3P058

Bond order

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1   Introduction

We have proposed new parameters named Bond order and Chemical potential in order to evaluate chemical bondings in moleculers. These values enable us to analyse stability and reactivity of aiming bondings. In this research, we have picked up small groupes of organic compounds and have calculated Bond orders and Chemical potentials. The relation between these values and structural parameters and the affects of substitutions have been investigated. The result indicates the effectiveness of proposed parameters, and now, we become able to understand chemical bondings from a new respect.

2   Theory and computational details

Tachibana proposed stress tensor density $\vec{\tau}^S(\vec{r})$ in his rigged QED theory. It is given by a 3×3 matrix, and its components $\tau^{Skl}(\vec{r})$ are given by

$$\tau^{Skl}(\vec{r}) = \frac{\hbar^2}{4m} \sum_i \nu_i \left\{ \Psi_i^*(\vec{r}) \frac{\partial^2 \Delta \Psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \Psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \Psi_i(\vec{r})}{\partial x^l} + \frac{\partial^2 \Delta \Psi_i^*(\vec{r})}{\partial x^k \partial x^l} \Psi_i(\vec{r}) - \frac{\partial \Psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \Psi_i(\vec{r})}{\partial x^k} \right\} \quad (1)$$

for $k, l = 1, 2, 3$. If the largest eigenvalues of $\vec{\tau}^S(\vec{r})$ are positive, there is a extensional stress at that point, and if the largest eigenvalues are negative, there is a compressional stress at that point.

The sum of eigenvalues are connected to quantum energy density with

$$E = \frac{1}{2} \sum_k \tau^{Skk}(\vec{r}) \quad (2)$$

Between bonding two atoms, this energy density has a maximum at a point called Lagrangean point. We reguard this values of energy density at Lagrangean point as the energy density which can characterize the bonding. Bond order b_ε is given by

$$b_\varepsilon = \frac{E_{AB}}{E_{H_2}} \quad (3)$$

This parameter is the devision of the energy density of aiming bonding at its Lagangean point by the same of hydrogen molecule. Therefore, it can evaluate the strength of the bonding relatively. And the devision of this enegy density by electron densty at same point shows the enegy which an electron might have at same point. This enegy indicates the reactivity of electron in the bonding, and we define it as Chemical potential. Another Bond order b_μ is given by

$$b_\mu = \frac{E_{AB}/\rho_{AB}}{E_{H_2}/\rho_{H_2}} \quad (4)$$

This parameter is the devision of the Chemical potential of aiming bonding at Lagrangean point by the same of hydrogen molecule. Therefore it can evaluate the reactiveness of the bonding relatively.

We chose ethan, ethen and ethyn as the basic structures, and chose Bromine, methyl group, Chlorine, Cyano group, Fluorine, Amino group, Nitro group, hydroxyl group, Phenyl group and thiol group as substituition groups. Each of three structures are substituted one terminated hydrogen by these substitution one by one, and we calculate Bond orders, Chemecal potentials and some structural parameters with 6-311++G** basis set and using Hartree-Fock and MP2 method. We also have investigated

the dependeny on basis sets, and have calculated these parameters with STO-3G, 6-31G, 6-311G basis sets(with polarization functions and diffusion functions added or removed) using Hartree-Fock and MP2 method. All calculation were achived by Gaussian03 and MRQED program packages.

3 Result and discussion

b_ε and b_μ of bondings between two carbon atoms have strong correlations with electron density for ethan and ethen substitution derivatives. From the respect to electronegativities, b_ε of the sustitution derivatives of Fluorine, Bromine and Chlorine are related to their erectoronagativities. This is because the atom which has a large electoronegativity make much localized the surrounding electron density. And bond orders also have strong correlation with distances of two carbon atoms. The other hand, substitution derivatives of ethyn have slightly different bahviors. The correlations between bond orders and distances of two carbon atoms are a little bit weaker than other two species. Due to the electronegativity of the substitution group, the electron density arround the boning of two carbon atoms decreases, and this makes bond orders ensmall. But methyl group and phenyl group have a large amount of electrons and they tend to supply their electrons to surroundings. Therefore that electron density increases and bond orders of these are a little bit larger than other substitution derivatives. Fig.1 shows that the bond order b_ε of triple bond of ethyn fluorine is especially different from other substitution derivatives'. The bond length is much shorter than others. This is because its small atomic radius, and its large electronegativity. And b_ε is much larger than other other substitution derivatives. Fluorine has a largest electronegativity among all atoms, and take away surrounding electrons, and make a very strong and also short bonding. This bonding is too small, so another interaction occurs and get back a part of removed electrons using the π orbitals. This is why b_ε of ethyn fluorine differs from others, and this is a well-known charactaristic of fluorine atom. Therefore this result shows that b_ε can reproduce theoretical charactaristics by itself.

4 Sammary

Acording to the results of substitution affects against bondings, the behaviors of Bond orders, b_ε and b_μ have good agreement with theoretical foreknowledges such as stablity and reactivity of the bonding. Threfore, for the small groups of organic compounds, the analysis of bonding affects based on these new parameters has enough validity against the way before. We will calculate these parameters with more and more compounds and discass the result in order to prove the stiff validity of proposed parameters.
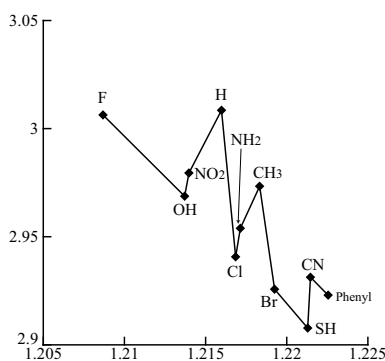

1: The affects of substitution against b_ε and atomic distance.