bonding electrons tend to form a toroidal structure around its atom helium core. This occurs until the next noble gas structure is fulfilled.

2 Experimental

By cutting the silhouette of the two separated sphere structure, involving the bonded atoms, the bond longitudinal cross section areas (bond area) were determined from the contour map of the Laplacian of its charge density. An example of such silhouette (green lines) can be observed in Fig. 3 for the fluorine molecule. They were printed on paper, cut and weighted. The bond length was used to calibrate the longitudinal cross section area measured in each bond. Then, these areas were correlated with their respective bond energies.

The contour map of the Laplacian of the charge density for fluorine, F₂ and dicarbon, C₂ molecules were found in [4], oxygen O₂ was found coordinated to a molybdenum atom in [5]. Nitrogen, N₂ is from [7]. Carbon monoxide, CO from [8]. Cyanide CN⁻ from [11]. Nitrogen monoxide, NO from [9] and carbon dioxide CO₂ was found in [10].

3 Results

Fig. 2 shows a straightforward correlation between the bond area divided by a number n and the bond energy of each bond. This number n is a whole number and it is interpreted as the

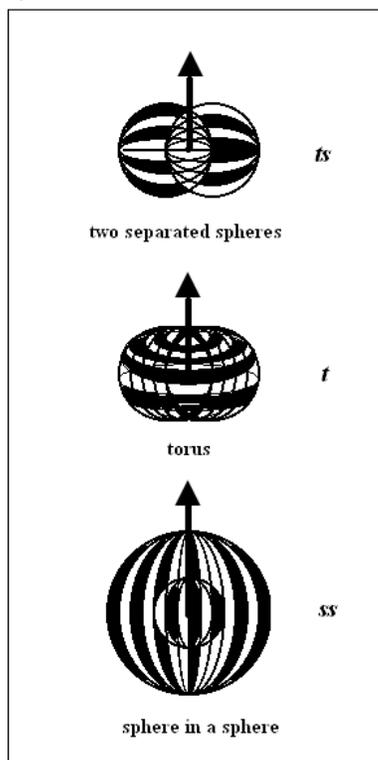


Fig. 1: Observables structures of the electron. This is after [3].

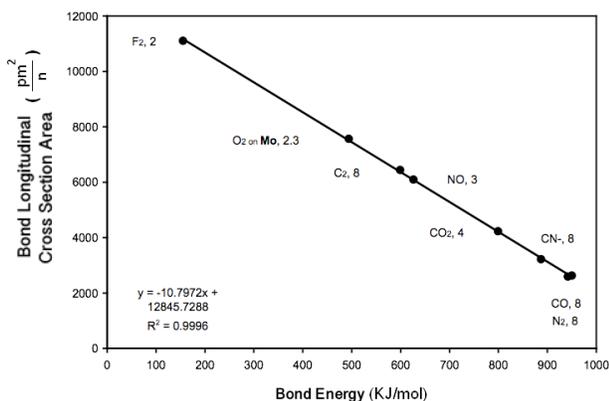


Fig. 2: Correlation between bond longitudinal cross section area and its energy for different diatomic molecules and CO_2 .

number of electrons involved in the bond. It has to be stressed that the y -axis location for each experimental point is very sensitive to the number n . Fractions of this number makes the r^2 get lower than 0.999. It is clear that as the normalized bond area diminishes, the bond energy increases.

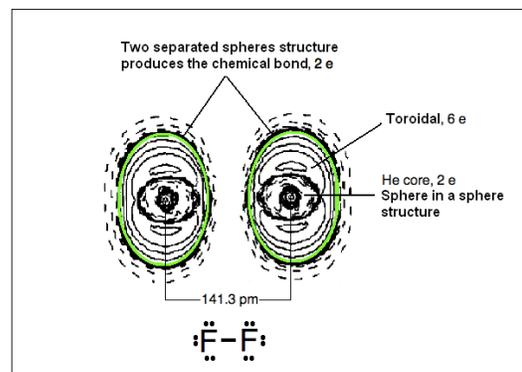


Fig. 3: Fluorine molecule. There is no discernible structures between the atoms. The different electron's structures are indicated. The green line shows where the bond was cut. The original figure is from [4]. Used under Creative Common License.

