

The Quantum Description of Halogen Bonds *via* a Generalized Empirical Potential

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Abstract: The Halogen Bonds are crucial to understand phenomena in several fields of science [1]. Recent works have shown strong evidences that non-classical interactions overcome simple electrostatic interactions supported by the σ -hole model [2,3]. Despite of an accurate description of the electronic effects in Halogen Bonds be needed, large systems are still a great challenge to electronic structure methods. In this perspective, we have proposed a new empirical potential designed to perceive the real nature of the Halogen Bonds under subtly modifications in the traditional empirical potentials [3,4].

The models in Figure 1 were used as training set to parameterize the new empirical potential. Our findings have shown that the orbital interactions are, in fact, predominant to minimize the steric repulsion [3]. Furthermore, we have shown that even with electrostatic repulsion, the interaction energies can be stronger in contrast to the σ -hole model predictions [3].

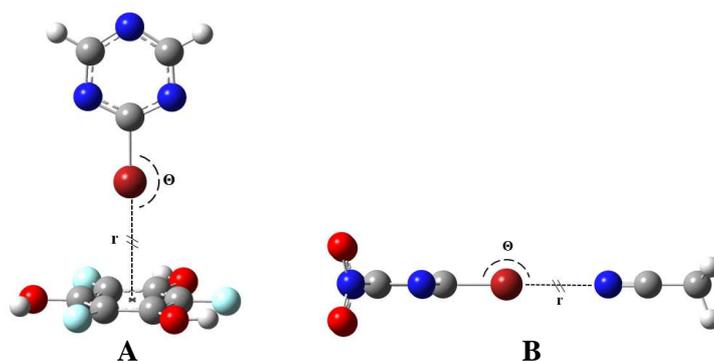


Figure 1. Structural models of $2\text{-XY}\cdots\text{ArZW}$ and $2\text{-XY}\cdots\text{NC}_2\text{H}_3$ interactions: $2\text{-Br_ArF}_3(\text{OH})_3$ (A) and $2\text{-BrNO}_2\text{-NC}_2\text{H}_3$ (B). Θ is the interaction angle and r is the interaction distance. X = Br, Cl and F; Y = NO_2 , NH_2 and H; W and Z = OH, F and H.

In the current work, a new empirical potential has been developed to describe Halogen Bonds, considering the F, Cl and Br atoms, in function of the quantum parameters δ and γ , as showed in equation (1) [3]. A crucial factor to design E_{mod} was to show the straight relationship between the maximum ESP value on σ -Hole (V_{max}) and the energies of LUMOs that contains the $\sigma^*_{\text{C-X}}$ orbital. This feature has allowed us to build parameters in function of V_{max} to describe the orbital interactions (eq. 2 and 3), that were the main responsible to lead the Halogen Bonds [3]. In (2), β is an empirical constant depending on the halogen bond acceptor and α is the van der Waals radii of the halogen.

$$E_{mod} = \varepsilon \left\{ \left(\frac{r_e + \delta \cos \theta / 6}{r} \right)^{10} - 2 \left(\frac{r_e}{r + \gamma} \right)^6 \right\} \quad (1)$$

$$\delta = \frac{\beta V_{max}}{4\pi\alpha^3} \quad (2)$$

$$\gamma = \left[\frac{2^{2-\delta}(1-\delta)}{25r} \right] \quad (3)$$

The new empirical potential E_{mod} have also demonstrated a great performance to describe systems in and out of the training set [3]. The traditional force fields have bad predictions on the equilibrium distances and interaction energies, mainly at low range situations (Figure 2). The PES showed in Figure 2 prints the E_{mod} behavior in contrast to the whole UFF and QM plots. In this scenario, we believe this study will be helpful to improve the force fields description of large systems containing Halogen Bond.

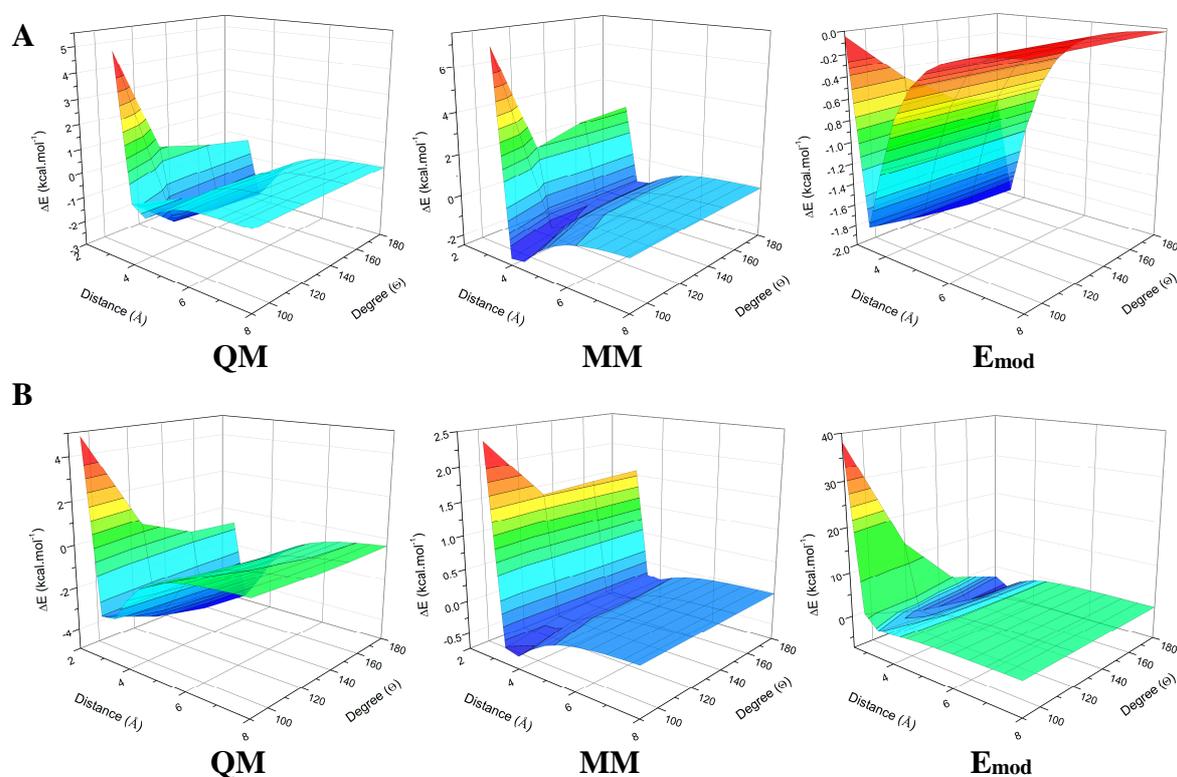


Figure 2. Potential Energy Surfaces of 2-Br \cdots Ar (A) and 2-BrNO $_2\cdots$ NC $_2$ H $_3$ (B) interactions calculated by B3LYP-D3BJ/aug-cc-pVTZ (QM), UFF (MM) and E_{mod} (eq. 1).

Key-words: Halogen Bonds, Force Fields, Empirical Potentials.

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