

Symmetry assignment in the distributed Gaussian functions method to study homonuclear rotating trimers

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Abstract

An approximate method based on the use of distributed Gaussian functions (DGF) to describe the interparticle distances is employed to study the rovibrational spectrum of trimers. Rotational energy levels are obtained by assuming that vibration and rotation are separated. Thus, eigenstates of the Hamiltonian for the zero total angular momentum, $J = 0$, are used as basis set to solve the rotational Hamiltonian. A procedure to identify the corresponding symmetry character for the rovibrational bound states is proposed. The DGF approach is applied to the case of the rotating Ar₃ trimer. The reliability of the method is tested by comparison with results from an exact hyperspherical coordinate calculation for $J = 0, 1$ and 6.

1 Introduction

Some years ago an exact variational method which employs distributed Gaussian functions (DGFs) to describe the interparticle distances R_1 , R_2 and R_3 was developed to tackle the study of weakly bound trimers. By means of this approach, the energy levels and geometrical structure of the bound states for a zero total angular momentum, $J = 0$, of systems such as He₃ [1,2] and LiHe₂ [3,4] were investigated. Successive applications have extended these studies of the vibrational spectrum to a large list of three-body (3B) systems [5,6]. The selection of Gaussian functions in the radial grids for the corresponding

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pair distances coordinates yields a basis set which is constituted, in essence, for functions describing different triangular arrangements. Such basis functions have been found to provide an adequate scheme to analyse the overall geometry of the bound states of the molecular trimers under study.

In order to extend this technique to study those cases in which, besides the vibrational motion, the 3B system also rotates, we propose here an approximate method based on the use of the R_1 , R_2 and R_3 coordinates. Although there certainly exists the possibility to deal with a Hamiltonian for nonzero total angular momenta, $J > 0$, written in terms of those interparticle distances [7], our intention is to develop a less demanding alternative than an exact method to perform reliable calculations of the rovibrational spectrum of rotating trimers for large values of J . A possible strategy consists on assuming the separation of the rotational and vibrational problems. Under such an assumption, the total Hamiltonian is expressed as the sum of a term containing the $J = 0$ contribution, H_{vib} , and the rotational Hamiltonian, H_{rot} , which vanishes for a zero total angular momentum. Once the $J = 0$ case is solved by means of the above mentioned vibrational version of the DGF method, the corresponding eigenfunctions of H_{vib} are employed, besides standard rotational basis functions $|J\Omega M\rangle$ (Ω and M being the projections of \mathbf{J} on the body- and space-fixed z -axis respectively), to diagonalise the rovibrational Hamiltonian.

The DGF approach has been employed before to estimate rotational constants for the cases of the Ne_2H^- and Ne_2Kr systems [8]. The calculation was done however with a mere average on the ground vibrational state configurations and no $J > 0$ rovibrational spectra were evaluated. The only attempt to calculate rotational energies by means of a DGF-based method was made in the past when the possible existence of rotationally excited states for He_3 was investigated [9]. However, in that case, the rovibrational basis set was assumed to contain exclusively the element $|J = 1, \Omega = 0, M\rangle$. In addition, the rotational contribution to the matrix elements of the total Hamiltonian was reduced simply to a diagonal term with the rotational eigenstate of an asymmetric rotor consistent with the above mentioned choice for J and Ω . Besides these limitations, there exists an additional issue to solve regarding the symmetry of the corresponding bound states. Since the total symmetry is not imposed within the DGF scheme, it is necessary to design a procedure to identify the symmetry associated with the $(2J + 1)$ rotational energy levels for each vibrational state k . In this work we propose an efficient method in which the symmetry of the rovibrational states is analysed in terms of the corresponding values of ℓ , the vibrational angular momentum number. The assignment of this quantum number to the bound states obtained in the DGF calculation is done simply by comparison with the spectrum for $J = 0$ obtained in an exact hyperspherical coordinates (HC) calculation. The method is applied in the case of the Ar_3 system. The rovibrational spectra for this trimer at $J = 0 - 6$ have been recently studied by means of an HC approach [10]. In

the work of Ref. [10], only rotational levels belonging to the fully symmetric irreducible representation A_1 were reported. In order to test the reliability of the approach proposed here we have extended those HC calculations to obtain, not only the physically acceptable bound states but those corresponding to all possible symmetry blocks included in the D_3 group, isomorphic with the permutational group for a three identical particles system.