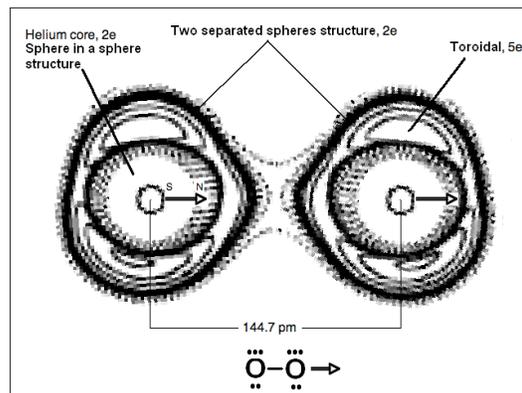


Fig. 4: Oxygen molecule coordinated by a Mo atom. The different electron's structures are indicated. The magnetic moments are shown with the arrow with North and South poles. The original figure is from [5]. Used with permission of the editors.

3.1 Homonuclear diatomic molecules

Fluorine, F_2 . Fig. 3 shows the fluorine molecule. The sphere in a sphere structure is clearly observed at the center of each F atom. This is due to the helium core and account for two electrons. The next six electrons are in the toroidal structure around each helium core. As observed in Fig. 2, the F-F bond has two electrons. The two bonding electrons belong to both nuclei in a ts structure. Due to this bonding, there is no discernible structure between the F atoms. Therefore, one can still put a stroke between these two atoms, understanding that there is a bond through this structure. Hence F-F is all right. The dots around each F atom just denotes the pairing of each atom's 6 toroidal electrons. This is the usual Lewis structure.

Oxygen, O_2 . Fig. 4 shows that the oxygen molecule highly resembles the fluorine one. The n number was not a whole

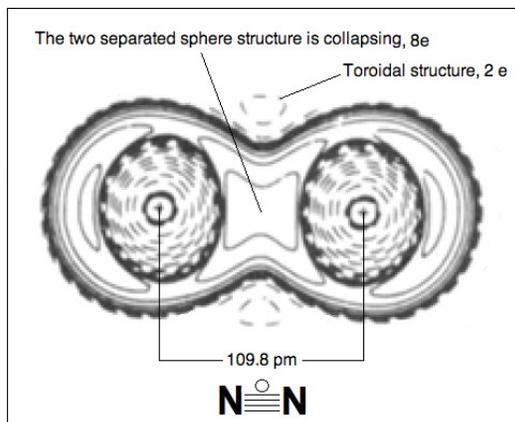


Fig. 5: Nitrogen molecule. The original figure is from [7]. Used with permission of the editors.

number giving 2.3. The uncoupled electrons in each oxygen atom will produce a magnetic attraction in the line of the bonding. Probably, this may distort the molecule in a way to make it digress from the experimental trend observed. However, the resemblance to the fluorine molecule and the closeness of the n number to 2, strongly suggests that the number of electrons involve in the O–O bond is 2.

As a consequence, the toroidal structure on the oxygen's helium core, previously observed in F_2 , necessarily have 5 electrons each. This odd number means two uncoupled magnetic momenta. One in each oxygen atom. They will align as indicated in the figure. This will create a net magnetic moment in the molecule, i.e. the oxygen molecule is paramagnetic.

The magnetic attraction is rendering a shorter bond area in this molecule. Probably, this is why this molecule is away from the general trend observed in Fig. 2. Dividing between a larger n number is just compensating this magnetic attraction. In other words, to have an $n = 2$ in this molecule, the energy of the O–O bond should be 410 kJ/mol and not the experimental 494 kJ/mol. There have not been any consensus about how the oxygen's Lewis structure should be written. The molecule's paramagnetism does not help. This is because an uncoupled electron structure has to be written, somehow contradicting Lewis pairing hypothesis. O–O, O=O and O÷O has been proposed. From these structures, the more pertinent is O÷O because the dots are the two uncoupled electrons observed in Fig. 4. The Lewis structure printed in Fig. 4 indicates the existence of odd pairing, which is supported by the molecule paramagnetism.

