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Look at the spatial confining effect on the molecular electrostatic potential (MEP). A case study of the HF and BrCN molecules

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Abstract: In this theoretical study we report on molecular electrostatic potential (MEP) of titled molecules confined by repulsive potentials of cylindrical symmetry mimicking a topology. Our calculations show that the spatial restriction significantly changes the picture of MEP of molecules in quantitative and qualitative sense. In particular, the drastic changes of MEP as a function of the strength of spatial confinement are observed for the BrCN molecule. This preliminary study is the first step in the investigations of the behavior of MEP of molecular systems under the orbital compression.

Keywords: molecular electric potentials; spatial confinement; intermolecular interactions

1. Introduction

Incorporation of the molecular electrostatic potential (MEP) concept into the chemistry and molecular physics community is owed to the pioneering works of Scrocco and Tomasi in the early 1970s [1]. Since then the MEP has advanced to the position of an important tool of computational chemistry in elucidating various properties of atoms, molecules and materials [2-5]. It results from the ease of interpretation of the MEP in terms of classical electrostatics: the initial tendency of an approaching positive point charge is to go to those parts of molecule where the MEP is most negative. In addition, the computation of molecular electrostatic potential from the wave function is not a very demanding task, thus it is feasible to obtain its values at various points around the molecule and represent the MEP as a three- or two-dimensional isopotential map or, by color, on the molecular envelope. It is therefore hardly surprising that introduction of the MEP was an important step toward domestication of quantum chemistry and making it more accessible to chemists and other experimentalists. The molecular electrostatic potential created in the space around a molecule by its nuclei and electrons is defined rigorously by the following equation (in terms of atomic units):

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|}, \quad (1)$$

where Z_A denotes the charge on nucleus A, located at a distance R_A , and $\rho(r')$ is the molecule's electronic density. In contrast to $\rho(r)$, which represents solely the electronic density at the point r , MEP involves contributions from each nucleus and electrons in the entire molecule, thus providing a total electrostatic picture. The first term of Eq. (1) brings in the positive contribution of the nuclei, while the second one represents the negative effect of the electrons. Hence, the sign of $V(r)$ in any particular region depends on whether the nuclear or the electronic term is dominant there. It is worth mentioning that MEP belongs to the quantities observable physically, thus it can be derived directly from the wave function or experimental electron densities available from, e.g., X-ray diffraction [6]. Typical

applications of MEP has expanded from primarily a focus on sites for electrophilic and nucleophilic attack to the interpretation of molecular electronic structure, structure-activity relationships or in the theory of solvent effects [2-5,7-10], just to name a few. One of the common applications of the molecular electrostatic potential is also the study of long-range interactions. An important type of such interactions, in the context of which the knowledge of MEP has been proven very useful, is the σ -hole bonding. Initially, the σ -hole concept was introduced to resolve the enigma of halogen bonding (XB) [5, 7-14]. The explanation of this phenomenon is based on the anisotropy of the electron density distribution around the halogen atom. As it has been demonstrated the distribution of electron density around the X atom adopts ellipsoidal form with the longer radius perpendicular to the direction of the R-X bond. This leads to the formation of the electron-deficient region, along the R-X direction, which consequently exhibits an excess of positive charge (the so-called σ -hole). The interactions involving σ -holes are highly directional, due to the localization of the electron acceptor site (σ -hole) on the extension of the covalent bond. As driving the molecular organization in the space, σ -hole interactions can control the properties of supramolecular entities and materials through the structure-properties relationship which make them of great importance in the fields of crystal engineering, supramolecular chemistry, nanotechnology and material science. However, it should be noticed that the prominent role of the σ -hole in the context of formation of the halogen bond was also criticized [15].

Recent years have seen a significant strengthening of studies concerning the description of noncovalent complexes exposed to the high pressure or embedded in confining environments (see refs. [16, 17] and the references cited therein). These investigations and observations open up the possibility of constructing molecular systems with entirely new properties, mostly determined by size effects (e.g., endohedral complexes, inclusion compounds or low-dimensional semiconductor structures). Recently, we have demonstrated that the effect of orbital compression, represented by the cylindrical harmonic potential, significantly influences the nature of hydrogen as well as halogen bonds interaction [16, 17]. Generally, in order to get the fundamental understating, in the context of quantitative and qualitative results, about the nature of spatially confined molecular complexes energetics, intermolecular distances or vibration properties are considered, which requires performing high level *ab initio* molecular orbital calculations. Hence, the search simplest solutions and model, for example based on the analysis of MEP is important and necessary challenge.

