Application of Fuzzy Theory for the Evaluation of Bond Nature

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Introduction

The concept of ionicity is directly associated with character of the chemical bond and thus provide means for explaining and classifying many basic properties to molecules and solid state in chemistry and physics. After the development of the modern ideas of chemical bonds in the early days of twenty century, as Pauling has stated in his classical book [1], the following question was formulated and rigorously discussed: "if it were possible to vary continuously one or more of the parameters determining the nature of a molecule or a crystal, such as the effective nuclear charges of atoms, then would the transition from one extreme bond type (ionic) to another (non-polar covalent) take place continuously or would it show discontinuities".

Before Pauling, Lewis in 1916 and later, believed that the transition would be continuous with the idea that the shared electron pair in general, attracted more strongly by one than by the other of two unlike bonded atoms, the bond having a corresponding amount of ionic or polar character.

A theoretical measure of the ionicity based on different mathematical concepts has been presented in this research. Considering the distribution of valence electrons on each atom in a bond, we assume that the chemical properties of the atom can be expressed by means of a probability. Using the introduced probability, fuzzy model has been employed to introduce new descriptors of bond ionicity. The ionicities were calculated for 12 heterodiatomic molecules and the bonds were classified in terms of covalency versus ionicity. It was found that our proposed ionicity descriptor correlates well with the partial ionic character of the bonds.

Theoretical Background

We assume that the chemical properties of each atom in a bond can be introduced by a probability and thus the whole bond is defined by a normal set of two probabilities (p_1,

p_2 and $\sum_{i=1}^{2} p_i = 1$). Considering the fact that the total number of valence electrons are distributed between two atoms, we define the quantity (p_i) for each atom as the ratio of its valence occupancy $(N_{occ})_i$ to the total number of valence electrons N_{val} :

$$p_i = \frac{(N_{occ})_i}{N_{val}} \qquad (1)$$

where $(N_{occ})_i + (N_{occ})_j = N_{val}$ leads to a value between 0 and 1 for p_i , giving a probabilistic nature to it. Thus we deal with a normalized probability set. Now we try to find a solution for evaluating the closeness of these two probabilities to each other. In the case of equal probabilities we face with a pure covalent bond while the ionic nature of the bond becomes more as the difference between the two probabilities increases.

Results and Discussion

As its name implies, the theory of fuzzy sets, is basically a theory of graded concepts in which every thing is a matter of degree. Since its inception by L. A. Zadeh , the theory of fuzzy sets has advanced in a variety of ways and in many disciplines.[2,3]. The application of this theory can be found in the whole entry of engineering and natural sciences.

A classical (crisp) set is normally defined as a collection of elements or objects ($x \in X$, X is a reference set) that can be finite or infinite, countable or overcountable. Each single element can either belong to or not belong to a set A. For a fuzzy set, a characteristic function allows various degrees of membership for an element of a given set. If X is a collection of objects denoted generically by x, then a fuzzy set $\tilde{A}$ is a set of ordered pairs:

$$\tilde{A} = \{(x, \mu_{\tilde{A}}(x)) \, x \in X\} \qquad (2)$$

$\mu_{\tilde{A}(x)}$ is called the membership function or grade of membership (also degree of compatibility) of x in $\tilde{A}$ that maps x to the membership space. Using the fuzzy logic the membership of an element in a classical set can be either 1 for member or zero for non-

member.

If a chemical bond can be considered as a set of pairs including our defined probabilities and an appropriate membership values, is it possible to transvalue the bond

characteristic by means of fuzzy criteria? To answer this question, first an appropriate membership function should be defined according to our expectation from the chemical nature of a bond. The membership function must indicate by how much degree an element belongs to a set. Second, a theoretical method is applied to each element of a set in order to attribute a certain quantity to it. This quantity must be able to indicate of the bond ionicity and be comparable in different sets.

A proper membership function in the current study is a function shows the amount of relative closeness of the two probabilities to each other or it shows the closeness of the atomic probabilities to the reference value of 0.5. In this work, the following general membership function has been used [4],

$$\mu_{\tilde{A}(x)} = \frac{1}{1 + (x - 0.5)^{2m}} \qquad m=1, 2, 3,\ldots \qquad (3)$$

where $x=P_i$.

