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Determining the Type of Bond between Diatomic Cluster of Platinum and Hydrogen: Quantum Mechanical Approach

(Penentuan Jenis Ikatan antara Kelompok Dwiatom Platinum dan Hidrogen: Pendekatan Mekanik Kuantum)

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ABSTRACT

Type of bond is vital to understand the mechanism of interaction between corresponds atoms. We used three kinds of method to determine the type of bond between diatomic cluster of platinum and hydrogen: types of element, electronegativity and electron distribution. In this work, we found that the results from these three methods are not unanimously agreed with each other for bond type forming in platinum-hydrogen diatomic cluster. Thus, we conclude that the type of bond is hybrid of both: mainly covalent and slightly ionic.

Keywords: Diatomic cluster; hybrid-bond; platinum; type of bond

ABSTRAK

Jenis ikatan adalah penting bagi memahami mekanisme sesuatu interaksi antara dua atom terbabit. Kami telah menggunakan tiga kaedah dalam menentukan jenis ikatan di antara kelompok dwi-atom platinum dan hidrogen: jenis unsur, keelektronegatifan dan taburan elektron. Dalam kajian ini, kami dapati bahawa keputusan daripada ketiga-tiga kaedah tidak sepakat mengenai jenis ikatan yang terbentuk antara kelompok dwi-atom platinum dan hidrogen. Oleh itu, kami menyimpulkan bahawa jenis ikatan yang terbentuk adalah campuran ikatan kovalen dan ionik.

Kata kunci: Ikatan kacukan; jenis ikatan; kelompok dwiatom; platinum

INTRODUCTION

Fuel cell is one of the promising renewable energy. It converts chemical energy into electrical energy with high efficiency. It also produces zero-waste of harmful emission, only water and heat. This idealistic system of energy has been setback due to the cost of manufacturing it. The main component which is too expensive but too important to ignore is the catalyst used. The heart of any fuel cell is the platinum catalyst.

The catalyst can cause electron to dissociate from hydrogen atom. This reaction happened due to the interaction between catalyst and reactant. The interaction can be understood in term of chemical bonding. Thus, information regarding chemical bonding between catalyst and reactant can help to understand the mechanism involved in the reaction. Subsequently, an alternative can be found to overcome the high-cost problem of fuel cell.

In search for an alternative catalyst, the alternative candidates must have the criteria like platinum catalyst. One of the criteria is the bond type formed between reactant and catalyst. This is to ensure the reaction mechanism will be like the original platinum catalyst. As stated by Wang et al. (2006), information of bond type is also important in energy calculation, which can be correlates with activation energy.

There are lots of research has been done regarding mechanism of adsorption between catalyst (platinum) and reactant. In 2007, Zhou et al. shows that the type of bond between platinum catalyst and hydrogen changing from metallic bond to covalent bond as the increment of H loading occurred.

Meanwhile, another work done by Arnadottir et al. (2010) stated that the type of bond formed between platinum and hydrogen is hydrogen bond. However, the hydrogen is not a single atom, but an atom in H_2O compound. Thus, with slightly differ structure, the type of bond can totally change. Thus, our work has been done with purely single hydrogen atom to assure its pureness.

In this research, only two types of bond will be referred, which are ionic bond and covalent bond. Moreover, we are also open to the idea of mixture of bond type. Pauling (1932) has proved this idea which can also be found in previous work done by Othman et al. (2015).

The objective for this research was to find the type of bond formed during interaction between platinum atom and hydrogen atom from the electron distribution using quantum mechanical approach. All the calculation is based on the density functional theory framework using the potential energy of exchange and correlation as proposed by Perdew and Zunger (1981) and Slater (1930) correlation functional where barely known as local density approximation (LDA).

Next, we will discuss in detail about our method and concept in Theory and Methods section. After that, presenting our finding in Result and Discussion section. Finally, we conclude our research in the Conclusion section.