Nitrogen, N_2 . As it is noticeable from Fig. 5, the nitrogen atoms are not separated. This is probably due to the lower electronegativity in comparison with fluorine and oxygen molecules. The well defined ts structure previously observed for fluorine and oxygen disappears, giving way to the

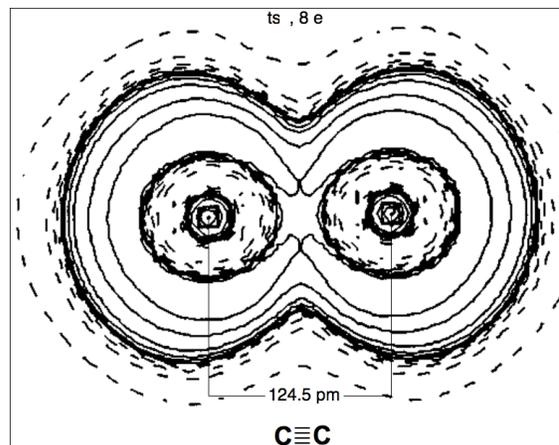


Fig. 6: Dicarbon molecule. The original figure is from [4]. Used under Creative Commons License.

same structure but with its spheres more collapsed; this is covering both nitrogen atoms' helium cores.

According to the results from Fig. 2, four of the five nitrogen valence electrons are compromised in the N–N bond. Since this molecule is diamagnetic, it is believed that the two remaining electrons join forming a toroidal lone pair structure around the N–N bond. This ring will occur in the midpoint between the bonding nitrogens. Structures like this have been observed, for example in the acetylene molecule [12]. As a consequence of this electron distribution, all nitrogen's five valence electrons are joined and this is why this molecule presents the highest bond energy in the series F, O, N, C.

The usual Lewis structure is a triple bond between the nitrogens and two lone pairs, one at each nitrogen atom. However, this molecule has one of the highest bond energies and also the smaller bond area measured from the pool of molecules tested. Therefore, it should not surprise that a very high number of valence electrons join for this bond. Furthermore, there is no structures in Fig. 5 to justify the presence of lone pairs on either N atoms. As it was observed in F–F or in O÷O. Hence, the Lewis structure pictured in Fig. 5 with four strokes and the lone pair making a ring (torus) around the middle of the N–N bond is a new Lewis structure.

Dicarbon, C_2 . Fig. 6 presents an even less collapsed ts structure in comparison with N_2 . This is due to less number of valence electrons to bond and to the lower electronegativity that carbon has. The C–C bond in dicarbon involves all valence electrons from each carbon, i.e. 8, and they are around each atom's helium core. The diamagnetism of this molecule reveals that all its bonded electrons are magnetically coupled. Again, no lone pair structures are noticeable in this molecule. Hence, the Lewis structure depicted in Fig. 6 is new.

Upon comparing these four molecules, one can arrive to the conclusion that the chemical σ bond is mostly performed

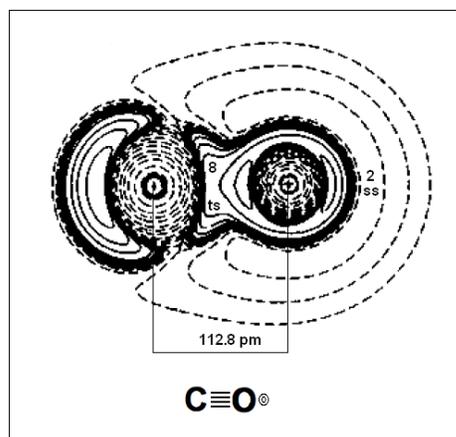


Fig. 7: Carbon monoxide. The two concentric semicircles in the Lewis structure represent an *ss* lone pair structure located on the oxygen atom. The original figure is from [8]. Used with permission of the editors.

by this *ts* structure and the separation between the spheres depends on the atom's electronegativity. As the electronegativity of the bonded atoms diminishes, more electrons are involved in the bond.

3.2 Heteronuclear diatomic molecules

Carbon monoxide, CO. As observed in Fig. 2, the C–O bond involves 8 electrons. Accordingly, Fig. 7 presents the electron distribution in CO. From the 10 valence electrons to share: 4 from the carbon and 4 from the oxygen are joined around the helium core of each atom. The other 2 oxygen's valence electrons are in a lone pair. This is the *ss* structure over the oxygen's helium core.