2 Theory

As mentioned in the previous section, the solution of the vibrational part is obtained by means of the DGF method for $J = 0$. The approach has been extensively described before [5,6], so we restrict ourselves to indicate that the total wave function is expressed as:

$$\Phi_k(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3), \quad (1)$$

where the ϕ functions are written in terms of the product of Gaussian functions φ as follows:

$$\phi_j(R_1, R_2, R_3) = N_{l_1 l_2 l_3}^{-1/2} \varphi_{l_1}(R_1) \varphi_{l_2}(R_2) \varphi_{l_3}(R_3), \quad (2)$$

with $N_{l_1 l_2 l_3}$ being normalization constants.

Details regarding the solution of the rotational part have been published elsewhere [6]. Here we limit the theoretical description to the most relevant aspects. In the general case of an asymmetric top, it is possible to write the rotational Hamiltonian as [11–13]:

$$H_{rot} = \frac{1}{2}(A + C)\mathbf{J}^2 + \frac{1}{2}(A - C)(J_A^2 + \kappa J_B^2 - J_C^2), \quad (3)$$

where the κ factor above corresponds to Ray's asymmetry parameter [14], defined as $\kappa = (2B - A - C)/(A - C)$.

The Hamiltonian matrix elements in the corresponding vibration-rotation basis take the form:

$$\langle k; J\Omega M | H_{rot} | k'; J'\Omega' M' \rangle = \sum_{jj'} a_j^{(k)} a_{j'}^{(k')} \langle \phi_j; J\Omega M | H_{rot} | \phi_{j'}; J'\Omega' M' \rangle. \quad (4)$$

The integration in each internal radial coordinate R_i of the corresponding product of DGFs $\varphi(R_i)$ involved in the matrix elements of Eq. (4) is solved,

in an approximate way, as the product of the overlaps between each pair of Gaussian functions in each radial coordinate and the value of the rotational Hamiltonian, $H_{rot}(R_1^\dagger, R_2^\dagger, R_3^\dagger)$, at the R_i^\dagger values. These R_i^\dagger are the centers of the Gaussian functions obtained as the product of the two DGFs depending on R_i [5,6].

The rotational Hamiltonian matrix, diagonal in the J and M quantum numbers, can be then further expanded as [11–13]:

$$\begin{aligned} \langle J\Omega M | H_{rot}(R_1^\dagger, R_2^\dagger, R_3^\dagger) | J\Omega' M \rangle &= \frac{A^\dagger - C^\dagger}{2} \mathcal{H}^\dagger \sqrt{f(J, \Omega \pm 1)} \delta_{\Omega \pm 2, \Omega'} \\ &+ \left[\frac{A^\dagger + C^\dagger}{2} J(J+1) + \frac{A^\dagger - C^\dagger}{2} \left[\mathcal{F}^\dagger J(J+1) + (\mathcal{G}^\dagger - \mathcal{F}^\dagger) \Omega^2 \right] \right] \delta_{\Omega, \Omega'} \end{aligned} \quad (5)$$

where

$$f(J, \Omega \pm 1) = \frac{1}{4} [J(J+1) - \Omega(\Omega \pm 1)] [J(J+1) - (\Omega \pm 1)(\Omega \pm 2)]. \quad (6)$$

In a near oblate basis: $\mathcal{F} = (\kappa+1)/2$, $\mathcal{G} = -1$ and $\mathcal{H} = (\kappa-1)/2$ [11,12]. The \dagger symbols in Eq. (5) indicates that the different quantities have been evaluated at the corresponding R_i^\dagger values. For the calculation of the quantities A , B , C in Equation (5) we have chosen the body frame formed by the instantaneous principal axes of inertia corresponding to the triangular system of R_1^\dagger , R_2^\dagger and R_3^\dagger sides. The rovibrational spectrum is then obtained by diagonalizing the Hamiltonian matrix of Eq. (4), which includes the effect of possible interaction between different vibrational states in those elements with $k \neq k'$. Analogously, according with Eq. (5), the Hamiltonian matrix is not diagonal in the Ω quantum number. As in the case of the HC calculation, the assignment of such number to the rovibrational eigenstates is done by considering the dominant value of Ω .