The main motivation of this work was to examine the spatial confinement effect on MEP of the titled compounds. This preliminary study is the first step in the investigations of the behavior of MEP of molecular systems under the orbital compression. This work is continuation of our investigations on this field devoted to theoretical description of the electrical properties (in particular linear and nonlinear) of atomic and molecular systems (see, e.g., refs. [16-21])

2. Results and Discussion

The choice of the BrCN molecule for our investigations was connected with the fact that this type of system are often discussed in the context of possibility of the forming halogen bonds (σ -hole concept based on MEP) in the molecular complexes. Additionally, the simplest of the HF molecule was included in our consideration in order to obtain more general conclusion. It is worth to underline that all computations of MEP have been performed for the molecular structures relaxed in the presence of cylindrical harmonic potential. It is connected with the fact that the bond distances in rigid molecules are shortened upon spatial confinement in comparison with the molecules in vacuum [21-23]. It has been shown that this effect strongly influences on the electrical properties of molecular systems (distribution of charges, dipole moment, polarizability etc.) [18-24]. MEP have

been calculated by using Eq. (1). It should be again noticed that MEP at given point around the molecule is defined as the force acting (or potential energy) on a positive test charge located at point through the electrical charge cloud generated through the molecules electrons and nuclei. The MEP is often visualized through mapping its values onto the surface reflecting the molecules boundaries. In our case molecules boundaries have been generated through a constant value of electron density (0.001 a.u.). The AIMAll program was used to process the data and generate MEP onto the molecular surface [25]. It should be noticed that in our visualization the negative MEP (red, green and yellow colors) corresponds to a situation when the positive test charge is attracted by electron density (see Figures 1 and 2). On the other hand, the blue color represents positive MEP. In this region proton is repelled by the atomic nuclei (there is low electron density in this region). The intensity of the colors corresponds to the absolute value of MEP (the most negative value is indicated by red color).

The results of the calculations of MEP (in the form of electrostatic potential maps) for investigated molecules (for $\omega = 0$ and $\omega = 0.6$) are presented in Figures 1 and 2. A short inspection of plots presented in this figures allows to conclude that the spatial restriction

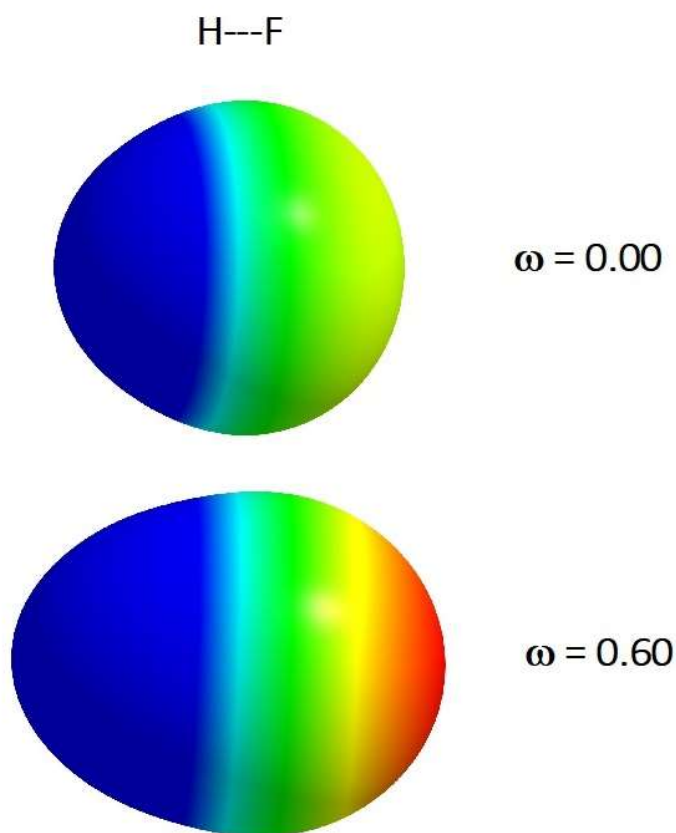


Figure 1. The ω B97X/ aug-cc-pVTZ calculated MEP on the 0.001 a.u. isodensity surface of HF molecule (for the free molecule as well as for molecule upon the confinement). The meaning of colors is explained in the text.

