

## ATOMIC CHARGES, ELECTRON DENSITY, ELECTRONEGATIVITY, AND BOND LENGTH OF LiH WITH GGA + U FUNCTIONAL

*Uko Ofe*

Department of Science,  
Laboratory Technology (Physics),  
Akanu Ibiam Federal Polytechnic,  
Afikpo, Nigeria

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**ABSTRACT:** In this paper, Bader atomic charges for LiH was calculated. Pauling electronegativity for Li, bond length and hydrogen ionic radius for LiH. were also calculated. Electron density difference between GGA+U and GGA-PBE was plotted. It was observed that the difference was positive, and this was symptomatic of the charge being more localized on S orbital of hydrogen for GGA + U functional calculations.

**KEYWORDS:** Electronegativity, Bader atomic charges and bond length.

### 1 INTRODUCTION

The following essential features of LiH and other AlkH have been studied: H-H interaction, Li-H and charge transfer. The influence of the exchange interaction was checked, using different approximations: Generalized Gradient Approximation (GGA), and Local Density approximation (LDA), using the full potential augmented plane wave extended with local orbitals (FP-APW + Lo) and the full potential linearized augmented plane waves (FP – LAPW) methods, as implemented by the WIEN 2K software package (Schwartz, 2001).

The charge distribution in the (100) plane contouring  $L^+$  and  $H^-$  was discussed (Novakovic et al, 2007). It was noticed that the charge depletion regions, in LiH, were narrow between H ions, but broad between Li ions.

In (111) plane, there was a clear sign of H-H bonding: bonds, obviously must have used some of Li charges (Novakovic, 2007).

The objective of this contemporary work is to study the atomic charges for LiH, using Bader electron decomposition method (Henkelman et al, 2006), anion-cation electronegativity difference, Li-H bond length and hydrogen ionic radius for LiH, using full-potential linearized augmented plane wave (FP-LAPW) method as embodied in WIEN2K code, with GGA and GGA + U used as exchange-correlation potentials, where U is the Hubbard correction term.

Proximity has been evaded by referring an avid reader to GGA+U calculations of LiH (Uko, 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 (Hirshfeld, 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).

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

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):

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

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 (Propelier, 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, 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 ELECTRON DENSITY

The true space charge distribution offers a fundamental penetration into bonding of the crystal. In ionic structures, the atomic charges are of basic interest.

As shown in Figure 1, atomic charges were determined using Bader electron density decomposition method (Tang et al, 2009). This method divides the total electron density into basins being separated by zero flux regions now create space division which maintains total charge.

The binary structure of LiH affirms that charges on Li and the hydrogen are equivalent but with opposite sign. The calculated Bader charges are displayed in Table 1. It was observed that charged transfer was 0.86e.

To exhibit features of the charge distribution that results in GGA and GGA + U calculations, comparison of the charge distribution were made: A cross-section of the charge density in the middle of the unit cell along (a, b) was cut.

For this correlation, the lattice constants of GGA calculations were used to provide direct subtraction of resulting charges (Uko, 2014).

The discrepancies in the charges density between GGA and GGA + U calculations are presented in Figure 1. It was observed that the difference is positive, and this indicated the charge being more localized on S orbital of hydrogen for GGA + U calculation.

Although there was large region of charge localized for LiH, but there was no spherical symmetry; the charge density was elongated toward Lithium (Li) which indicated non-ionic interaction, and this is in agreement with Novakovic et al 2007.

For lucidity, only regions of charge clustering are presented. The charge density plot delineates only improvement of localized charges owing to application of GGA + U.