This molecule is isoelectronic with N_2 . However, the difference between the atoms' electronegativity makes the lone pair to form over the oxygen. In the case of N_2 , there is no difference in electronegativity, and thus it is believed that its lone pair will be at the mid point between the N–N bond in a toroidal shape.

The current Lewis structure of CO is a triple bond between the carbon and the oxygen and one lone pair on each atom. Somehow trying to achieve the octet rule. The new Lewis structure is a quadruple bond for the C–O bond and one lone pair only on the oxygen in an *ss* structure. This last feature has been noted as two concentric circles in the new Lewis structure (see Fig. 7).

Finally, there is a controversy about the dissociation energy of CO. The values can be 881, 926, 949, 941 or 1070 KJ/mol coming from different kind of experiments [13]. In the case of Fig. 2, the value 926 KJ/mol from electron impact experiments or 949 KJ/mol from pre-dissociation data produced the best linear correlation with the other molecules of the group.

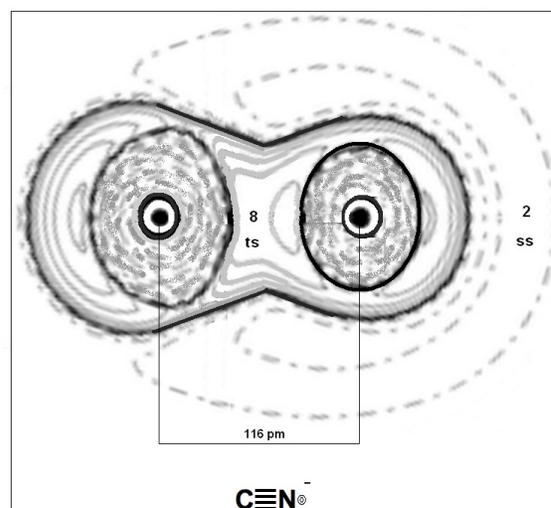


Fig. 8: Cyanide molecule. The two concentric semicircles in the Lewis structure represent an *ss* lone pair structure located on the nitrogen atom. The original figure is from [11]. Used with permission of the editors.

Cyanide, CN^- . As in the case of carbon monoxide, the C–N bond involves 8 electrons. Fig. 8 presents the electron distribution in the molecule: 4 valence electrons from carbon and 4 more from the nitrogen make this bond in an *ts* structure around the atoms' helium cores. The nitrogen however, remains with one uncoupled electron. Since this molecule is diamagnetic, an extra electron is needed to couple and cyanide finish with a negative charge. This charge is a *ss* lone pair, clearly observed on the nitrogen. This occurs on the nitrogen atom because it is more electronegative than carbon. The current Lewis structure is a triple bond between the carbon and the nitrogen and two lone pairs; one on each atom. This is to try to achieve the octet rule. Again, just like in the CO molecule, the new Lewis structure is a quadruple bond and the lone pair repeats on the more electronegative atom.

Nitrogen monoxide, NO. Fig. 9 presents the NO molecule. As observed in Fig. 2, the N–O bond involves three electrons. This will imply that one of those three electrons is not magnetically coupled with the other two and therefore, this molecule will be paramagnetic. In this join of three electrons, the nitrogen shares 1 and the oxygen shares 2. By this way, the nitrogen can couple the other 4 electrons as one toroidal structure around its helium core. The oxygen will arrange its other 4 electrons in the same manner. The current Lewis structure depicts an uncoupled electron on the nitrogen and a double bond between the nitrogen and the oxygen. The new Lewis structure leaves the odd electron in the N–O bond. Thus, this would be an example of a three electron bond and therefore, this bond is paramagnetic. Thus, the new Lewis structure draws a magnetic moment vector over the single N–

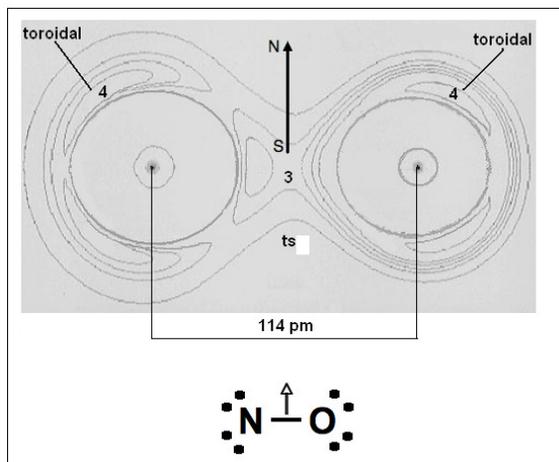


Fig. 9: Nitrogen monoxide molecule. It has a three electron σ bond. 4 electrons forms a toroidal structure around each atom's helium core. The original figure is from [9]. Used with permission of the editors.