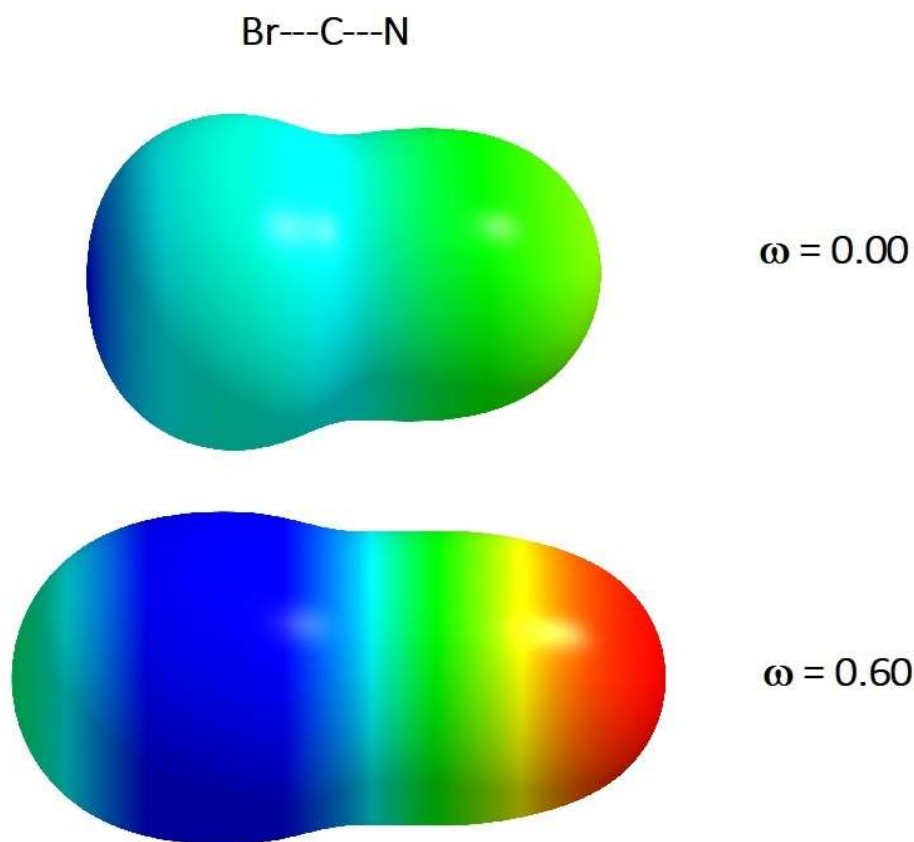


Figure 2. The ω B97X/ aug-cc-pVTZ calculated MEP on the 0.001 a.u. isodensity surface of BrCN molecule (for the free molecule as well as for molecule upon the confinement). The meaning of colors is explained in the text.

significantly changes of MEP in two aspects. Firstly, we can observed the change of shape of MEP of both the HF and BrCN molecules. In particular, it is clearly visible in the case of the BrCN molecule. The shape is more extended in axial direction and simultaneously becomes thinner in the equatorial direction. Due to cylindrical symmetry of the confining potential this result is not rather unexpected. The dependence of the values of MEP around the space of the molecules is more significant and complex. The results depicted in Figures 1 and 2 demonstrate also how the cylindrical harmonic confining potential influences the location of the maximum ($V_{s,max}$) and minimum ($V_{s,min}$) values of MEP. It should be noticed that $V_{s,max}$ and $V_{s,min}$ corresponds to the positive and negative of MEP of the investigated molecules, respectively. In Figure 1 we cannot precisely observed that the value of $V_{s,max}$ of the confined HF molecule significantly decreases in comparison with the situation without spatial restriction. This finding becomes clear after analyzing results presented in Figure 3. Here, the decrease of the values of $V_{s,max}$ (from $V_{s,max}^{\omega=0} = 68.7 \frac{\text{kcal}}{\text{mol}}$ to $V_{s,max}^{\omega=0.6} = 44.9 \frac{\text{kcal}}{\text{mol}}$) upon the increase of confinement strength is clearly observed and this relation is almost linear. It should be noticed that $V_{s,max}$ is always located on extension of the covalent bond H-F (left side of the H atom, Figure 1). On the other hand, $V_{s,min}$ becomes more negative in the same conditions (from $V_{s,min}^{\omega=0} = -20.6 \frac{\text{kcal}}{\text{mol}}$ to $V_{s,min}^{\omega=0.6} = -32.7 \frac{\text{kcal}}{\text{mol}}$). However, in this case we observe significant qualitative changing connected with location of $V_{s,min}$. For the free HF molecule $V_{s,min}^{\omega=0}$ is located around the F atom but already for the potential strength ($\omega \approx 0.3$) $V_{s,min}$ is located on extension of the covalent bond H-F (right side of the F atom, Figure 1).

