

INVESTIGATION OF THE ATOMIC CHARGES, ELECTRON DENSITY, ELECTRONEGATIVITY, AND BOND LENGTH OF BeH₂ WITH GGA + U FUNCTIONAL

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ABSTRACT: In this paper, Bader atomic charge for BeH₂ was calculated. Pauling electronegativity for Be, bond length and hydrogen ionic radius for BeH₂ were also determined. Electron density difference GGA + U and GGA-PBE was plotted. It was observed that GGA + U does not notably charge the charge state of the ions. As expected, the charge difference between the two hydrogen ions was 0.05e (approximately).

KEYWORDS: Electronegativity, Bader atomic charges and bondlength.

1 INTRODUCTION

The Chemical bonding property of BeH₂ has been explored through first principle DFT-GGA calculations (Bao-Tian, et al, 2010). It was established that Be-H bond displays a mixed ionic/convalent character. It was also observed that the ionicity in the Be-H bond is mainly featured by charge transfer from Be 2s to H 1s atomic orbital's Bao-Tian, et al, 2010).

Profound perception into the nature of Be-H bonding in the orthorhombic BeH₂, and valence charge density distribution have also been investigated, using two contour plots, both of which, it was found, that the hydrogen charge density shape was deformed toward the direction to the nearest-neighbour atoms: the charge density around H atoms was higher than that around Be atoms, thus indicating the aforementioned significant ionic-type charge transfer from Be 2s to H 1s state (Bao-Tian, 2010).

The purpose of this up-to-date work is to examine the atomic charges for BeH₂, using electron decomposition method (Henkelman *et al*, 2006), anion-cation electronegativity difference, Be-H bond length and hydrogen ionic radius for BeH₂, using full potential linearized augmented plane wave (FP-LAPW) as code embodied in WIEN 2k (Schwartz, 2001) with GGA and GGA + U, used as exchange-correction potentials, where U is the Hubbard correction term.

This improved method obviates the problem encountered by Yu and Lam (1988) in determining the ionic radius of Be in Be-H distance.

Superfluidity has been avoided by referring a perspicacious reader to GGA + U calculations of BeH₂ in orthorhombic crystal system (Uko, et al, 2014).

2 THEORETICAL CONSIDERATION

Atomic charges in molecules or solids are not observables, and therefore, not defined by quantum mechanical theory (Biegler et al, 2001). The output of quantum mechanical calculations is continuous electronic charge density, and it is not clear how electrons, among fragments of system such as atoms or molecules, should be partitioned.

Many different schemes, however, have been proposed, some based on electronic orbitals: Mulliken population analysis (Mulliken, 1955); Density matrix based on normal population analysis (Lemin & Robert, 1986); Bader analysis (Bader, 1990) and, Hirshfeld analysis (Hirschfeld, 1977).

For the purpose of this work, two of these methods will be discussed, and Bader Decomposition method, for its palpable advantage will be used for the calculation of atomic charges.

2.1 MULLIKEN POPULATION ANALYSIS

This method was proposed by Robert S. Mulliken (Mulliken, 1955), after whom the method was designated. It provides a means of estimating partial atomic charges from calculation found or linear combinations of atomic orbital.

The density matrix are expressed as (Mulliken, 1955).

$$D_{\mu\nu} = +2 \sum_{\mu} C_{\mu\nu} C_{\nu\mu}^* \quad (1)$$

Where $C_{\mu i}$ are the coefficients of the basis functions in the molecular orbitals for the LiH basis function and $D_{\mu\nu}$ is for a closed shell system where each molecular orbital is doubly occupied (The matrix P_{UV} then has the terms (Mulliken, 1955):

$$P_{\mu\nu} = D_{\mu\nu} S_{\nu\nu} \quad (2)$$

Where S is the overlap matrix of the basis functions. The atomic charges, charges, Q_A , are therefore, calculated directly for the expansion of the basis functions:

$$Q_A = Z_A - \sum_{\mu,\nu} D_{\mu\nu} S_{\mu\nu} \quad (3)$$

One of the most prominent impediments of this method is that it cannot provide physically meaningful absolute magnitude of the atomic charges owing to the sensitivity of the results to the choice of the basis set (Popelier, 2001).

The instability of the charge with increased basis set size is another major disadvantage to this method, for there is no account for the differences in electronegativity of atoms within the molecule.

2.2 BADER CHARGE DECOMPOSITION METHOD

In this method found by Bader (Bader, 1990), his idea was to use charge density $P(r)$ to divide space within the molecular system into atomic volumes (Bader volumes).

Each Bader volume contains a single charge density maximum and is separated from other volumes by surface on which the charge density is a minimum normal to the surface (Henkelman *et al*, 2006).