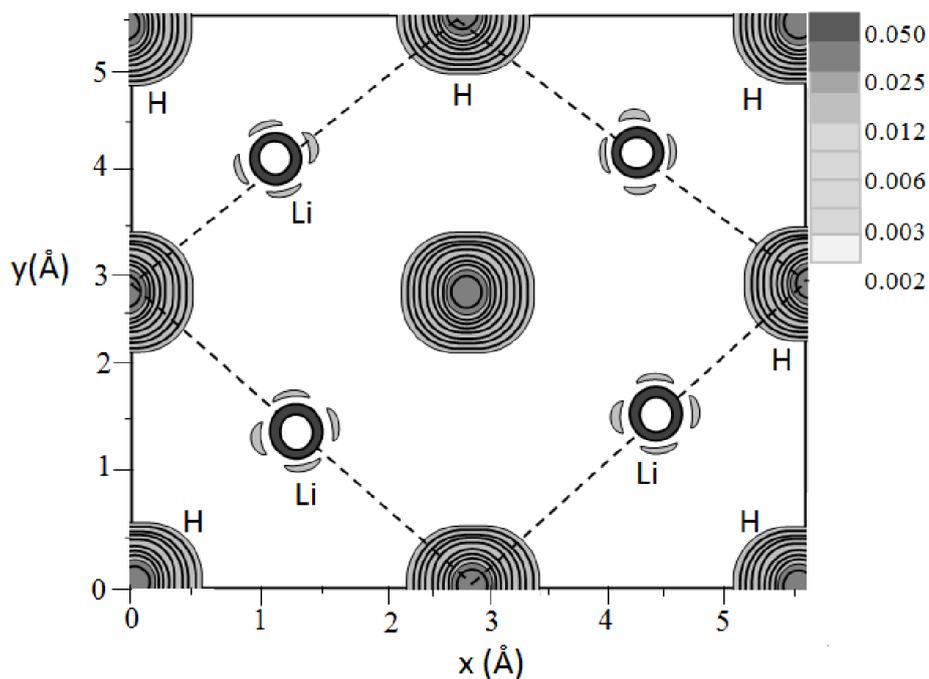


Figure 1: Electron density difference between densities of GGA + U and GGA – PBE functional for LiH.

**Table 1: Bader atomic charges for LiH**

Compound	Method	Li <sup>+</sup> Cation	H <sup>-</sup> Anion
	GGA	0.86	-0.86
LiH	GGA + U	0.87	-0.86

### 3.2 PAULING ELECTRONEGATIVITY, BOND LENGTH AND IONIC RADIUS

The above parameters were determined. For calculations with GGA + U, it was observed, that charge transfer, does not change within exactness of calculations as shown in Table 2.

The Li-H distance (bond length) was calculated as the half of the lattice constants (Uko, 2014), and the Pauling electronegativity (Pauling, 1960) for the compound was also calculated and presented in Table 2.

On the foundation of the charge localization region, the ionic radius of hydrogen (H<sup>-</sup> radius) was estimated, and compared to the Pauling radius (Pauling, 1960), and was found to be 0.875 Å, approximately, but was smaller than the radius computed from the structural information (Holleman, 1995) which increasingly has the contrary direction.

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

Compound	Electronegativity	Li-H bond length	Hydrogen ionic radius present work	Other work
LiH	0.91 <sup>(a)</sup>	2.04 <sup>(b)</sup>	0.88	1.14 <sup>c</sup>

Ref<sup>(a)</sup>: Web Elements Periodic Table of Elements (2010). <http://webelements.com>

Ref<sup>(b)</sup>: Uko (2014): Calculated bond lengths equal the half of the Lattice constants in Table 1

Ref<sup>(c)</sup>: Holleman (1995): Calculated as a difference between Li-H bond length and Pauling ionic radius of Li atom.

## 4 CONCLUSION

In this paper, the quantities calculated were done using FP-LAPW within GGA and GGA + U as implemented in WIEN2K code. The atomic charges were calculated; it was observed that the charge transfer in LiH was 0.86e, and this indicated strong ionicity.

Lithium hydrogen distance and Pauling electronegativity were determined. The charge distributions between GGA and GGA + U calculations were done, and the difference compared. It was observed that this difference was positive, indicating the charge being more localized on S orbital of hydrogen for GGA + U calculation. It was also noticed that charge density was elongated toward Lithium ions, indicating non-ionic interaction, which had been reported by Novakovic et al, 2007.

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