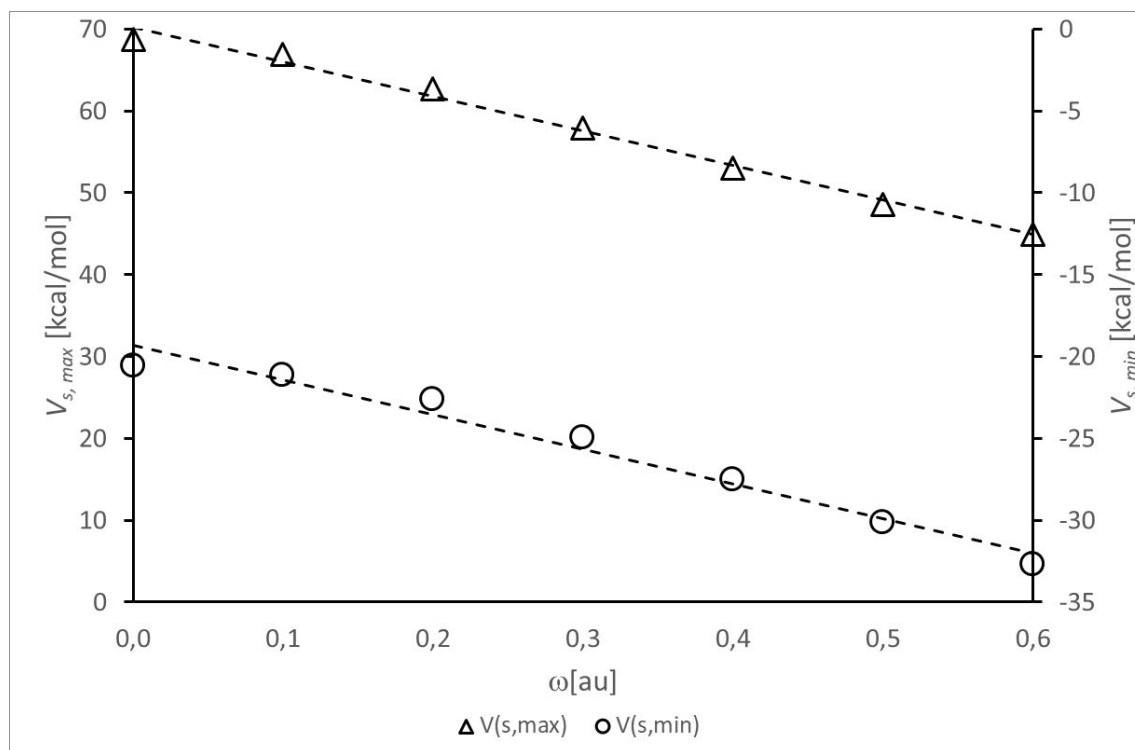


Figure 3. The $V_{s,max}$ (the maximum values of MEP) and $V_{s,min}$ (the minimum values of MEP) as a function of the strength confinement (ω) for the HF molecule. R^2 is equal to 0.9912 and 0.9712 for $V_{s,max}$ and $V_{s,min}$, respectively.