THEORY AND METHODS

Three molecules have been studied, which is sodium chloride molecule, hydrogen molecule and platinum-hydrogen diatomic cluster to determine the type of bond formed. Sodium chloride molecule and hydrogen molecule have been chosen to validate the method used by accurately determine their bond type which is ionic bond and covalent bond respectively. After that, the calculation is done onto platinum-hydrogen diatomic cluster to determine its type of bond.

To determine type of bond, theoretically there were three simplified approach which can be used throughout the computational approach. The simplest way of determining types of bond is by deducing at the type of elements involved in the compound. Basically, if a non-metal element interacts with the non-metal element, it will experience the Van der Waals interaction resulting into formation of covalent bond. Meanwhile, metal with non-metal will produce ionic bond.

Secondly, by involving the calculation of the electronegativity differences between the diatomic clusters, we can also deduce the types of bond involved. All different combination can be resulting into different types of bond which can be simplified in Table 1.

TABLE 1. Determine type of bond based on difference in electronegativity of the corresponding atoms

Difference in electronegativity	Type of bond
Less than 0.5	Nonpolar covalent bond
Between 0.5 and 1.6	Polar covalent bond
Between 1.6 and 2.0	If there is metal involved, its ionic bond
	If there are only nonmetal involved, its polar covalent bond
More than 2.0	Ionic bond

Naturally, the phenomena of all the compound who's experiencing the ionic and covalent bond can be describe directly as the transition of electron donation-acceptance or sharing between two elements as follows:

Covalent: A chemical bond formed by sharing a pair of electrons; Ionic: A chemical bond formed by transferring electron from one atom to another.

Unfortunately, this simple understanding of the natural phenomena is unusable to define the exact electron donator or acceptor in a complex heavy element (in our case is platinum element). This deficiency led us to take an intensive care on determining the types of bond involve by simulating the electron density distribution using quantum mechanical approach. We have decided to calculate the electron density distribution through the quantum mechanical approach under the framework of density functional theory (DFT). The difficulties of complex heavy element, makes this method worth to be used. In this method, we intensively analyze the bond type involved, by carefully looking at the distribution of electron density throughout the system. In explanation, if the electron density is covered all surround the two interacting atoms, it can be deduced as covalent bond type occurred. Meanwhile, if the electron density localized only around one of the two atoms, it is clearly shown that the bond types can be directly considered as an ionic bond.

Based on all those three methods, the most accurate method is by looking at the electronic distribution. This method has been reviewed by Bader in 1991, in which the quantum theory of molecular structure can be used to determine the type of bond accurately. In microscopic world, strange phenomena might happen where the phenomena involved in light metal might be totally different with heavy metal. Those differences occur contributed by the different number of electron in an element. Thus, in this computational study, three combination of software has been used to get the electronic distribution. The software used throughout the research are Octopus version 5.0.1 for quantum mechanical calculations under DFT framework, Avogadro version 1.0.1 and VESTA version 3.3.2 used for technical support and result analysis.

All the three methods have been used to determine the bond type for each of the compounds; hydrogen molecule, sodium chloride and platinum-hydrogen diatomic cluster. First, for the third method (electronic distribution), the diatomic cluster was constructed using Avogadro software by positioning an atom using the interatomic distance (bond length) which is equal to the sum of the radii for both atoms. Next, by using Octopus software, we begin our calculation studies from the geometry optimization step by applying the conjugate gradient Broyden-Fletcher-Goldfarb-Shannon (CG-BFGS) algorithm with a few enhancements known as CG-BFGS2 for better efficiency. After that, the electronic ground state calculation of a compound was proceeds using the same software, Octopus. This step is crucial and resulted a very important parameter which is the electron density distribution in the system. The parameter used for geometry optimization and ground state calculation in Octopus for all molecules is stated as in Table 2. Finally, the electronic density is displayed and analyzed by using the Vesta software.

