The spherical-harmonics representation for the interaction between XOY-AB molecules: the general case and applications to HOH-B$_2$ and HOH-HB.

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To calculate the potential energy surface (PES) of van der Waals interactions, the general case of XOY-AB molecules were represented through hyperspherical harmonics expansion, that is a mathematically rigorous procedure and a powerful tool for these interacting molecular systems, with applications also to classical and quantum molecular dynamics simulations. This technique consists in the construction of the expanded potential interaction up to terms that provide the generation of a number of leading configurations sufficient to explain faithful geometrical representations. The full general description of the method of the spherical harmonics expansion applied to the systems of nonlinear molecules interacting with diatomic molecules and applications to interaction for H$_2$O with Hydrogen and Halogens atoms is also presented in this article.

Keywords Potential Energy Surface; Van der Waals clusters; XOY-AB molecules; Interaction Energy; Spherical harmonics.

1. Introduction

In molecular dynamics simulations of reactive and non-reactive systems [Aquilanti and Cavalli 1986, Aquilanti et al. 1986], the potential energy surfaces have been lately generated by spherical and hyperspherical harmonics expansions [Palazzetti et al. 2011]. These expansions are best suited for the calculation of matrix elements, which are needed in quantum mechanics. In classical molecular dynamics simulation, a specific requirement is a suitable representation of the interactions by a convenient analytical form, which permits a simple calculation of derivatives and a full account of the involved symmetries. Multipolar expansions have been applied to several areas, including representation of potential energy surfaces, showing as a major feature the fast convergence of the series (see [der Avoird et al. 1994]). The multipolar expansion that we describe here is an exact transformation of quantum chemical (or experimental) input data related to a minimal number of configurations, called "leading configurations", selected on the basis of geometrical and physical characteristics of the system. Since the transformation is exact, the number of terms of the expansion corresponds to the number of leading configurations. The method permits interpolation and extrapolation as needed in dynamical and structure calculations. Spherical harmonics expansion has been largely used to characterize potential energy surfaces of a series of van der Waals aggregates using information from molecular beam studies and/or quantum chemical calculations. The mathematical procedure consists in solving a finite dimensional linear algebra

system, where the elements of the known vector are the input data, in this case the single energy points determined by quantum mechanical calculations, and the elements of the unknown vector are the expansion moments, thus the expansion in spherical harmonics of a certain configuration gives exactly the single point energy. The expansion moments provide interpolation among the potential curves corresponding to the leading configurations, to the whole configuration space. The key points of the method are expansibility by inclusion of further leading configurations and replacing of the input data, when more accurate ones are available. In the characterization of the potential energy surface of a generic XOY-AB van der Waals cluster (one nonlinear molecule interacting with one diatomic molecule composed by five different atoms), we limit our considerations to non-reactive interactions and assume that the interatomic bonds are kept "frozen" i.e. the interacting molecules are considered as rigid in their equilibrium position in the electronic ground state. The functional form depends on a radial coordinate R between centers-of-mass of the two molecules, and the azimuth, the polar and dihedral angles $(\alpha, \theta_1, \theta_2, \phi)$(see Figure 1 in Section 2). The moments of the hyperspherical harmonics expansion are determined by choosing for the quantum chemical calculations a certain number of representative configurations (we call the leading configurations - see Figure 2), with a minimal number, depending on the type of system, based on geometrical and symmetry considerations. The leading configurations allow the solution of a system of linear equations for which the unknown values are the expansion moments and the known values are the interaction potentials determined by *ab initio* calculations. The method allows extension whenever further configurations are available and considered appropriate to improve the representation of the full potential energy surface. The paper is organized as follows. In Section 2 we discuss the representation of the PES and leading configurations. In Section 3 we show results on the application of this method on the HOH-HB system, where B equal to H, F, Cl and Br atoms. We close the paper in Section 4 with Conclusions.

