

## Potential Energy Surfaces for Interactions of H<sub>2</sub>O...HX Systems, with X = H, F, Cl and Br, using a Hyperspherical Harmonics Representation.

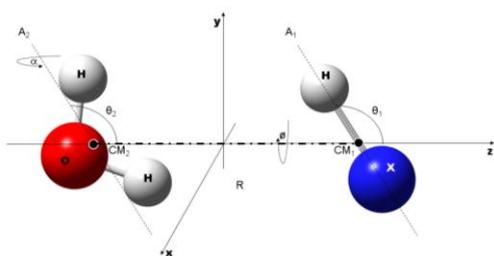
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### INTRODUCTION

In this work we report the explicit representation of the potential energy surfaces for interactions of H<sub>2</sub>O...HX systems, with X representing the atoms H, F, Cl and Br, based on orthogonal vectors, via harmonic expansion functional depending on the distance between the centers of mass of the two molecules and on four angles, assuming that the two molecules are rigid<sup>1-3</sup>. In this way, account for two contributions: an external one depending on the three angle variables which define the mutual orientation of the two molecules and an internal one expressed by the angle which describes the position of the oxygen atom in H<sub>2</sub>O with respect to the H<sub>2</sub>O...HX system.



**Figure 1.** The mutual position of the H<sub>2</sub>O and HX molecules is expressed by five coordinates in the Cartesian coordinate framework *xyz*. The axes *A*<sub>1</sub> and *A*<sub>2</sub> are also defined, respectively, as the axis parallel to the H-X bond and the axis passing through the center of mass of the H<sub>2</sub>O molecule and parallel to the vector joining the H atoms in H<sub>2</sub>O. The radial coordinate *R* is defined as the distance between the center of mass of H<sub>2</sub>O (*CM*<sub>2</sub>) and the center of mass of HX (*CM*<sub>1</sub>).  $\theta_1$  and  $\theta_2$  are the angles between the *A*<sub>1</sub> and *z* axes and *A*<sub>2</sub> and *z* axes, respectively;  $\phi$  is the dihedral angle between the plane going through the *A*<sub>2</sub> and *z* axes and the plane going through the *A*<sub>1</sub> and *z* axes. Finally,  $\alpha$  is the angle that describes the rotation of H<sub>2</sub>O around the *A*<sub>2</sub> axis.

### METHODS

The surface was generated in the framework of the supermolecular approach, using the counterpoise-corrected interaction energies at the CCSD(T), auc-cc-pVQZ level with the Molpro code. Comparisons with the atoms involved are presented and their features are discussed. The analytical form of the potential energy surfaces, for each of the leading configurations, is constructed by fitting the energies to a fifth degree generalized Rydberg function<sup>4,5</sup> into the *ab initio* points.

### CONCLUSIONS

The PES was computed for about one hundred for each of the 27 leading configurations, whose number reduces to 24 because of symmetry properties. The results for the system, presented here, reduced the number of degree of freedom, reducing the computational cost simplifying the fitting of the potential energy surface.

### ACKNOWLEDGMENTS

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