The dividing surface (also called zero flux surfaces) separating these volumes lie in the bonding regions between atoms (Henkelman *et al*, 2006).

One of the advantages of Bader partitioning over Mulliken population method is that the former is based on the charge density, which is an observable quantity that can be measured experimentally or calculated.

3 RESULTS AND DISCUSSION

3.1 ATOMIC CHARGES AND ELECTION DENSITY

Atomic charge of BeH_2 was calculated with Bader election density decomposition method (Henkelman *et al*, 2006) and presented in table 1.

In this method, according to Bader's work, a subsystem such as atoms in crystalline compound is bond by the surface of zero flux of electron-density-gradient vector field. This allows the determination of charge distribution among the atom within molecules (Bader 1990).

For more complex crystal structure of BeH₂, a large number of non-equivalent charges ensue: non two-equivalent beryllium atoms and two hydrogen atoms were observed. The charge of the two hydrogen aims differed by 0.05e (approximately), as expected.

To exhibit features of charge distribution that results in GGA and GGA + U calculations comparisons of the charge distribution were made: the cross sections of the difference of the charge density for GGA + U and GGA calculations were made along crystallographic plane passing through hydrogen atoms as presented in figure 1.

It was observed that GGA functional does not prominently change the charge state of ions. It was also noticed that hydrogen atoms do not have spherical symmetry and charge distribution changed on Be atoms. These effects indicate that direct bonding, which had covalent features, exist between atoms; moreover, the change in charge distribution in the region between hydrogen atoms also indicated interaction of H in BeH₂ as had been reported by Bao-Tian *et al*, 2010.

It is pertinent to mention that on the contour plot, for clarity, only regions of charge aggregation are presented.

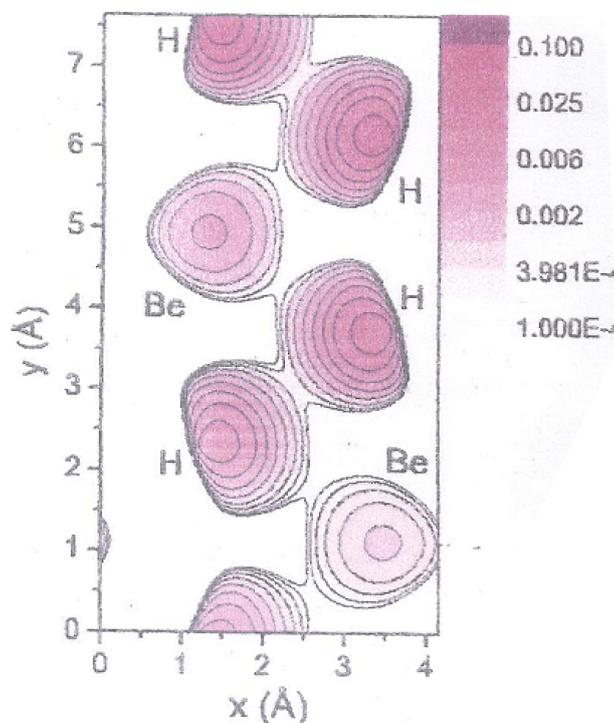


Figure 1: Electron density difference between the densities of GGA + U and GGA-PBE

Table 1: Bader atomic charges for BeH₂

Compound	Method	Be + Cation	H ⁻ anion	H ⁻ anion
	GGA	1.62,1.63	-0.86	-0,79
Be H ₂	GGA +V	1.61,1.63	-0.86	-0.79

3.2 PAULING ELECTRONEGATIVITY, BOND LENGTH AND IONIC RADIUS

The above properties were determined. For calculation with GGA + U it was observed that the charge transfer was small, decreasing with increasing mass of Be. Such influence recounts the decreasing Pauling electronegativity that is smaller in other metals than in Be.

The calculated Be-H distance (bond length) and the ionic radius were found to be in agreement with the result of Holleman, 1995.

Table 2: Pauling electronegativity bond length (Å), ionic radius (Å)

Compound	Electronegativity	Be-H bond length	Hydrogen ionic radius (present work)	Other work
Be H ₂	1.58 ^(a)	1.33 ^(b)	0.88	0.88 ^c

Ref^(a): Web Elements Periodic Table (2010)

Ref^{(b), (c)}: Holleman (1995). Calculated as the difference between Be-H

4 CONCLUSION

In this paper, the quantities calculated were done using FP-LAPW within GGA and GGA + U as implemented in WIEN 2k code. The atomic charges were calculated. It was noticed that GGA + U functional does not significantly change the charge state of ions. It was also, as expected, noticed that charge difference between the two hydrogen anion was 0.05e.

The shape of the atoms in BeH₂ indicated direct bonding, which had covalent features as had been reported by Bao-Tian, *et al* 2010.

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