The present DGF approach consists on the description of the rotating trimer by means of “instantaneous” images of the system defined by the geometry formed with the $(R_1^\dagger, R_2^\dagger, R_3^\dagger)$ sizes. Given that those configurations might correspond, in principle, to any possible triangular arrangement, the employed rotational Hamiltonian, shown in Eq. (3), which corresponds to the most general possible case of an asymmetric rotor, seems a sensible choice. In this sense, this scheme is similar the separation of rotation and vibration proposed by Jellinek and Li [15], in which the time evolution of the rotation of a nonrigid system is represented by the rotational motion of a changing rigid body. In our case, due to the use of of finite width Gaussian functions instead of strict Delta functions, the corresponding A , B and C rotational quantities can be assumed as not completely rigid but affected by the different k vibrational states

employed in the matrix representation of the rotational Hamiltonian. The instantaneous separation of the rotational and vibrational energies suggested in Ref. [15] leads to zero Coriolis terms in the corresponding Hamiltonian.

The exact calculation of the rovibrational states of Ar₃ has been performed by using the HC coordinates of Pack and Parker [16] described in previous applications [17,18]. The basis set employed in the calculation is adapted to the permutation symmetry. Bound states obtained with the HC method are classified according with the values of the (v_1, v_2^ℓ) and Ω quantum numbers, where v_1 and v_2 describe the symmetric and antisymmetric vibrations.

3 Approximate assignment of the symmetry

The full symmetry of the wave functions of the bound states obtained with the present DGF approach can be expressed as the product of the symmetries of a “vibrational” part, $\Gamma_v^{\Omega\ell}$, which, due to its dependence on the Ω and ℓ numbers, we will denote hereafter as rovibrational symmetry, and of a rotational part, Γ_R , as $\Gamma = \Gamma_v^{\Omega\ell} \times \Gamma_R$. Γ is, for the case of homonuclear trimers, an irreducible representation of the permutation inversion group isomorphic with D_{3h} .

On the one hand, symmetry adapted rotational functions are built as linear combination of Wigner rotation matrices as

$$D_{M\Omega}^{J\Gamma_R}(\alpha, \beta, \gamma) = A_{M\Omega}^{J\Gamma_R} D_{M\Omega}^{J*}(\alpha, \beta, \gamma) + B_{M\Omega}^{J\Gamma_R} D_{M-\Omega}^{J*}(\alpha, \beta, \gamma), \quad (7)$$

where α, β, γ are the Euler angles which relate the principal axes of inertia with the space-fixed frame. The application of the corresponding symmetry operators on the Wigner functions [19] leads to the following expression for the coefficients $A_{M\Omega}^{J\Gamma_R}$ and $B_{M\Omega}^{J\Gamma_R}$:

$$A_{M\Omega}^{J\Gamma_R} = \begin{cases} \chi^{\Gamma_R}(E) + 2\chi^{\Gamma_R}(C_3), & \Omega \neq 0 \\ \chi^{\Gamma_R}(E) + 2\chi^{\Gamma_R}(C_3) + 3(-1)^J \chi^{\Gamma_R}(C_2), & \Omega = 0 \end{cases} \quad (8)$$

$$B_{M\Omega}^{J\Gamma_R} = \begin{cases} 3(-1)^{J-\Omega} \chi^{\Gamma_R}(C_2), & \Omega \neq 0 \\ 0, & \Omega = 0 \end{cases} \quad (9)$$

where E , C_3 and C_2 are the classes of the D_3 group. The substitution of the characters χ^{Γ_R} for the corresponding irreducible representations [20] leads to the conclusion that Γ_R can only be A_1 or A_2 , since the E representation is

not allowed. Furthermore, one obtains that: (i) for $\Omega = 0$, $\Gamma_R = A_1$ for even values of J and $\Gamma_R = A_2$ for odd J , and (ii) for $\Omega \neq 0$, both A_1 and A_2 representations are possible. The expressions shown in Eqs. (8) and (9) are subject to the precise choice of the Euler angles, identical, in this case, to the selection adopted in Refs. [17] and [18].