2. Spherical harmonic expansion and Representation of the potential energy surface (PES)

2.1. Coordinates

The parametrization of the nonlinear molecule$\cdots$linear molecule system (XOY$\cdots$AB) requires four orthogonal vectors and a total of nine coordinates [Barreto et al. 2009]. The system is embedded in the Cartesian coordinate frame xyz, whose origin coincides with the center-of-mass of the whole system (see Figure 1 for the general case where XOY is the nonlinear molecule and AB is the diatomic molecule). The lengths of three atomic bonds are frozen and correspond to the two bonds of the molecule XOY and to the AB bond. Next, we define the coordinates of the system: the distance between the centers of mass (CM_1 and CM_2) of the two molecules is the coordinate R, i.e., the vector joining the center of mass of the XOY molecule and the center of mass of the AB molecule, it is denoted by $\vec{R}$ and has module R. In a reference system for bodies fixed, the Z axis is chosen as the axis coincides with the direction of $\vec{R}$. E_1 is the axis parallel to the AB bond of the diatomic molecule and E_2 is along the Jacobi vector of the nonlinear-molecule XOY. The description of the system requires also four angular variables: α, θ_1, θ_2 and $\phi = \phi_1 - \phi_2$ [Barreto et al. 2009, Barreto et al. 2011], while the angle of bending of the XOY molecule is also held fixed at the equilibrium distance. The azimuth is expressed by

the α, whose value varies between 0 and 2π and describes the motion of the AB molecule around XOY (or equivalently the motion of XOY around the E_2-axis. The angle formed by the intersection of the $Z-$ and $E_1 - axes$, along the AB bond is the θ_1, while the θ_2 is the angle formed by the intersection between the axes Z and E_2 along the Jacobi vector of XOY. Their values vary between 0 and π. In this work, we consider the bond length held fixed because we treat the molecules as rigid rotors. Lastly, the dihedral angle ϕ represents the angle formed by the plane passing through the E_1 and Z axes relative to the plane passing through the E_2 and Z axes, and its range varies between 0 and 2π.
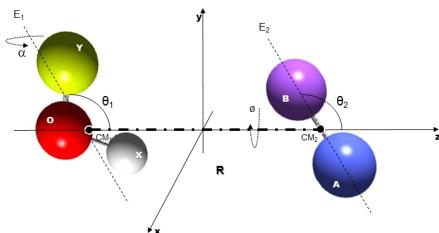
Figura 1. Definition of coordinates (R; α; θ_1, θ_2 and ϕ) in a Cartesian Coordinate system specifying the position of the XOY $\cdots$ AB system.

2.2. Hyperspherical harmonics expansion for the HOX $\cdots$ AB system

In this paper we focus on aspects more relevant for this work in relation to the hyperspherical harmonics expansion of the interaction potential, thus the bond lengths of the molecules are considered "frozen", in such a way that this interaction depends only on four variables: $R; \alpha, \theta_1, \theta_2, \phi$, and then the potential energy surface (PES), V, is given as an expansion of angular functions and the corresponding radial functions:

$$V(R; \alpha, \theta_1, \theta_2, \phi) = \sum_{m,n} \upsilon_{m,n}(R) F_{m,n}(\alpha; \theta_1, \theta_2, \phi) \tag{1}$$

where the $\upsilon_m(R)$ coefficients are the expansion moments depending on the R coordinate (intermolecular distance) and $F_{m,n}(\alpha; \theta_1, \theta_2, \phi)$ are the angular functions, which can be written in terms of the bipolar spherical harmonic, $Y_{L_1 L_2}^{L0}(\theta_1, \theta_2, \phi)$ [Aquilanti and Cavalli 1986] for the "exterior"angles, while the angle α is the argument of functions $w(\alpha)$ accounting for the position of XOY with respect to the largest moment-of-inertia axis:

$$V(R; \alpha; \theta_1, \theta_2, \phi) = \sum_{L_1, L_2, L} \upsilon_{L_1 L_2 L}(R) w(\alpha) Y_{L_1 L_2}^{L}(\theta_1, \theta_2, \phi) \tag{2}$$

with L_1, $L_2 = 0, 1, 2, \cdots, |L_1 - L_2| \leq L \leq L_1 + L_2$. The Equation 1 can be rewritten as:

$$V(R; \alpha; \theta_1, \theta_2, \phi) = \sum_i w_i(\alpha) \sum_{L_1, L_2, L} \begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix} \upsilon_{L_1 L_2 L}(R) Y_{L_1}^{m}(\theta_1, 0) Y_{L_2}^{-m}(\theta_2, \phi) \tag{3}$$

