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The Concept of Bond Order : Rapid and New Innovative Methods for Prediction of Bond Order of Diatomic and Polyatomic Molecules / Ions Without Using Molecular Orbital Theory in a Very Short Time

KEYWORDS: In the Classroom; Physical Chemistry; Molecular Orbital Theory; Diatomics, Polyatomics; Bond Order; Lewis Structures; Active Learning.

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ABSTRACT *For the prediction of electronic and molecular properties of a substance a clear understanding of the concept of bond order is vitally important to students of chemistry in undergraduate, graduate and also in postgraduate level. Knowing the values of bond order students are able to solve different kinds of problems related to bond length, bond strength, bond dissociation energy, thermal stability and reactivity of the molecules/ ions. Several studies have noted that the prediction of bond order using molecular orbital theory (MOT) for diatomic and polyatomic molecules / ions is very difficult for students at all levels of learning chemistry. The methods generally used to find the bond order of diatomic and polyatomic molecules / ions are time consuming because these are based on MOT and electronic structure of the molecules / ions. On the basis of our investigation of a large number of diatomic and polyatomic molecules / ions, we report here new innovative methods for prediction of bond order in a very short time without using MOT and electronic structure of the molecule / ion. We can strongly recommend that these methods will be very useful and rapid for the prediction of bond order of a large number of diatomic and polyatomic molecules / ions.*

Introduction

The nature of chemical bonding and molecular geometry is mainly described in terms of valence bond theory (VBT). The main postulate of valence bond theory is that bonds result from the sharing of electrons in overlapping of orbitals of bonded atoms. These orbitals may be *pure atomic orbitals* or *hybridized atomic orbitals* of individual atoms. VBT describe the electrons in overlapping orbitals of bonded atoms as being localized in the bonds between the two atoms involved in bonding. The concept of hybridization based on VBT is used to predict the geometry of a molecule or ion.

In molecular orbital theory (MOT), we postulate that molecular orbitals (MOs) are formed by the combination of atomic orbitals on different atoms, so that electrons in them belong to the molecule as a whole. In some polyatomic molecules, a molecular orbital may extend over only a fraction of the molecule. So, the prediction of bond order between bonded atoms using MOT might be not as accurate as predicted by VBT. VBT is descriptively attractive and it lends itself well to visualization. MOT gives better descriptions of electron cloud distributions, bond energies and magnetic properties, but its results are not as easy to visualize. VBT and MOT are alternative descriptions of chemical bonding. They have strengths and weaknesses, so they are complementary.

What is a Chemical Bond ?

We define chemical bond as "when attractive and repulsive forces between two atoms are well balanced or when these attractive and repulsive forces are in equilibrium then chemical bond formation takes place".

Need of Chemical Bond Formation :

Each atom has a tendency to acquire the electronic configuration of its nearest inert gas, if possible, that is why, it forms a number of bonds. But, there are so many molecules and ions in which atoms are not having inert gas configuration. If we go through the electronic configurations of some atoms, and molecules formed by them then we find that, in general, an atom forms an equivalent number of bonds to the number of unpaired electrons present in it. For example, hydrogen, oxygen and nitrogen atoms are having one, two and three unpaired electrons, respectively, and these atoms form the same number of bonds i.e. one, two and three respectively. So, we can say that each atom has a tendency to complete the duet of its each and every atomic orbital, if possible, by bond formation and this is called 'duet rule' or 'law of duet'.

Utility of Bond Order :

For the prediction of electronic and molecular properties of a substance a clear understanding of the concept of bond order is vitally important to students of chemistry in undergraduate, graduate and also in postgraduate level. Knowing the values of bond order students are able to solve different kinds of problems related to bond length, bond strength, bond dissociation energy, thermal stability and reactivity of the molecules / ions.

Several studies have noted that the prediction of bond order using molecular orbital theory (MOT) for diatomic and polyatomic molecules / ions is very difficult for students at all levels of learning chemistry. The methods generally used to find the bond order of diatomic and polyatomic molecules / ions are time consuming [1,2,3,4,5] because these are based on MOT and electronic structure of the molecules / ions.

Recently, Arijit Das [6,7] reported new innovative methods for prediction of bond order of diatomic molecules / ions and oxide based acid radicals in a very short time but when we go through the research articles we found that the methods were not common for all the species and are not applicable for polyatomic molecules such as BF_3, CH_4, CO_2 etc. [6,7]. On the basis of our investigation of a large number of diatomic and polyatomic molecules / ions, we report here new innovative methods for prediction of bond order in a very short time without using MOT and electronic structure of the molecule / ion. We use concepts and rules of atomic structure as basic approach for finding

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the bond order of different diatomic and polyatomic molecules and ions. By knowing the electronic configurations of bonded atoms in a covalent molecule or ion we can easily predict the bond order between two bonded atoms.