Our focus will be the diatomic cluster of platinum and hydrogen. However, to properly distinguish which type of bond is formed between the diatomic clusters, we have created a baseline with few molecules, which is already confirmed its type of bonds. The chosen molecules are H_2 and NaCl, which correspond to covalent and ionic molecule respectively.

One thing to be noted is that diatomic cluster of platinum and hydrogen is an open shell. Thus, we treated the extra electron as free electron but confined to platinum atom. This will reenact the behavior of electron in metal as a sea of free moving electron.

TABLE 2. Parameter used in geometry optimization (GO) and ground state (GS) calculation using Octopus software for all molecules under studies

Geometry optimization	Ground state
CalculationMode = GO	CalculationMode = GS
Units = eV_Angstrom	Units = eV_Angstrom
%Species	%Species
'Cl'|35.453|spec_ps_hgh|17	'Cl'|35.453|spec_ps_hgh|17
'Na'|22.989769|spec_ps_hgh|11	'Na'|22.989769|spec_ps_hgh|11
'Pt'|195.078|spec_ps_hgh|78	'Pt'|195.078|spec_ps_hgh|78
'H'|1.00794|spec_ps_hgh|1	'H'|1.00794|spec_ps_hgh|1
%	%
XYZCoordinates = "molecule.xyz"	XYZCoordinates = "molecule.xyz"
Radius = 2.50	Radius = 2.50
Spacing = 0.175	Spacing = 0.175
GOMethod = cg_bfgs2	Output = wfs + density + elf + potential
	OutputHow = cube

Finally, with all the result from the methods as stated before, we will conclude the bond type possess by diatomic cluster of platinum and hydrogen.

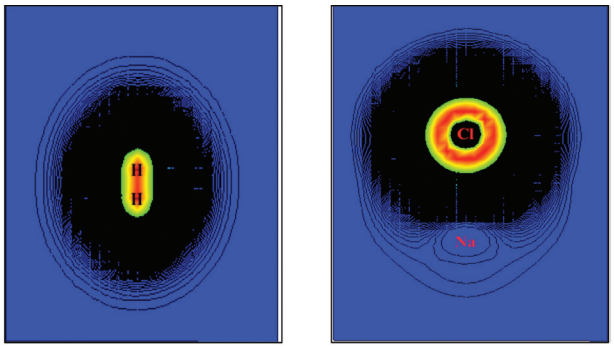
RESULTS AND DISCUSSION

Figure 1 shows the electronic distribution for the guideline, which are H_2 and NaCl:

From Figure 1, the region with dense contour line is corresponds to higher electron density. Since, the electron density in hydrogen diatomic is equally divided. Thus, it means that hydrogen diatomic cluster having a covalent bond. Meanwhile, for NaCl diatomic cluster, the electron density is not equally divided and tendency more to Cl atom. This means that Cl atom receive an electron from Na atom. Thus, it proves that NaCl diatomic cluster is having an ionic bond. By using Methods 1 and 2, it is proven that the type of bond is consistent with the result shown in Figure 1. It can be simplified as in the Table 3.

Based on Figure 1 and Table 3, the method in determining the type of bond via electronic distribution is validated. Thus, the calculation of electronic distribution for platinum-hydrogen diatomic cluster can be accepted. Table 4 shows the summary of method 1, 2 and 3, which applied to platinum-hydrogen diatomic cluster:

From Table 4, we may conclude that the type of bond between platinum and hydrogen is mainly covalent and slightly ionic. Since the result is not unanimously agree with one type of bond but mix of both. To explain this, we may look at the reaction occurred between platinum and hydrogen. In the reaction between hydrogen and platinum, hydrogen will ionize by releasing electron. However, the released electron will not transfer or accepted by the platinum but will be a free moving electron. This is consistent with the mechanism in fuel cell, which free moving electron will go through the outer circuit and recombine with hydrogen ion at the other end of the fuel cell. In other word, the covalent properties are for adsorption, while the ionic properties are for electronic dissociation.



