Explore the Nature of Chemical Bonds in the Scope of a Donor-Acceptor Model Using Density Functional Theory

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Abstract

The key to understanding the physical and chemical properties of materials lies in the nature of chemical bonds. With the help of electronic structure theories such as the Density Functional Theory, people can approach the quantum mechanical behaviors of electrons. But it is still difficult to extract the nature of chemical bonds out of the electron based quantities. In this work, an algorithm, which is derived from the donor-acceptor model is discussed and applied. With the help of the algorithm, molecules of halogen acid and ionic compounds are studied and characters of bonds are visualized.

Keywords

Nanocluster, Nanoalloy, Sulfur-metallic interaction.

1. Introduction

The investigation of chemical bonds is important in understanding the formation, physical and chemical properties of materials[1,2]. The classical way to understand a chemical bond, for example, is to assume a pair of shared electrons move in between two atoms as the covalent bond[3]. Such a description is frequently used in the early days of development in chemistry and is still used in the education for its reasonable accuracy in the description of the inter-atomic bindings. However, with the emergence of quantum mechanics in the last century, it is difficult to relate such a chemical picture of bonds to the description of electrons in quantum mechanics which is a wave function based description[4]. Although the electronic density can be obtained using the wave function for the probabilistic description of electrons, it is still not related to the binding between atoms. Such a problem is not solved until the concept of "electron localization function" (ELF) is introduced[5,6]. The ELF by definition measures the localization of electrons in atoms, molecules, and bulk systems. When the value of ELF is larger than 0.8, the corresponding region is the chemical bond resides. If the value of ELF is close to 0.5, the corresponding region is filled with electron gas[7]. So the ELF is a way to map the wave function based on the classical concept but not the only picture to rely on. Other methods are developed later on[8-11]. In this work, another electronic density based method will be introduced and demonstrated.

2. Algorithm

Originated from the donor-acceptor model[12-15], for a system with more than 1 atom, it is always possible to treat it as the combination of two parts to study the interaction of the two. For example, we can assume the electrons in a whole molecule forms the electronic density $n(\vec{r})$. And the molecule can be considered as a complex of two parts A and B. In the scope of "donor" and "acceptor", the molecule can be described in the distribution of the probability of electrons and holes as $c(\vec{r})$,

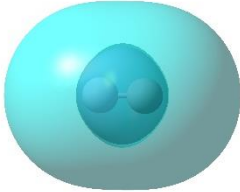$$c(\vec{r}) = n(\vec{r}) - [n_A(\vec{r}) + n_B(\vec{r})] \tag{1}$$
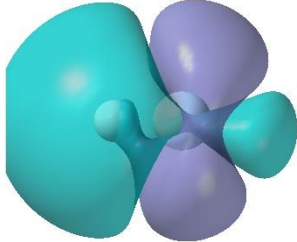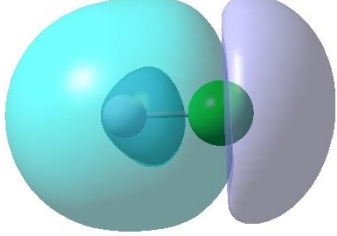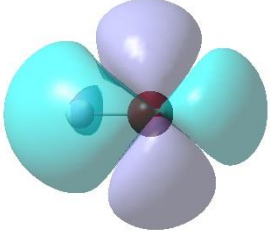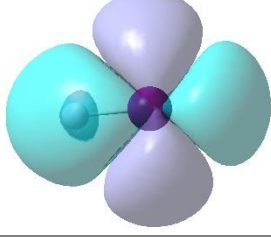
And the charge conservation is guaranteed,

$$\int_V c(\vec{r}) = 0. \tag{2}$$

This model can be integrated into Density Functional Theory (easily) and its accuracy is at the same level of DFT as a density-based algorithm. The DFT assumes the electron-electron introduction can be represented by a background potential such that the Schrodinger equation is transformed into the Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + v_s[n(\vec{r})](\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \tag{3}$$

Table 1 The images of electrons and holes for the halogen acid. Color codes: cyan=iso surface of the probability density of electrons; purple=iso surface of the probability density of holes.

	Bond length (Å)	Images of electrons and holes
H2	0.7435	
HF	0.9487	
HCl	1.3183	
HBr	1.455	
HI	1.6393	

The electron-electron interaction is turned into the Kohn-Sham potential, vs which is a functional of the electronic density. The solution of the equation contains the wave functions and energies, $\phi_i(\vec{r})$ and ε_i.

In a standard procedure of DFT simulations, the electronic density can be obtained after the geometry is relaxed[16,17]. With the known atomic position, one can manually split the system into two pieces, A and B to meet a particular research interests[18,19]. Then the electronic density for part A and B, $n_A(\vec{r})$ and $n_B(\vec{r})$ can be calculated independently without relaxation. Then the redistribution $c(\vec{r})$ is calculated using Equation 1.