How to determine Bond Order ?

Bond order is a number which is used to define the degree of covalent character present between two bonded atoms in a molecule / ion. It is mainly based on MOT. In order to figure out the bond order of a diatomic molecule / ion , first we need to know the molecular orbital (MO) energy level diagram or molecular electronic configuration of the molecule / ion then we can predict the bond order of concerned molecule / ion using the following general formulation :

Bond order = ½ **(Ne BMO – Ne ABMO)**

Where Ne BMO = Number of electrons present in bonding molecular orbitals (BMO),

Ne ABMO = Number of electrons present in anti-bonding molecular orbitals (ABMO),

But the drawback of this formulation is that first we have to draw the MO energy level diagram or write the molecular electronic configuration of the molecule / ion which is time consuming process. For example in case of O_2 molecule if we draw MO energy level diagram then we find that there are 10 electrons in BMO and 6 electrons in ABMO, hence the calculated bond order using above formulation comes out to be two and this whole process is very much time consuming.

For polyatomic molecules / ions, bond order can be calculated using following equation :

Bond Order = Nb / Nrs

Where Nb = total number of bonds present between two concerned bonded atoms in all resonating structures,

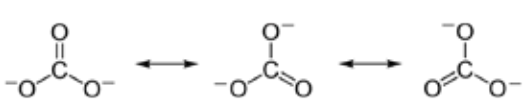
Nrs = total number of resonating structures of given molecule / ion.

This formulation also requires all possible canonical electronic structures of the molecule / ion which is again very much time consuming process. For example, if we want to predict the bond order between carbon and oxygen atom in CO_2 and CO_3^{2-}, then first we have to draw their all possible electronic structures, which are as follow:

$$O_1{=}C_1{=}O_2 \leftrightarrow {}^{+}O_1{\equiv}C_1{-}O_2^{-} \leftrightarrow {}^{-}O_1{-}C_1{\equiv}O_2^{+}$$

(1) (2) (3)

So, bond order between carbon atom (C_1) and oxygen atom (O_1) comes out to be (6÷3) =2 . Similarly for carbonate ion bond order can be predicted as :



(1) (2) (3)

There are 3 canonical structures of carbonate ion and total number of bonds present between carbon and oxygen atom is 4. Hence the calculated bond order comes out to be (4÷3) = 1.33. This method for calculation of bond order takes at least 4 to 5 minutes.

Methodology and Results

To simplify the calculation of bond order in a very short time we predict a method in which we require only one canonical structure of the molecule / ion.

Bond Order = 1 + (Number of π bonds ÷ Number of σ bonds)

But the disadvantage of this formulation is that first we have to draw at least one electronic structure of the molecule / ion which is time consuming process. So, to keep the matter in mind, we formulate here new innovative methods for calculation of bond order of molecules / ions in a very simple way and these methods are not based on MOT or do not require the electronic structure of the molecules / ions and are also less time consuming.

For diatomic and mono centric molecules/ ions we formulate the following equation :

Bond Order = [½ {(CEA ± C) + (PEA ±A)}] / Np

CEA = Number of unpaired electrons present in the central atom after loosing one or more electrons,

PEA = Total number of unpaired electrons present in peripheral atoms after gaining one or more electrons,

C = Charge on cation or number of electrons lost by central atom,

A = Charge on anion or number of electrons gained by peripheral atoms,

Np = Total number of peripheral atoms.

Values of predicted bond order using above equation for different systems are given in tables 1-4.

Table 1. Predicted Bond Order of Some Diatomic Molecules.

S. No.	Formula of DiatomicMolecules	CEA	PEA	Bond Order
1.	H_2	1	1	1
2.	He_2	0	0	0
3.	Li_2	1	1	1
4.	Be_2	0	0	0
5.	B_2	1	1	1
6.	C_2	2	2	2
7.	N_2	3	3	3
8.	O_2	2	2	2
9.	F_2	1	1	1
10.	CN	2	3	2.5
11.	NO	3	2	2.5
. 12.	CO	4	2	3
13.	HF	1	1	1
14.	Ne_2	0	0	0
15.	HCl	1	1	1

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Table 2. Predicted Bond Order of Some Diatomic Ions.