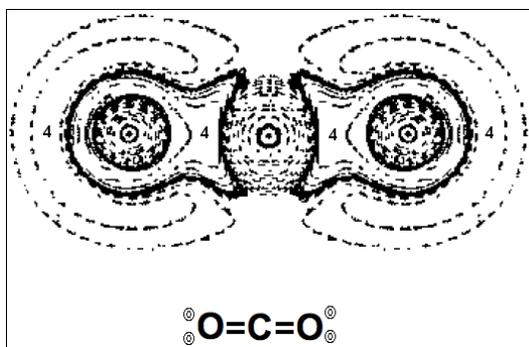


Fig. 10: Carbon dioxide, CO_2 . The new Lewis structure specifies that the two lone pairs on the oxygen atoms are in an ss structure. The original figure is from [10]. Used with permission of the editors.

O bond. The two lone pair on each atom are also depicted.

Carbon dioxide CO_2 . Fig. 10 shows that the 4 valence electrons of carbon are used at each side of the molecule to produce two C–O bonds with 4 electrons each. The remaining 4 electrons of the oxygen go to an ss lone pair over each oxygen atom. The current Lewis structure presents a double bond towards each oxygen atom and two lone pairs on each oxygen. The new Lewis structure just stresses that these lone pairs are in an ss structure.

4 Discussion

The three shapes observed in Fig. 1 are the “attractors” identified by Bader *et al* after the topological analysis of a large number of molecules [6]. Specifically, the core attractor can be identified as the ss shape; the bonding attractor as the ts

shape and the non-bonding attractor as the toroidal shape. Given that the same shapes have been observed for the deuteron [3], it is inferred that these attractors are actually different shapes of the electron.

The results presented in Fig. 2 are paramount to understand the chemical bond. The bond area was found to be inverse proportional to the correspondent bond energy. Something similar has been observed before. It is common knowledge that as the number of bonds increases between two carbon atoms, the interatomic distance diminishes. By this way, a single bond is larger than a double bond and a double larger than a triple bond. Thus, it is not strange that another dimensional relationship does occur between the bond area and the bond energy. However, as observed in Fig. 2, the same number of bonding electrons, 8, produced the main chemical bond between the bonded atoms in: C_2 , CN^- and CO , rendering different bond areas and bond energies. This means that those electrons are changing sizes in the bond and their longitudinal cross section area corresponds to different energies.

How all these electrons are together in a progressively smaller place? Electrostatic repulsion is non-existent in these arrangements. This is because, all these electron charges are neutralized by the counter charge from their atom nuclei. This will certainly help to have all of them in just one location. In a given molecule, most of the time an even number of electrons are found in the bond between two atoms. This is because the magnetic coupling between valence electrons magnetic momenta renders such even number and diamagnetism to the bond. Paramagnetism occurred in two cases O_2 and NO , to which, the electron distribution helped to locate where is the uncoupled electron producing it.

Another example of inverse proportion between the occupied longitudinal cross section area and the bond energy can be found in nuclear isotopes, where it is observed the general trend of reduction in the isotope radius as the number of neutrons increases in the isotope. Reference [14] presents such relationship for oxygen isotopes. This means more nuclear bonding energy to keep all those neutrons in the nucleus in a progressively smaller longitudinal cross section area. Just what was observed in Fig. 2 with electrons instead. Therefore, it is believed that no repulsive electric forces manifest in the chemical bond situation. More likely, the bonding electrons behavior is controlled by the properties of their masses, i.e. mass fusion.

Hence, before the bond can occur, valence electrons will naturally repel each other because of mass repulsion. Thus, an activation energy would be needed to overcome such repulsion. After that, the bond occurs as a consequence of valence electrons mass fusion. Consequently, this mass fusion defect or gain will translate to an energy release or increase respectively. This answers what in a molecule changes in mass to account for the chemical energy.

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