The terms $\begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix}$ is the Wigner $3 - j$ symbol, with $-min(L_1, L_2) \leq m \leq min(L_1, L_2)$, $Y_{L_1}^{m}(\theta_1, 0)$ and $Y_{L_2}^{-m}(\theta_2, \phi)$ are the spherical harmonics. The $w_i(\alpha)$ establishes the weight of each set of leading configurations according to the value of the α

angle, defined by the subscript i (i=0, $\pi/2$, and π) and the general form for $w_i(\alpha)$ is given by $w_i(\alpha) = a_i + b_i \cos(\alpha) + c_i \cos(2\alpha)$ allowing us to compute a_i, b_i, c_i as follow

$$
\begin{aligned}
w_1(\alpha) &= (1/4)+(1/2)\cos(\alpha)+(1/4)\cos(2\alpha) \\
w_2(\alpha) &= (1/2)-(1/2)\cos(2\alpha) \\
w_3(\alpha) &= (1/4)-(1/2)\cos(\alpha)+(1/4)\cos(2\alpha)
\end{aligned}
\tag{4}
$$

For the general case when the molecules are antisymmetric, both the odd and even moments will contribute to the sum in Equation 3 and it will be shown adequate that the sum can be truncated for $L_1 = L_2 = 2$. Explicitly, after extensive algebraic manipulations, one obtains a system of linear equations that depends on angles and moments for $XOY \cdots AB$. In order to evaluate the expansion moments of the interaction potential $V(R, \alpha, \theta_1, \theta_2, \phi)$ and according to [Novillo et al. 2011], we can identify a number of leading configurations (possible positions of the molecules in the system - see Figure 2 in the Subsection 2.3), whose choice is due to physical and geometric considerations. The advantage of such a choice is to select a number of configurations which permit interpolation to account fully for the symmetries of the interactions between the molecules forming the system. The leading configurations depends on their values on α, θ_1, θ_2 and ϕ (shown in 1 for details). We have a system with "n"equations and "n"leading configurations that can be algebraically inverted by Cramer's rule, and get the moments depending on the geometries terms, determined by *ab initio* calculations. And then, we obtain the isotropic term of potential energy, which is important because it can be measured by molecular beam experiments with rotationally hot molecules and can be compared with other systems [Aquilanti et al. 2005, Cappelletti et al. 2010].

2.3. Leading Configurations

We have seen that in order to obtain the Potential Energy Surface it is necessary to find the values of the moments of the expansion of the angular function and their corresponding radial functions. With the *ab initio* calculations we obtain the points of the interaction distances necessary to obtain the radial terms of the potential function, V. Therefore, it is necessary to present possible equilibrium geometries (configurations) that depend only on the angles, allowing us to solve the angular terms of the function. The choice of the minimal number these configurations (leading configurations) is selected based on the geometric and physical characteristics of the system, in order to simplify and converge the calculations. Since the transformation is exact, the number of terms of the expansion corresponds to the number of leading configurations. The method permits interpolation and extrapolation as needed in dynamical and structure calculations. Spherical harmonics expansion has been largely used to characterize potential energy surfaces of a series of van der Waals aggregates using information from molecular beam studies and/or quantum chemical calculations.