S. No.	Formula of Diatomic Ions	CEA	PEA	C	A	Bond Order
1.	H_2^+	0	1	1	-	0.5
2.	H_2^-	1	0	-	1	0.5
3.	He_2^+	1	0	1	-	0.5
4.	Li_2^+	0	1	1	-	0.5
5.	Be_2^+	1	0	1	-	0.5
6.	B_2^+	0	1	1	-	0.5
7.	C_2^+	1	2	1	-	1.5
8.	N_2^+	2	3	1	-	2.5
9.	O_2^+	3	2	1	-	2.5
10.	CN^+	1	3	1	-	2.0
11.	NO^+	4	2	1	-	3.0
. 12.	CO^+	3	2	1	-	2.5
13.	C_2^-	2	3	-	1	2.5
14.	O_2^-	2	1	-	1	1.5
15.	O_2^{2-}	2	0	-	2	1.0
16.	CN^-	4	2	-	1	3.0
17.	NO^-	3	1	-	1	2.0
18.	N_2^-	3	2	-	1	2.5

Table 3. Predicted Bond Order of Some Polyatomic Molecules.

S. No.	Formula of Polyatomic Molecules	CEA*	PEA	Np	Bond Order
1.	BeF_2	2	2	2	1
2.	$BeCl_2$	2	2	2	1
3.	CH_4	4	4	4	1
4.	CH_2	2	2	2	1
5.	CCl_2	2	2	2	1
6.	NH_3	3	3	3	1
7.	NF_3	3	3	3	1
8.	H_2O	2	2	2	1
9.	OF_2	2	2	2	1
10.	O_3	2	4	2	1.5
11.	PH_3	3	3	3	1
12.	PCl_3	3	3	3	1
13.	PCl_5	5	5	5	1
14.	SO_2	4	4	2	2
15.	SO_3	6	6	2	2
16.	SF_4	4	4	4	1
17.	SF_6	6	6	6	1
18.	ClF_3	3	3	3	1
19.	IF_3	3	3	3	1
20.	IF_5	5	5	5	1
21.	IF_7	7	7	7	1
22.	XeF_2	2	2	2	1
23.	XeF_4	4	4	4	1
24.	XeF_6	6	6	6	1
25.	XeO_3	6	6	3	2

* Number of unpaired electrons vary with electronegativity and number of peripheral atoms.

Table 4. Predicted Bond Order of Some Polyatomic Ions..

S. No.	Formula of Polyatomic Ions	CEA*	PEA	C	A	Np	Bond Order
1.	BO_3^{3-}	3	3	-	3	3	1
2.	CH_3^+	3	3	1	-	3	1
3.	CH_3^-	4	2	-	1	3	1
4.	CO_3^{2-}	4	4	-	2	3	1.33
5.	NH_4^+	4	4	1	-	4	1
6.	NH_2^-	3	1	-	1	2	1
7.	NO_2^+	4	4	1	-	2	2
8.	NO_2^-	3	3	-	1	2	1.5
9.	NO_3^-	3	5	-	1	3	1.33
10.	H_3O^+	3	3	1	-	3	1
11.	SiO_4^{4-}	4	4	-	4	4	1
12.	PO_4^{3-}	5	5	-	3	4	1.25
13.	SO_4^{2-}	6	6	-	2	4	1.5
14.	SO_3^{2-}	4	4	-	2	3	1.33
15.	$S_2O_3^{2-}$	6	6	-	2	4	1.5
16.	ClO_2^-	3	3	-	1	2	1.5
17.	ClO_2^+	4	4	1	-	2	2.0
18.	ClO_3^-	5	5	-	1	3	1.66
19.	ClO_4^-	7	7	-	1	4	1.75

* Number of unpaired electrons vary with electronegativity and number of peripheral atoms.

Discussion

On comparing our predicted values of bond orders with those reported by Arijit Das [6,7] we find that our methods are much better and less time consuming. On the other hand our methods can be applied for a large number of molecules / ions where as his methods have limitations [6,7] The value of bond order of nitrate ion reported by him i.e. 1.66 was incorrect because nitrogen atom can not form five covalent bonds due to absence of 'd' orbitals. Our method correctly predicts the value of bond order of nitrate ion i.e. 1.33. Moreover, our methods are based on basic concepts and rules of atomic structure i.e. electronic configurations of bonded atoms and it is very easy to find out the number of unpaired electrons in bonded atoms by simply knowing the electronic configurations of atoms.

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Conclusion

We use concepts and rules of atomic structure as basic approach for finding the bond order of different diatomic and polyatomic molecules and ions. By knowing the electronic configurations of bonded atoms in a covalent molecule or ion we can easily predict the bond order between two bonded atoms. We expect that this article will be very helpful to students of chemistry in undergraduate, graduate and also in postgraduate level. These innovative methods for prediction of bond order are very less time consuming and using these methods student can predict bond order in a very short time without knowing the electronic structure of the molecule / ion or MOT.

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