The charge redistribution shows the electronic probability change in forming the complex of A and B. The region of negative values show the deficiency in electron which can be regarded as (the distribution of) "holes". In contrast, the region of positive values shows the surplus of (the distribution of) electrons. Such an algorithm clearly shows the charge transfer from one side to another: it causes surpluses in electrons and leaves holes behind.

3. Simulation Results

This algorithm can be applied to a series of compounds to study the polarization of electrons and holes. For simplicity, the family of halogen acid will be investigated first, including H_2, HF, HCl, HBr, and HI. The results are summarized in Table 1.

Most of the halogen acid including the H2 molecule does show the covalent character except the HCl molecule: electrons and holes are not separated but stay tangled with each other. Such character indicates that the covalent binding is just the redistribution of electrons without electrostatic features.

On the other side, the ionic bonds behave differently than the covalent bonds. For comparison, some compounds of ionic bonds are simulated including KBr, NaOH, and CuSO4.

Table 2 The images of electrons and holes for some ionic compounds. Color codes: cyan=iso surface of the probability density of electrons; purple=iso surface of the probability density of holes.

	Bond length (Å)	Images of electrons and holes
KBr	2.9984	
NaOH	1.9151	
CaSO4	2.9099 (Ca-S)	

The ionic compounds show significant characters than the covalent compounds including significant longer bond lengths between the donor and acceptor and well-separated electrons and holes. From the donor-acceptor model, the HCl is closer to the ionic compounds but with a much smaller bond.

We can then summarize the results and quantify the type of bond out of the donor-acceptor model by a score, the "score of ionic". The results are represented in Figure 1.
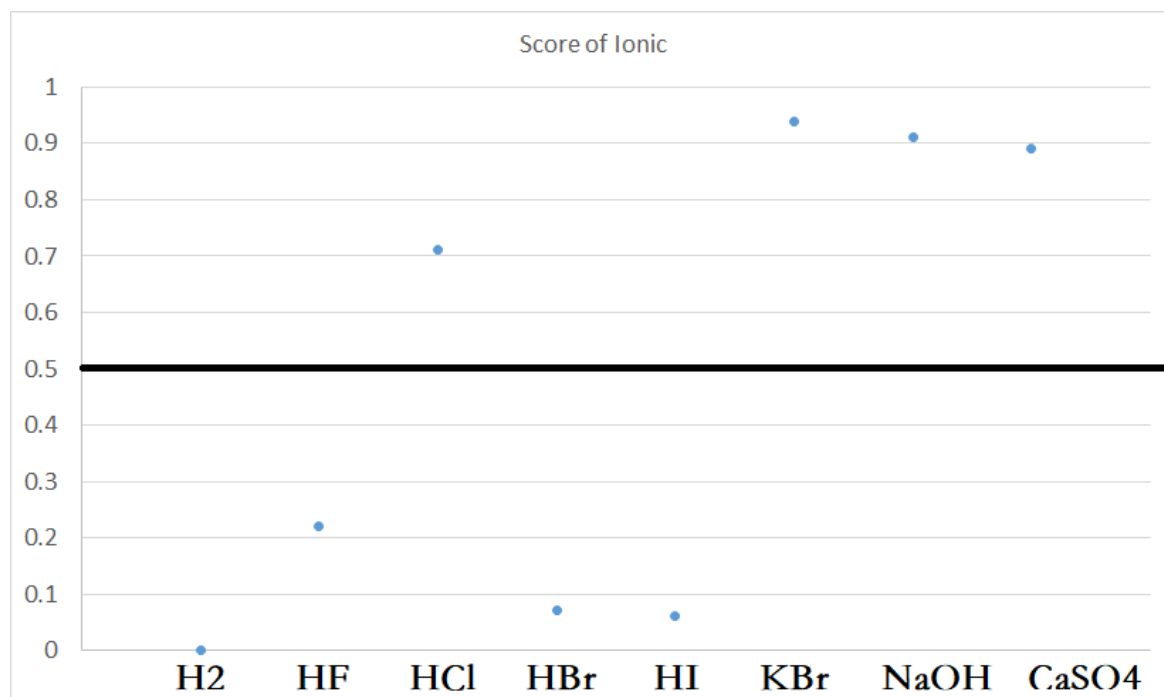

Figure 1 Score of the compound to evaluate the property of the bond.

4. Summary

In this work, the donor-acceptor model is extended with the electronic probability density simulated by DFT. The results show the redistribution of the electronic density and can be interpreted as electrons and holes. With the help of the donor-acceptor model, we investigated halogen acid and some ionic compounds. The model clearly shows the characters of charge redistribution and the interactions. The covalent bonds are normally constituted of tangled electrons and holes while the ionic bonds are constituted of well-separated electrons and holes. Integrated with DFT, the donor-acceptor model provided details of the bonds within molecules. The algorithm can also be extended to other systems.

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