

## HYPERSPHERICAL COORDINATE POTENTIAL ENERGY SURFACE FOR THE Rg<sub>3</sub> COMPLEX, WITH Rg=Ne, Ar, Kr AND Xe

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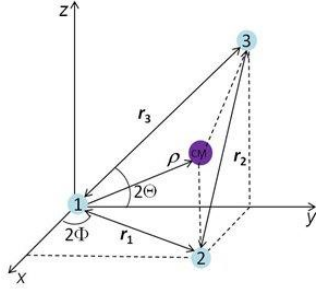
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### 1. Introduction

Since the appearing of first work on He<sub>3</sub> in 1972[1], several theoretical papers have been published using different methods: Monte Carlo [2, 3], specific functions [4] and hyperspherical coordinates [5]. Nevertheless, unfortunately, an analytic form of the PES simple enough to be used for all the purposes were missing. On a previous paper [6], we had fill out the above gap by furnishing a very simple and accurate analytical expression of the PES for the He<sub>3</sub> and now we use it for all the rare gas series. In the literature we can find different approach to different systems, as Ne<sub>3</sub> studied by variational approach, which uses atom pair coordinates and a distributed Gaussian function (DGF) basis set by Baccarelli et. al, [7].

### 2. Theoretical and Computational Details

The coordinate system is made by three variable, the hyperradius ( $\rho > 0$ ) and two hyperangles ( $0 \leq \Theta \leq \pi/4$  and  $0 \leq \Phi \leq \pi/3$ ). The hyperangle  $\Theta$  represents the area of the triangle and the hyperangle  $\Phi$  is related with the shape of it, the hyperradius,  $\rho$ , is the vector pointed out from the center-of-mass (CM) of the system, see Fig.1.



**Fig. 1** Definition of the hyperspherical coordinates ( $\rho, \Theta, \Phi$ ). The vector  $r_i$  ( $x_i; y_i; z_i$ ) ( $i = 1; 2$  and  $3$ ) representing the internuclear distances of the rare gas atoms,  $\rho$  is the vector with representing the distance between the center-of-mass of the molecule system.

In this figure, the vectors  $r_i$  ( $x_i; y_i; z_i$ ) ( $i = 1; 2$  and  $3$ ) representing the interatomic distances in space. We have obtained the PES using the mass unscaled hyperspherical coordinates. Note that the ranges of  $\Theta$  and  $\Phi$  are lower than their standard values. Symmetry restrictions are, indeed, needed to account for the exchange of identical particles. The definition of the hyperradius and hyperangles can be find in our previous work [6].

Using the coordinates system, presented in Fig.1, the PES can be expanded into a series of angular functions multiplied by radial coefficients (expansion moments):

$$V(\rho, \Theta, \Phi) = \sum_m v_m(\rho) F_m(\Theta, \Phi) \quad (1)$$

where the  $v_m(\rho)$  coefficients are the expansion moments depending on the  $\rho$  coordinate and  $F_m(\Theta, \Phi)$  are angular functions which can be written as the real Wigner D-functions [8] with the  $\gamma$  angle equal to zero, where the D-function is given by:  $D_{m,n}^l(\Theta, \Phi, \gamma) = e^{-im\Theta} d_{m,n}^l(\Phi) e^{-im\gamma}$ , and  $d_{m,n}^l(\Phi)$  is tabulated function. In that, way the term  $F_m(\Theta, \Phi)$  can be written as:

$$F_{m,n}^l(\Theta, \Phi, \gamma) = \sqrt{\frac{8\pi^2}{2(2l+1)}} \left( D_{m,n}^l(\Theta, \Phi, \gamma) + \epsilon D_{-m,-n}^l(\Theta, \Phi, \gamma) \right) \quad (2)$$

Truncating equation (1) at  $m = 1$ , which is enough to represent a three-body system, we have:

$$V(\rho, \Theta, \Phi) = \sqrt{2} \{ v_{0,0}(\rho) d_{0,0}^0(4\Phi) + v_{0,1}(\rho) [d_{0,0}^1(4\Phi) + d_{0,1}^1(4\Phi)] + v_{1,1}(\rho) \cos(6\Theta) [d_{1,0}^1(4\Phi) + d_{1,1}^1(4\Phi)] \} \quad (3)$$

This shows that three not dependent radial functions are needed for  $V(\rho, \Theta, \Phi)$ , thus we considered three different arrangements (leading configurations) of the Rg<sub>3</sub> complex: the linear disposition, the equilateral triangle and a scalene triangle. The expansion moments are, then, obtained by a linear combination of the potential profiles calculated for the leading configurations. The moments  $v_{m,n}(\rho)$  are related to the potentials of the leading configurations by:

$$\begin{aligned} V_{eq}(\rho) &= \sqrt{2} (v_{0,0}(\rho) - v_{0,1}(\rho)) \\ V_{sc}(\rho) &= \sqrt{2} v_{0,0}(\rho) + \frac{1}{2} (\sqrt{3} - \sqrt{2}) v_{0,1}(\rho) \\ V_{lin}(\rho) &= \sqrt{2} (v_{0,0}(\rho) + v_{0,1}(\rho) + v_{1,1}(\rho)) \end{aligned} \quad (4)$$

