Chemical Physics Letters 652 (2016) 40–45

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Molecular partitioning based on the kinetic energy density

Siamak Noorizadeh

Chemistry Dept., Faculty of Sciences, Shahid Chamran University, Ahwaz, Iran

ARTICLE INFO

Article history:
Received 7 March 2015
Revised 3 March 2016
In final form 2 April 2016
Available online 22 April 2016

Keywords:
AIM theory
Non-nuclear attractor
Gradient kinetic energy density
Density functional theory

ABSTRACT

Molecular partitioning based on the kinetic energy density is performed to a number of chemical species, which show non-nuclear attractors (NNA) in their gradient maps of the electron density. It is found that NNAs are removed using this molecular partitioning and although the virial theorem is not valid for all of the basins obtained in the being used AIM, all of the atoms obtained using the new approach obey this theorem. A comparison is also made between some atomic topological parameters which are obtained from the new partitioning approach and those calculated based on the electron density partitioning.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A wide range of experimental observations could be predicted by Atoms in Molecules (AIM) theory [1–5], which attempts to provide a clear definition for bond path using solutions of the Schrödinger equation via the topology of the electron density [6]. In this theory the pronounced maxima in the electron density at the positions of the nuclei give rise to a rich topology, which embodies a natural partitioning of the molecular space into individual separate *mononuclear* regions or basins (Ω) called "atoms" [7]. Therefore in the commonly used AIM theory the molecular space is discretely so partitioned that any point can be attributed to only one atom. The surfaces bounding such atoms in a molecule (Interatomic Surface; IAS) are zero-flux in the gradient vector field of the electron density, $\nabla\rho(r)$; i.e. they are not crossed by any of the gradient vectors at any point (zero-flux condition) [1]. Therefore for this surface:

$$\nabla\rho(r_s)\cdot\mathbf{n}(r_s)=0 \quad r_s \text{ belongs to the surface } \Omega \tag{1}$$

where r_s is the position vector on the surface of Ω and $\mathbf{n}(r_s)$ is the unit vector normal to this surface. The atoms defined in this manner, i.e. based on the topology of the electron density (called Bader or AIM atoms), are brought into coincidence with the quantum mechanically derived atoms in a molecule [8] starting from Schwinger's principle of stationary action [9].

Although in AIM theory each atom or nucleus is expected to be associate with a determined spatial domain delimited by a surface, in some cases it also predicts the existence of local maxima of electron density at points distinct from nuclear positions; called non-nuclear attractors (NNAs). These points are called NNA because they behave like 3D attractors of the gradient paths so do the nuclei, but clearly without a cusp at the NNA position since they are not nuclei. For this reason, a NNA and its associated basin bounded by zero-flux surfaces are also termed "pseudoatoms". Usually these pseudoatoms possess a significant portion of the excess electrons within the cavity, consistent with the cavity-bound model of the solvated electron. These points are usually observed in the highly symmetric clusters, and therefore the occurrence of them is rare and was first theoretically predicted in alkali metal clusters [10–12] and later observed experimentally in metallic beryllium and magnesium [13,14]. Some quantum mechanical calculations were also performed for analyzing the occurrence of non-nuclear maxima in the electron density of crystals and molecules, which is due to the shell structure of atoms contained in promolecular densities [15]. It should be mentioned that in theoretical studies, the appearance of NNA has not something to do with the inclusion of electron correlation in calculations [16].

The techniques of topological analysis allow one to perform distribution of a molecular property into the Bader domains providing suitable descriptions of atomic related quantities. The occurrence of non-nuclear attractors hampers the interpretation of decomposition of a given molecular property (such as energy, electron density and atomic dipolar polarization) mainly by the monoatomic and diatomic terms involving non-nuclear attractors, which have not a clear chemical meaning. Therefore it turns out to be difficult to interpret the resulting bondings between a domain associated to an ordinary atom and the one corresponding to a non-nuclear attractor. On the other hand, the appearance of non-nuclear

---

E-mail address: noorizadeh_s@scu.ac.ir

http://dx.doi.org/10.1016/j.cplett.2016.04.005
0009-2614/© 2016 Elsevier B.V. All rights reserved.

attractors breaks the one-to-one correspondence between atoms and Bader domains, which is generally admitted in the topological treatments [1]. Therefore in these cases some modifications are needed to calculate precisely the atomic properties or it is necessary to partition the molecular space into real atoms.

In this work it is attempted to partition a given molecule to its individual basins using the gradient vector field of kinetic energy density instead of the electron density. This approach is applied to a number of chemical species included B_6C^{2-} molecule, some lithium clusters, a complex of magnesium and a series of acetylene with nitrosyl hydride complexes. A comparison is also made between some atomic topological parameters obtained from the new partitioning approach and those which are evaluated based on the electron density partitioning.

2. Computational details

All of the considered molecules included Li_2 (B3LYP/6-311G*), Li_4 (B3LYP/6-311G*), Li_6 (B3LYP/6-311G*), B_6C^{2-} (B3LYP/6-311G* and MP2/aug-cc-pvtz), a complex of magnesium (B3LYP/6-311G*) and some complexes of acetylene with nitrosyl hydride (B3LYP/6-311G* and MP2/aug-cc-pvtz) are optimized at the mentioned levels of theory using Gaussian03 suite of program [17]. In all cases the vibrational frequency analyses calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima. The calculations for partitioning the molecular space and obtaining the molecular graphs together with the integration of the considered properties over the obtained basins are all performed using Multiwfn 3.0 program [18,19].