The fuzziness of our defined probability can be obtained according to De Luca and Termini measurement by [5]

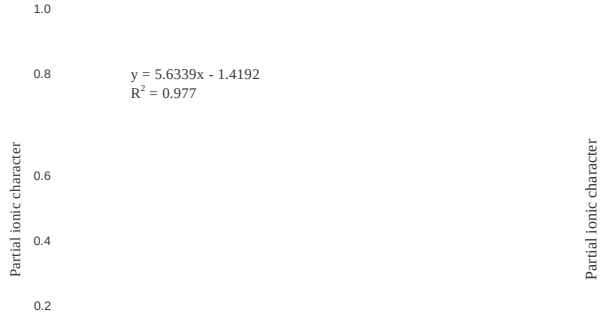
$$\Gamma_{Del} = K \sum_{i=1}^{2} \mu(x_i) \ln (\mu(x_i)) - (1 - \mu(x_i)) \ln (1 - \mu(x_i)) \qquad (4)$$

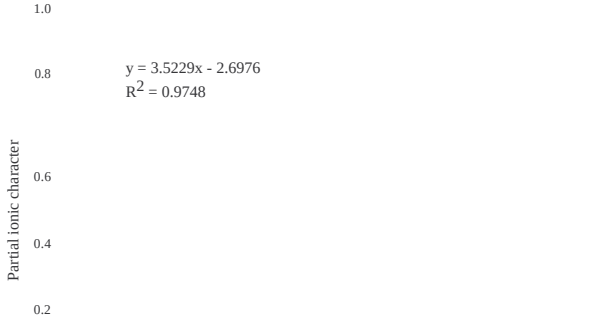
and Yager measurement by [6]

$$\Gamma_{Yag} = \frac{1}{2} \sum_{i=1}^{n} 2\mu(x_i) - 1 \qquad (5)$$

where $\mu(x_i)$ is defined in Eq. (3) with m=1.

The ionicities were obtained for different bonds in 12 heterodiatomic molecules and were compared with their partial ionic characters. The obtained results for Γ_{Del} and Γ_{Yag} are reported in Table 1 and the correlation lines are presented in Figures 1.





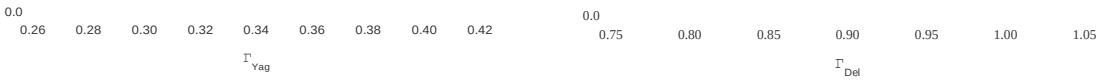


Figure 1. Correlation between partial ionic character and $\Gamma_{Yagl}\,\Gamma_{Del}$ for 12 heterodiatomic molecules

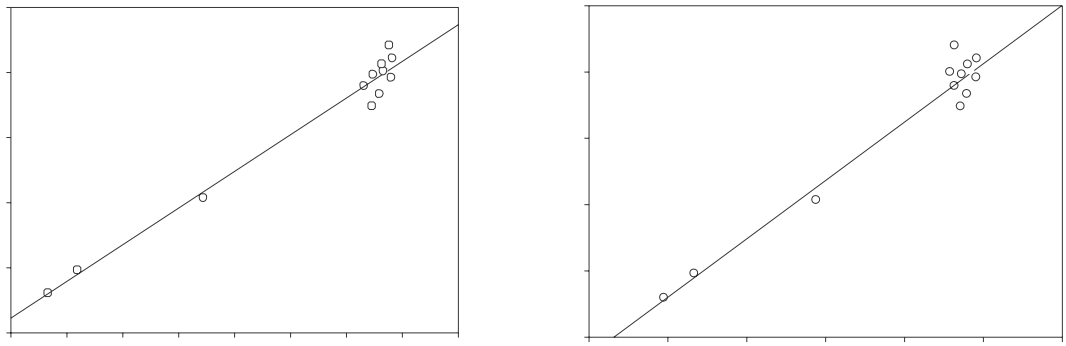


Table 1. Valence shell occupancies, atomic probabilities and ionicity values based on fuzzy theory

A-B	$(N_{occ})_A$	P_1	$(N_{occ})_B$	P_2	Γ_{Del}	Γ_{Yag}
HF	7.5424	0.9428	0.4462	0.0558	0.8937	0.3287
HCl	7.2425	0.9053	0.7398	0.0924	0.8164	0.2837
HBr	7.1746	0.8968	0.8087	0.1011	0.7977	0.2733
LiF	7.9593	0.9949	0.0031	0.0004	0.9959	0.3965
LiCl	7.9219	0.9902	0.0246	0.0031	0.9893	0.3918
LiBr	7.9019	0.9877	0.0396	0.0049	0.9853	0.3890
NaF	7.9676	0.9959	0.0221	0.0028	0.9947	0.3956
NaCl	7.9247	0.9906	0.0567	0.0071	0.9860	0.3895
NaBr	7.9023	0.9879	0.0757	0.0095	0.9814	0.3862
KF	7.9660	0.9957	0.0164	0.0020	0.9952	0.3960
KCl	7.9404	0.9925	0.0213	0.0027	0.9918	0.3935
KBr	7.9346	0.9918	0.0288	0.0036	0.9903	0.3927

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