3. Aplications

In this section, we report an overview of some case studies of water molecule $\cdots$ diatomic molecule systems. We will represent PES for the case of interaction between the water molecule with diatoms, HOH$\cdots$AB, where A represents the Hydrogen atom and B the Hydrogen, Fluor, Chlorine and Bromine atoms. To construct the PES, *ab initio*
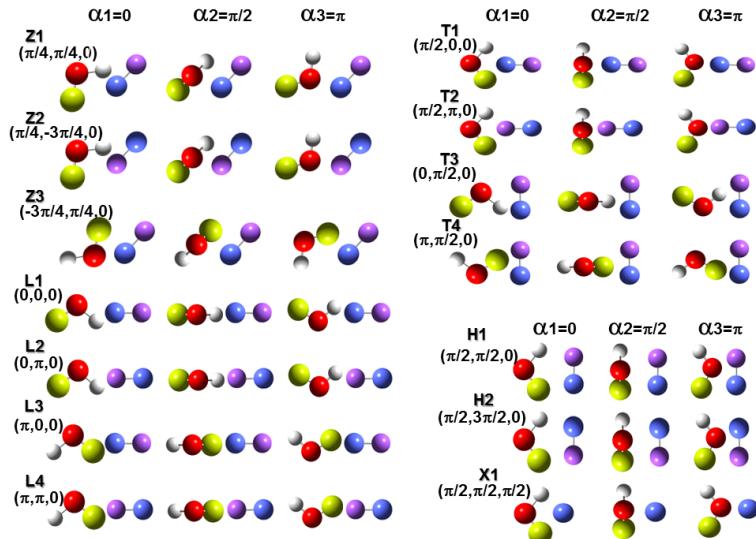
Figura 2. **The fourteen leading configurations for the general case of nonlinear molecule$\cdots$linear molecule system ($\mathrm{XOY}\cdots\mathrm{AB}$). Within parenthesis we reported the three angles θ_1, θ_2 and ϕ, where H1, H2, L1, L2, L3, L4, T1, T2, T3, T4, X1, Z1, Z2 and Z3 are the nomenclature given to the leading configurations in the three positions chosen for the α angle, inserted at the top of the image**

calculations were performed using the MOLPRO code [Werner et al. 0121] and in order to eliminate the basis set superposition error, the full counterpoise Boys and Bernardi method [Boys and Bernardi 2002] was used too. The analytical form of the PES, for each of the leading configurations (see Figure 2) is constructed by fitting the following fifth degree generalized Rydberg function [Rydberg 1931] and Improved Lennard Jones [Pirani et al. 2008] respectively into the *ab initio* points, taking advantage of the parameters also obtained as source of comparisons.

3.1. Interaction between water diatomic molecules

In general case where all atoms differ from each other, the surface can be adequately represented using 42 main configurations, as presented in this paper. For XOX-B_2 systems, eighteen leading configurations are required and only the even terms of the expansion contribute to the sum in equation 3, well explained in the literature [Barreto et al. 2009, Palazzetti et al. 2011]. For XOX-AB systems, twenty seven leading configurations are required and both the even terms of L_1 and the even and odd terms of L_2 in equation 3 contribute to the summation, as well as the interaction of the water molecule with diatomic molecules, when this number of the leading configurations decreases due to symmetries in the system. After extensive algebraic manipulations, one obtains:

$$V_{XOY\cdots AB}(R;\alpha,\theta_1,\theta_2,\phi) = \sum_i w_i(\alpha)\cdot[v_{000}(i;R)+\sqrt{3}v_{011}(i;R)\cos(\theta_2)+\tfrac{\sqrt{5}}{4}v_{022}(3\cos(2\theta_2)+1)$$

$$+\tfrac{\sqrt{5}}{4}v_{202}(i;R)(3\cos(2\theta_1)+1)-\tfrac{\sqrt{6}}{4}v_{211}(i;R)((3\cos(2\theta_1)+1)\cos(\theta_2)+3\sin(2\theta_1)\sin(\theta_2)\cos(\phi)))$$

$$+\tfrac{3}{4}v_{213}(i;R)((3\cos(2\theta_1)+1)\cos(\theta_2)-2\sin(2\theta_1)\sin(\theta_2)\cos(\phi))$$

$$+\tfrac{\sqrt{5}}{16}v_{220}(i;R)((3\cos(2\theta_1)+1)(3\cos(2\theta_2)+1)+3(1-\cos(2\theta_1))(1-\cos(2\theta_2))\cos(2\phi)+12\sin(2\theta_1)\sin(\theta_2)\cos(\phi))$$