More drastic changes are observed for the BrCN molecule. The significant reorganization of MEP is observed in the presence of spatial restriction in the comparison with free molecule ($V_{s,max}^{\omega=0} = 43.9 \frac{\text{kcal}}{\text{mol}}$ and $V_{s,min}^{\omega=0} = -31.9 \frac{\text{kcal}}{\text{mol}}$). For the strongest spatial confinement considered here, $V_{s,max}^{\omega=0.6}$ is equal to $56.6 \frac{\text{kcal}}{\text{mol}}$ and is located from the side of molecule (lateral blue belt in Figure 2) in opposite to the free molecule, where the maximum (and also minimum) value of MEP is located on the opposite sites of the BrCN molecule being an extension of the covalent bond. However, this phenomenon (i.e., the change of location of $V_{s,max}$) is already observed for $\omega \approx 0.3$. It is important finding, which may have very serious consequences in the theoretical description of molecular complexes, where σ -hole idea is applied (see introduction). Because of the σ -hole, in the classical meaning, disappears under strong spatial confinement (in this conditions ($\omega = 0.6$) the value of MEP on the extension of the covalent bond Br-CN is negative and equal to $-2.6 \frac{\text{kcal}}{\text{mol}}$), our results suggest that the BrCN molecule may significantly lose their ability to form of the stable and linear halogen bonds in such conditions. Probably, the same effects are expected for similar class of compound (FCN, ClCN and ICN). This finding is subtle supported by our results presented in ref. [17]. However, this conclusion has to be confirmed in additional studies. The other point that is worth noticing is connected with behavior of $V_{s,min}$. The location of $V_{s,min}$ for BrCN is not changed but their value is more negative, i.e., $V_{s,min}^{\omega=0} = -31.9 \frac{\text{kcal}}{\text{mol}}$ and $V_{s,min}^{\omega=0.6} = -73.9 \frac{\text{kcal}}{\text{mol}}$ (red area in Figure 2). This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

4. Materials and Methods

In this work all calculations were performed using density functionals theory (DFT). In particular the semi-empirical, range-separated hybrid functional ω B97X as approximation the exchange–correlation energy functional in DFT [26] combined with the aug-cc-pVTZ basis set [27] were employed in our theoretical considerations. The numerical results have been obtained using the Gaussian 16 Rev. C01 package [28]. In order to render the impact of the spatial restriction (orbital compression) on MEP of investigated molecules two-dimensional harmonic oscillator potential, mimicking a cylindrical confinement was applied. Hence, the effect of orbital compression was modeled by the one-electron operator in the form [16-18, 20, 21-22,24]:

$$V(\mathbf{r}_i) = \frac{1}{2}\omega^2\mathbf{r}_i^2 = \frac{1}{2}\omega^2(x_i^2 + y_i^2) \quad (2)$$

added to the Hamiltonian of a free molecule. This type of model confining potential allows to mimic a smoothly varying potential. The ω , which is related to the quadratic force constant of the applied harmonic oscillator potential, defines their strength. The ω values considered in this work vary from 0 to 0.6 au. In all calculations it was assumed that the principal axis of the cylindrical harmonic oscillator potential overlaps with the molecular axis of HF and BrCN, taken to be the z-axis. The cylindrical symmetry of the repulsive potential ensures that there is no net interaction between the confining potential and the nuclei.

5. Conclusions

In summary, the present study focuses on the investigation of behavior of MEP as a function of the strength of spatial restriction (orbital compression). In order to model this effect the cylindrical symmetry of the repulsive potential (two-dimensional harmonic oscillator) was applied. Our preliminary studies showed that that the spatial restriction may significantly change the picture of MEP of molecules in quantitative and qualitative sense. This finding suggests that many processes occur in such conditions (in which electrostatic interactions play important role) may show a different faces in comparison with the ambient conditions. However, it should be noted that the two-dimensional harmonic oscillator model is rather hypothetical approximation. It is mainly connected with the fact that the presented model describes only repulsive forces (this type of interaction is a results of the Pauli exclusion principle and increases rapidly when the wave functions of guest and host molecules start to overlap) but neglects the van der Waals force of attraction from the neighboring molecules. Thus, this simple model of the spatial confinement correspond rather to a non-polarizable, electronically inert environment. This important restriction should of course be taken into account. However, it should be underlined that this is the first study analysing the effect of spatial confinement on MEP of molecular systems. Authors would like to express their hope that more studies will follow, so it will be possible to generalize the conclusions presented in this work.

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