3. Results and discussion

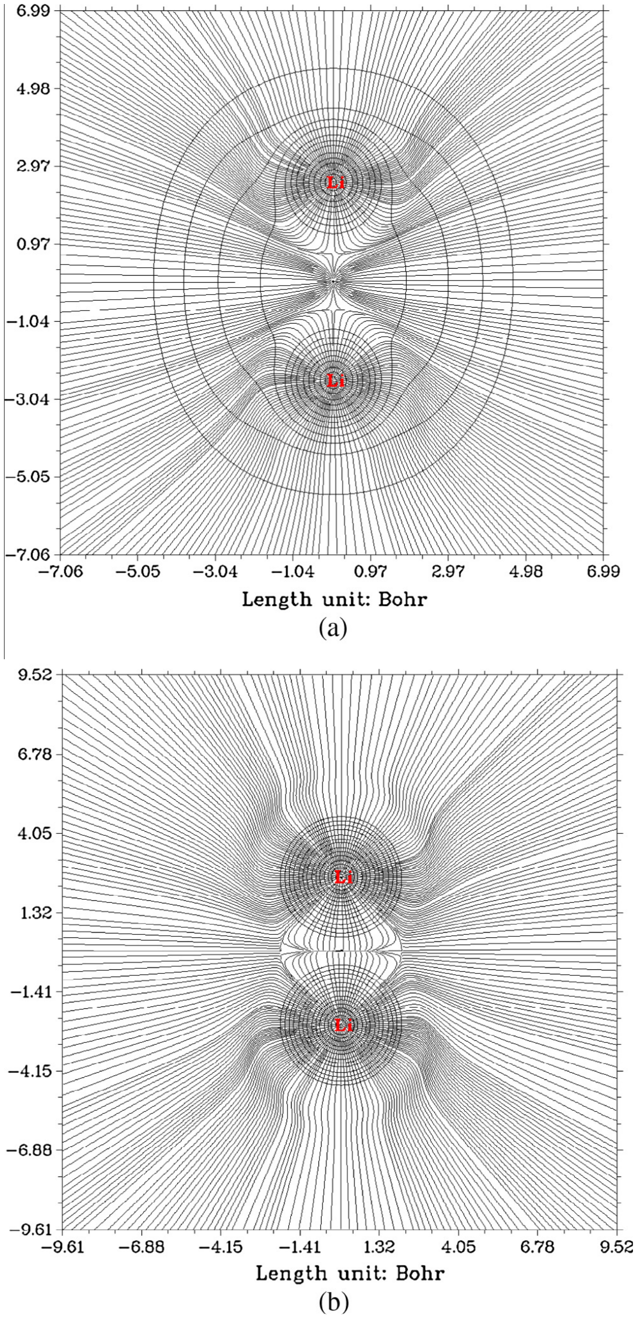
Recently, Liu introduced the concepts of steric energy and steric potential energy within the DFT framework [20]. In this article it is discussed that the steric energy is a nonnegative property which is similar to the Weizsäcker kinetic energy $\left(T_W = \frac{1}{8}\frac{|\nabla\rho(r)|^2}{\rho(r)}\right)$ and is vanished for homogenous electron gas. It is also claimed that the atoms in a molecule are interfaced with each other with the surface of a vanished steric energy density. Therefore this idea comes in mind that the kinetic energy density, which is positive everywhere and defines as:

$$G(r) = \frac{1}{2}\sum_i n_i|\nabla\varphi_i|^2 \tag{2}$$

could be also used for partitioning a given molecule to its constituted atoms. In this equation n_i and φ_i are the occupation number and the wavefunction of the ith molecular orbital, respectively.

The first chosen molecule is Li_2 as one of the simplest known systems which shows non-nuclear attractor (NNA) [10]. It should be recalled that the presence of the NNA is expected to be sensitive to the bond length of two atoms which the NNA is appeared between them and hence it is observed just by using some levels of theory. For example the analysis of topological parameters of Li_2 cluster shows that a NNA is present at the middle of metal bond when B3LYP/6-311G* method is used for the partitioning of the molecule [16]. Therefore this level of theory is used in both partitioning approaches (based on electron density and kinetic energy density) for this molecule.

The obtained gradient line maps of electron density (1a) and kinetic energy density (1b) with contour lines for Li_2 molecule are shown in Fig. 1. Based on the evaluated maps, all gradient vector field lines converged to one nucleus, form an atomic basin. Therefore, the surface bounding an atom is one of zero-flux in the gradient vector field of the kinetic energy density. This means that this surface is not crossed by any of the gradient vectors ($\vec{\nabla}G$) at any point. It seems that the atoms in this molecule are interfaced with each other with the surface of a vanished gradient kinetic energy density. This satisfy the condition:



(a)

(b)

Fig. 1. The gradient line maps of the (a) electron density and (b) kinetic energy density using B3LYP/6-311G* method for Li_2 molecule.

$$\nabla G(r_s)\cdot \mathbf{n}(r_s) = 0 \quad r_s \text{ belongs to the surface } \Omega \tag{3}$$

This is similar to the boundary condition necessary for application of Schwinger's principle of stationary action to an open system [8]. Since the boundary condition is defined in terms of the gradient kinetic energy density, the quantum subsystem is defined in real space.

Fig. 1 shows that, although an accumulation of electron density occurs between two lithium atoms (note to the appeared NNA in

Download English Version:

https://daneshyari.com/en/article/5378996

Download Persian Version:

https://daneshyari.com/article/5378996

Daneshyari.com