$$-\tfrac{5}{8\sqrt{14}}v_{222}(i;R)((3\cos(2\theta_1)+1)(3\cos(2\theta_2)+1)-3(1-\cos(2\theta_1))(1-\cos(2\theta_2))\cos(2\phi)+6\cos(\phi)\sin(2\theta_1)\sin(2\theta_2))$$

$$+\tfrac{3}{16}\sqrt{\tfrac{5}{14}}v_{224}(i;R)(2(3\cos(2\theta_1)+1)(3\cos(2\theta_2)+1)+(1-\cos(2\theta_1))(1-\cos(2\theta_2))\cos(2\phi)-16\sin(2\theta_1)\sin(2\theta_2)\cos(\phi))]$$

Since one of the molecules involved here are antisymmetric (HB when B is the F, Cl and Br atoms), the even and odd moments contribute to the sum in Equation 3 and because these interactions with the water molecule, we can identify twenty-seven terms that must be obtained through the only twenty-seven leading configurations (H1, L1, L2, T1, T2, T3, X, Z1 and Z2), taking into account the symmetry presented in the system, this number decreases to twenty-three because the geometries L1 and L2 are invariant with respect to the $w_i(\alpha)$ (Figures 1 and 2 for details). We have a system with equations that can be algebraically inverted by Cramer's rule and we have:

$$
\begin{aligned}
v_{000}(i;R) &= \tfrac{1}{18}(4V_{H1}(i;R)+V_{L1}(i;R)+V_{L2}(i;R)+2(V_{T1}(i;R)+V_{T2}(i;R)+2(V_{T3}(i;R)+V_X(i;R)))) \\
v_{011}(i;R) &= \tfrac{1}{6\sqrt{3}}(V_{L1}(i;R)-V_{L2}(i;R)+2(V_{T1}(i;R)-V_{T2}(i;R))) \\
v_{022}(i;R) &= \tfrac{1}{9\sqrt{5}}(-2V_{H1}(i;R)+V_{L1}(i;R)+V_{L2}(i;R)+2(V_{T1}(i;R)+V_{T2}-V_{T3}(i;R)-V_X(i;R))) \\
v_{202}(i;R) &= -\tfrac{1}{9\sqrt{5}}(2V_{H1}(i;R)-V_{L1}(i;R)-V_{L2}(i;R)+V_{T1}(i;R)+V_{T2}-4V_{T3}(i;R)+2V_X(i;R)) \\
v_{211}(i;R) &= \tfrac{1}{30\sqrt{3}}(6V_{H1}(i;R)+(3-2\sqrt{2})V_{L1}(i;R)+(3+2\sqrt{2})V_{L2}(i;R)+(3+2\sqrt{2})V_{T1}(i;R)+ \\
&\quad + (3-2\sqrt{2})V_{T2}(i;R)+6(V_{T3}(i;R)-2(V_{Z1}(i;R)+V_{Z2}(i;R)))) \\
v_{213}(i;R) &= \tfrac{1}{30}(2\sqrt{2}(V_{H1}(i;R)+V_{T3}(i;R)-2(V_{Z1}(i;R)+V_{Z2}(i;R)))+ \\
&\quad + (2+\sqrt{2})(V_{L1}(i;R)+V_{T2}(i;R))+(-2+\sqrt{2})(V_{L2}(i;R)+V_{T1}(i;R))) \\
v_{220}(i;R) &= \tfrac{1}{45\sqrt{5}}(2(7V_{H1}(i;R)-2V_{T3}(i;R)-5V_X(i;R)+6V_{Z1}(i;R)-6V_{Z2}(i;R))+ \\
&\quad + (2-3\sqrt{2})(V_{L1}(i;R)-V_{T2}(i;R))+(2+3\sqrt{2})(V_{L2}(i;R)-V_{T1}(i;R))) \\
v_{222}(i;R) &= \tfrac{1}{45\sqrt{7}}(2\sqrt{2}(5V_{H1}(i;R)+2V_{T3}(i;R)-7V_X(i;R)-3V_{Z1}(i;R)+3V_{Z2}(i;R))+ \\
&\quad + (3-2\sqrt{2})(V_{L1}(i;R)-V_{T2}(i;R))+(3+2\sqrt{2})(V_{T1}(i;R)-V_{L2}(i;R))) \\
v_{224}(i;R) &= \tfrac{2}{15}\sqrt{\tfrac{2}{35}}(2(V_{H1}(i;R)-V_{T3}(i;R)-2V_{Z1}(i;R)+2V_{Z2}(i;R))+ \\
&\quad + (1+\sqrt{2})(V_{L1}(i;R)-V_{T2}(i;R))+(1-\sqrt{2})(V_{L2}(i;R)-V_{T1}(i;R)))
\end{aligned}
\tag{5}
$$