Solving the above system of equations for  $v_{0,0}(\rho)$ ,  $v_{0,1}(\rho)$  and  $v_{1,1}(\rho)$ , gives:

$$\begin{aligned}
 v_{0,0}(\rho) &= \left( \sqrt{\frac{3}{2}} - 1 \right) \left( (\sqrt{3} - \sqrt{2})V_{eq}(\rho) + 2\sqrt{2}V_{sc}(\rho) \right) \\
 v_{0,q}(\rho) &= -\sqrt{2}(\sqrt{6} - 2) \left( V_{eq}(\rho) + V_{sc}(\rho) \right) \\
 v_{1,1}(\rho) &= \left( 4\sqrt{3} - \frac{9\sqrt{2}}{2} \right) V_{eq}(\rho) + 4(\sqrt{2} - \sqrt{3})V_{sc}(\rho) + \frac{\sqrt{2}}{2}V_{lin}(\rho)
 \end{aligned}
 \tag{5}$$

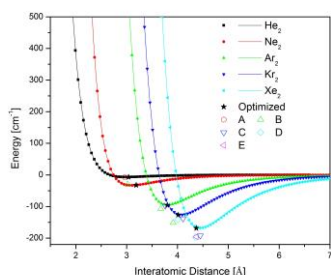
Therefore, by substituting eq. (5) into eq. (4), the full potential is obtained provided analytical expressions for  $V_{lin}(\rho)$ ,  $V_{eq}(\rho)$  and  $V_{sc}(\rho)$  are available. To get  $U(\rho)$ , where  $U(\rho) = V_{sc}(\rho)$ ,  $V_{sc}(\rho)$ ,  $V_{sc}(\rho)$ ; we have computed the energies of 151 points having different values of  $\rho$  for each of the three leading configurations, then we have fitted the energies vs  $\rho$  by means of a nonlinear least-square procedure, using a fifth degree generalized Rydberg potential as the fitting function. The complex energy is expressed as:  $E_{int} = E_{Rg_3} - 3E_{Rg}$ .

### 3. Results and Discussions

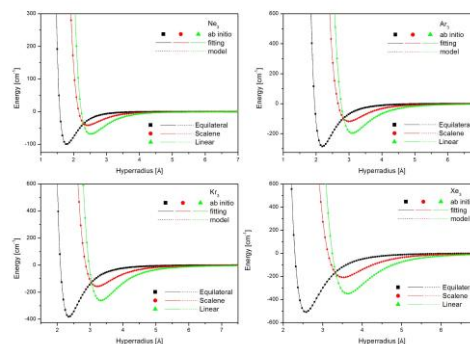
The ab initio calculations were carried out by using the Molpro2010 program. The CCSD(T)/aug-cc-pVQZ for all  $Rg_3$  system, except for  $Xe_3$  where the basis set aug-cc-pvQZ-PP was used. First, a simple optimization and frequency calculation for all dimers and trimers were carried out to determine the equilibrium configuration. It will be used as a guide for the PES calculation. For all trimers, we have computed 151 energies to different values of distance, while for the dimers we calculated 101 energies. A nonlinear least-squares procedure was used to obtain the values of the adjustable parameters that minimize the differences between the analytical energies obtained with the fifth degree generalized Rydberg function.

Fig.2 compared the PES for the dimers. The optimized data are, also, included in this figure, with the reference data. It is possible to observe that our optimized data are in good agreement with the reference data. The biggest error in the ab initio fitting is for the Xenon dimer, with a rms of  $0.033252 \text{ cm}^{-1}$ .

Fig.3 present the ab initio and the Rydberg fitting for leading configuration of each rare gas trimer. The smallest and biggest rms among all the fittings are  $0.006707$  and  $0.158722 \text{ cm}^{-1}$  for the scalene  $Xe_3$  and equilateral  $Kr_3$ , respectively.



**Fig. 2:** Dimers potential energy surface, [A] *J. Chem. Phys.* 1972, 56, 5801, [B] *J. Chem. Phys.* 1976, 65, 3242, [C] *J. Mol. Spectr.* 1973, 46, 454, [D] *J. Chem. Phys.* 1974, 61, 3081, [E] *J. Chem. Phys.* 1974, 61, 4880



**Fig. 3**  $Rg_3$  leading configurations

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