Chemical Physics 434 (2014) 11–14

Contents lists available at ScienceDirect

Chemical Physics

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

Exploring the role of steric effect in the stability of clusters: Water hexamer as a test case

Mojtaba Alipour *

Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran

ARTICLE INFO

Article history:
Received 30 November 2013
In final form 17 February 2014
Available online 27 February 2014

Keywords:
Steric effect
Cluster
Water hexamer
Stability
DFT

ABSTRACT

Steric effect is one of the most widely used concepts in chemistry and has long been known to play imperative roles in various phenomena. In this paper, on the basis of a quantitative description of steric effect, which is based on a new energy partition scheme where the total electronic energy is decomposed into contributions from three independent effects of steric, electrostatic, and the Fermionic quantum, the steric effects in different conformers of water hexamer have been investigated. It is shown that the steric repulsion has a strong effect on conformations stability. Reasonable correlations between relative electronic energies and steric energies are revealed. We find that more stable structures of water hexamer prefer to have smaller size and less steric repulsion.

1. Introduction

According to the title, this paper examines the role of steric effects in the structural analysis and relative stability of clusters. The steric effect is an essential and widely used concept in various fields such as chemistry, biochemistry, pharmacology and so forth. It is basically associated with the fact that atoms and molecules occupy a certain region of space [1,2]. The hindrance induced when they are brought together changes the energy, shape, reactivity, and other properties of systems. Although qualitative reference to the steric effect is commonplace in the literature, like many other concepts in science there is no exact quantitative definition of this effect. Quantitative description of the steric effect has just been proposed by Liu [3] in the framework of density functional theory (DFT) [4,5]. A number of applications of this approach to various chemical processes have recently been investigated [6–19]. We have also shown that the quantitative definition of steric effect can be used as an effective descriptor in predicting the rate constant of a reaction [20]. Moreover, in our recent communication on the present subject [21], the utility of momentum space in the density-based quantification of the steric effect has been analyzed. Now, one might ask whether the quantitative definition of steric effect provides a description for the trend of relative stability of clusters. The answer is the affirmative and we clarify this issue through the study on structural isomers of water hexamer as a working model.

The current paper is organized as follows. In the next section, a brief overview for the theoretical background of DFT definition of steric effect is given. Thereafter, the computational procedures involved in this work are described. Then, we present our results on the role of steric effects in the stability of structural isomers of $(H_2O)_6$ cluster. Finally, the main conclusions will be drawn in the last section.

2. Theory

Since in the present work we have focused on the quantitative approach of steric effect, it is worth to outline the underlying theory. In DFT, the total energy density functional of an atom and molecule, $E[\rho]$, has the form below

$$E[\rho] = T_S[\rho] + V_{ne}[\rho] + J[\rho] + V_{nn}[\rho] + E_{xc}[\rho] \tag{1}$$

where $T_S[\rho]$, $V_{ne}[\rho]$, $J[\rho]$, $V_{nn}[\rho]$, and $E_{xc}[\rho]$ denote the non-interacting kinetic, nuclear-electron attraction, classical interelectron Coulomb repulsion, nuclear–nuclear repulsion, and exchange–correlation energy density functionals, respectively. Three terms $V_{ne}[\rho]$, $J[\rho]$, and $V_{nn}[\rho]$ are of the electrostatic nature,

$$E_e[\rho] = V_{ne}[\rho] + J[\rho] + V_{nn}[\rho] \tag{2}$$

To separate the steric contribution, the total energy density functional can also be partitioned as [3]

$$E[\rho] = E_S[\rho] + E_e[\rho] + E_q[\rho] \tag{3}$$

Here $E_S[\rho]$, $E_e[\rho]$, and $E_q[\rho]$ stand for the independent energy contribution from the steric, electrostatic, and quantum effects, respectively. The quantum energy contribution due to the

---

* Tel.: + 98 711 6137160; fax: +98 711 6460788.
E-mail address: malipour@shirazu.ac.ir

http://dx.doi.org/10.1016/j.chemphys.2014.02.008
0301-0104/© 2014 Elsevier B.V. All rights reserved.

exchange–correlation effects, $E_q[\rho]$, is sum of the exchange–correlation energy $E_{xc}[\rho]$, which includes a kinetic counterpart of the dynamic electron correlation [22–24] and the Pauli energy, $E_{Pauli}[\rho]$, which is the contribution to the kinetic energy from the anti-symmetric requirement of the many-electron wave function (Pauli exclusion principle) [25,26]

$$E_{\mathrm{Pauli}}[\rho] = T_{\mathrm{S}}[\rho] - T_{\mathrm{W}}[\rho] \tag{4}$$

where the $T_W[\rho]$ is the Weizsäcker kinetic energy [27]

$$T_{\mathrm{W}}[\rho] = \frac{1}{8}\int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \tag{5}$$

Therefore,

$$E_{\mathrm{q}}[\rho] = E_{xc}[\rho] + E_{Pauli}[\rho] = E_{\mathrm{xc}}[\rho] + T_{\mathrm{S}}[\rho] - T_{\mathrm{W}}[\rho] \tag{6}$$