The same applies to homonuclear systems (HB when B is the H atom), where the potential energy surface can be adequately represented by eighteen leading configurations because the diatomic molecule involved here presenting symmetric characteristics that decrease the number of leading configurations necessary to solve the systems of equations, since only the even moments will contribute to the sum in the Equation 3.

3.2. Results for interaction between water and diatomic molecules

In Figures 3(a), 3(b) and 3(c) it is shown a cut of the representation through hyperspherical harmonics expansion of the potential energy surface (PES) of van der Waals interactions for HOH$\cdots$H$_2$, HOH$\cdots$HF and HOH$\cdots$HCl systems. The Figure 4 report the isotropic components of the interaction potential of HOH$\cdots$H$_2$ system with minimum at -46.8 cm^{-1} located at 3.5 Å, HOH$\cdots$HF system with minimum at -121.4 cm^{-1} located at 4.3 Å, and HOH$\cdots$HCl system with minimum at -174.2 cm^{-1} located at 3.7 Å. These components, which can be measured experimentally, would allow comparison and evaluation of the reability of the theoretical method.

4. Conclusions

In this paper we study the possibility of representing the potential energy surface for a general case of interaction between XOY-AB molecules and we present some applications where the water molecule represents XOY and the diatoms HH, HF and HCl represent

(a) HOH$\cdots$H$_2$.

(b) HOH$\cdots$HF.

(c) HOH$\cdots$HCl.
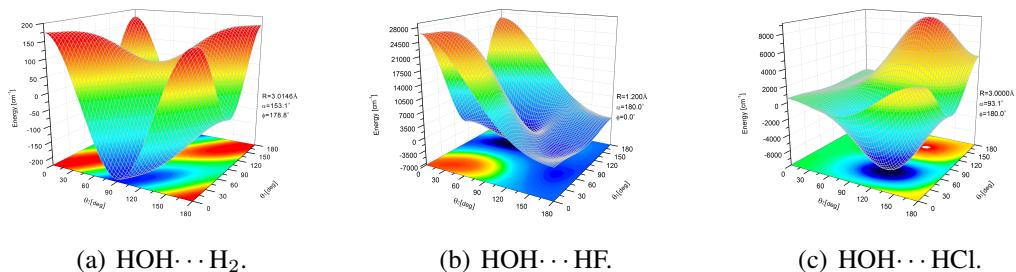
Figura 3. Representation of the potential energy surface near the global minimum configuration .
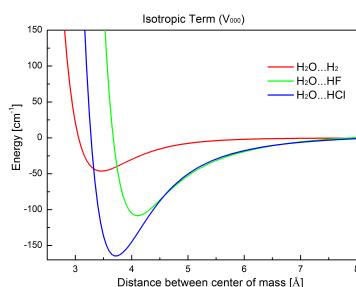
Figura 4. Isotropic Term for the HOH$\cdots$HB System, with B = H, F and Cl.

AB. In these applications, the PES was computed for about one hundred points for each of the leading configurations, whose number reduces from 42 to 23 for HOH$\cdots$HB (where B equal to F and Cl atoms) and to 18 for HOH$\cdots$B$_2$ (where B equal to H, F and Cl atoms), because of symmetry properties. The results for the system reducing the computational cost simplifying the fitting and the representation of the potential energy surface for other applications also to classical and quantum molecular dynamics simulations.

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