(a) Hydrogen diatomic cluster (covalent)

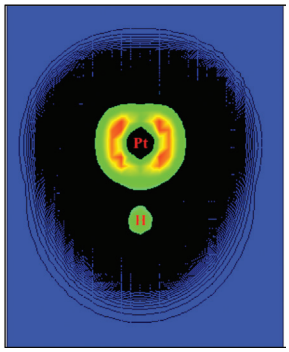
(b) NaCl diatomic cluster (ionic)

FIGURE 1. Electronic distribution of hydrogen diatomic cluster and NaCl diatomic cluster

TABLE 3. Summary of implementation of Methods 1 and 2 for H_2 and NaCl

Diatomic cluster	Method 1: Types of element	Method 2: Electronegativity
Hydrogen	Hydrogen - nonmetal Since, nonmetal interact with nonmetal will produce covalent bond	Hydrogen: 2.2 **Δ: 2.2-2.2 = 0** Since, less than 0.5. Thus, nonpolar covalent bond
Sodium Chloride	Sodium - metal Chloride - nonmetal Since, metal interact with metal will produce ionic bond	Sodium: 0.93 Chloride: 3.16 **Δ: 3.16-0.93 = 2.23** Since, more than 2.0. Thus, ionic bond

TABLE 4. Summary of Methods 1, 2 and 3 for platinum-hydrogen diatomic cluster

Method	Calculation	Result
Method 1: Type of elements	Platinum: Transition metal Hydrogen: Nonmetal	Ionic
Method 2: Electronegativity	Platinum: 2.28 Hydrogen: 2.2 Δ: 2.28 – 2.0 = 0.08	Nonpolar covalent
Method 3: Electronic distribution		Mainly covalent and slightly ionic

Another point noted from Table 4 is the value of electronegativity for platinum. As a metal, platinum is one of the few metals that possess high electronegativity values. Higher electronegativity values mean that the atom tendency to attract electron. Unlike a normal ionic molecule such as sodium chloride, which sodium as metal transfer electron to nonmetal chloride, hydrogen as nonmetal have more tendency to release electron than platinum itself. Thus, this contrast proves that platinum-hydrogen interaction is not simply an ionic molecule but having both types of bond, ionic and covalent.

Finally, if we compared graphically between the diatomic cluster with hydrogen molecule and the diatomic cluster with sodium chloride molecule, we can observe that the electronic distribution for platinum-hydrogen diatomic cluster have both characteristic. For an ionic compound, the electron completely transfers from one atom to another. This can be clearly seen from red region for both sodium chloride and the diatomic cluster. Both regions only tribute in one of the two atoms. The red region indicates higher electron density of valence shell. Meanwhile, for ionic compound, the electron is shared between both atoms. This can be observed by the shape of the contour line. As in hydrogen molecule and the diatomic cluster, both have similar shape of contour line. Both contour line is equally distributed between the two atoms, indicates that the electron is shared rather than transferred. Thus, with this mix result, this would be another evidence that the type of bond forming between diatomic cluster of platinum and hydrogen is mix of both type of bond; ionic and covalent bond.

CONCLUSION

We have calculated and determined the bond type for hydrogen molecule, sodium chloride molecule and platinum-hydrogen diatomic cluster using the three methods: type of element, electronegativity and electron distribution. For hydrogen molecule and sodium chloride, both are just a typical molecule having a chemical bond of covalent and ionic respectively.

However, based on the three methods, we are having a non-normal type of bond for platinum-hydrogen diatomic cluster. The bond formed between the atoms is mainly covalent but slightly ionic. This is consistent with the behavior of such interaction in a fuel cell system.

The next approach in the future is to relook at this type of bond in bigger structure such as a bulk phase platinum surface adsorption attached with a single hydrogen atom to improve the hydrogen dissociation mechanism in fuel cell system.

In conclusion, we have succeeded in determine the type of bond between diatomic cluster of platinum and hydrogen, which is mainly covalent and slightly ionic.

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