Using Eqs. (1)–(3) and Eq. (6) one obtains

$$E_{\mathrm{S}}[\rho] = T_{\mathrm{W}}[\rho] \tag{7}$$

The physical nature of the steric effect within this approach is as follows. If electrons in an atom or molecule behave as bosons, they would be crowded into the lowest ground state orbital. Assume that the density of the hypothetical boson state is the same as that of the Fermion state, $\rho(\mathbf{r})$. Then, the total wave function of the hypothetical state will be $(\rho(\mathbf{r})/N)^{1/2}$, where N is the number of electrons and corresponding kinetic energy density, from which Weisskopf's kinetic energy pressure [25] is derived, is as follows

$$t_{\mathrm{W}}[\rho] = \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \tag{8}$$

Thus, $T_W[\rho]$ represents the kinetic energy of the electrons in the hypothetical boson-like state and the energy $E_S[\rho]$ measures of the intrinsic dimensions peculiar to the system, when the quantum and electrostatic effects are completely excluded. This definition of steric effect is consistent with the original Weisskopf's attribution of the steric effect to the kinetic energy pressure because $T_W[\rho]$ is indeed a kinetic energy, exact for one electron systems.

3. Computational details

Usually, the richness of stable local minima that characterizes the potential energy surface (PES) of clusters makes any structural study a challenging task. In such kind of PES, determination of the

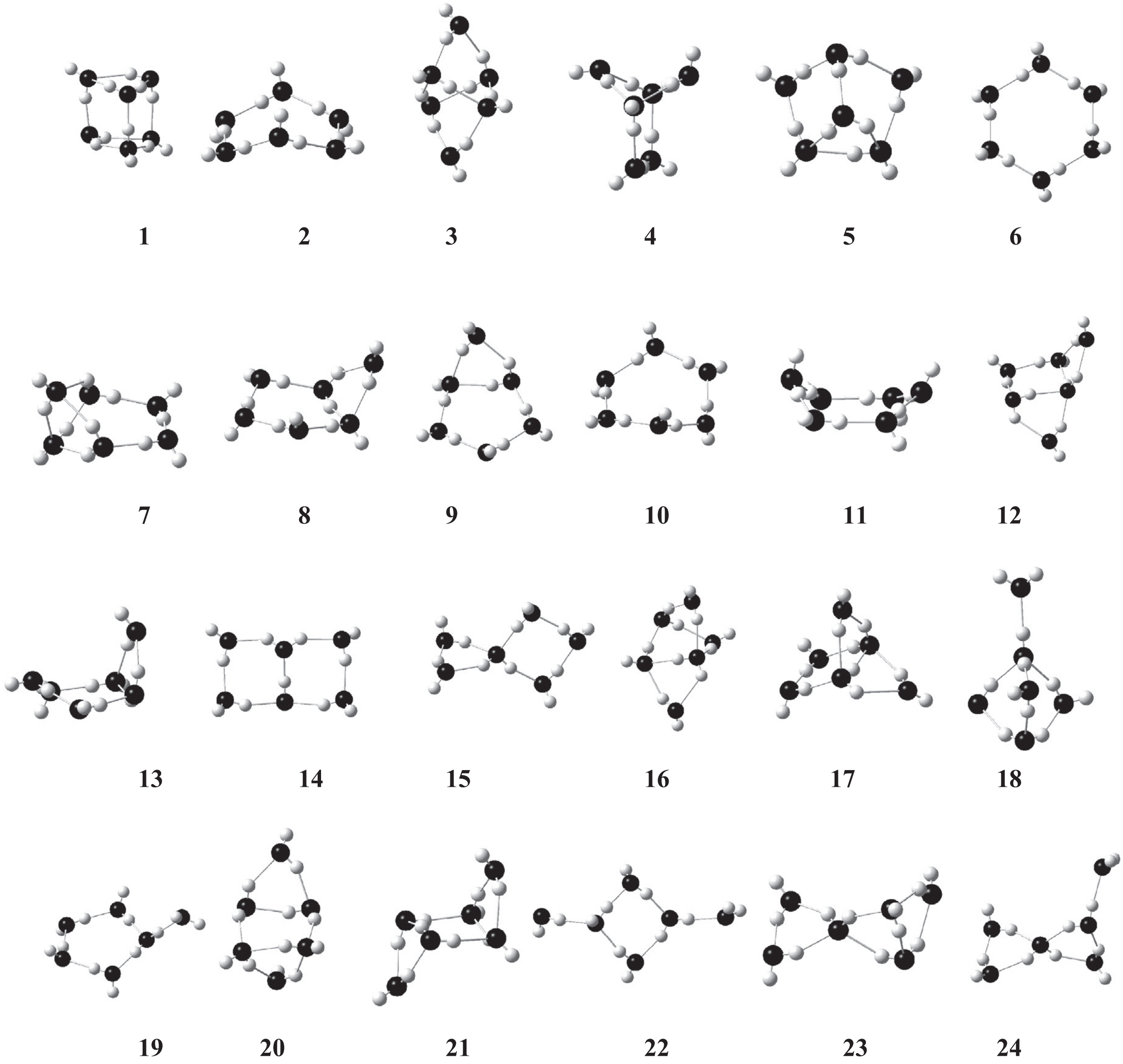

Fig. 1. Structures of the water hexamers under study. Black and light gray vertices are oxygen and hydrogen atoms, respectively. The numbers below the structures show the rank of stability of each isomer: structure **1** is the most stable conformer followed by **2**, **3**, etc.