A similar analysis of the rovibrational part can be done in terms of the n quantum number, defined as $n = |\pm 2\ell - \Omega|$ with $\ell \geq 0$ and $\Omega \geq 0$. Although this definition differs slightly from the value that one would obtain according with Ref. [17], for the purpose of the present discussion, once the relative sign between ℓ and Ω is distinguished, the above selection for n should be sufficient. The definition of the symmetry adapted vibrational functions:

$$f_n^{\Gamma_v^{\Omega\ell}}(\phi_\tau) = A_n^{\Gamma_v^{\Omega\ell}} e^{-in\phi_\tau} + B_n^{\Gamma_v^{\Omega\ell}} e^{in\phi_\tau}, \quad (10)$$

ϕ_τ being one of the two hyperangles employed in the HC approach, and the subsequent application of the symmetry operators yields the following expression for the $A_n^{\Gamma_v^{\Omega\ell}}$ and $B_n^{\Gamma_v^{\Omega\ell}}$ coefficients:

$$A_n^{\Gamma_v^{\Omega\ell}} = \chi_v^{\Gamma_v^{\Omega\ell}}(E) + \chi_v^{\Gamma_v^{\Omega\ell}}(C_3) 2 \cos \frac{4\pi}{3} n \quad (11)$$

$$B_n^{\Gamma_v^{\Omega\ell}} = \chi_v^{\Gamma_v^{\Omega\ell}}(C_2) \left(1 + 2 \cos \frac{2\pi}{3} n \right). \quad (12)$$

As in Eqs. (8) and (9), the substitution of the corresponding values of the $\chi_v^{\Gamma_v^{\Omega\ell}}$ characters [20] enables us to establish the dependence of $\Gamma_v^{\Omega\ell}$ on the values of n as follows: (i) For $n = 0$, it is found that $\Gamma_v^{\Omega\ell} = A_1$; (ii) for n multiple of 3, $\Gamma_v^{\Omega\ell}$ can be expressed as a linear combination of A_1 and A_2 , and finally (iii) for n not multiple of 3, $\Gamma_v^{\Omega\ell} = E$.

One needs therefore a procedure to estimate the corresponding value of n for each bound state of the DGF calculation. According with the definition of n and considering that Ω is included in the basis set of the DGF scheme, all we have to do is to assign the ℓ label. This is done simply by comparison of the predicted spectrum for $J = 0$ with the exact result provided by the HC calculation. Once we manage to establish the values (ℓ, Ω) to each rovibrational state we are capable to classify the different bound states according with symmetry considerations. The ℓ quantum number is then found, as we will see below, to label as well the rovibrational part of the bound states for $J > 0$. Besides the separation in the A_1 , A_2 and E irreducible representations, states are labelled with ' or ' ' depending on whether Ω is even or odd respectively. Finally, those situations in which, due to the $\pm 2\ell$ term in the definition of n , two different values of n are obtained with the same $\ell \neq 0, \Omega \neq 0$ pair, are solved by assigning the lowest n to the level with the lowest energy. The uncertainty

on the sign of 2ℓ is connected with the fact that, whereas the approximate symmetry assignment is explicitly based on ℓ and the z component of the total angular momentum, the precise choice for the x and y axes remains undefined. The above mentioned criterion enables us however to overcome the possible uncertainties in the elucidation of the correct symmetry.

The present strategy, suggested for the DGF method, should be, in principle, applicable as well in those general cases in which the assignment of the symmetry character of the rovibrational spectra is required. In Section 4, we apply this procedure on the $J = 0, 1$ and 6 rovibrational spectra of the Ar_3 system.

4 Results: Application to the Ar_3 system

In the present study, we have used 23 DGFs, with the first one centered at $6.21 a_0$, which generate 12167 ϕ_j functions (see Eq. (2)). Numerical parameters of the HC calculation, on the other hand, have been optimised to ensure convergence and the reproduction of those bound states at $J = 0-6$ belonging to the fully symmetric representation reported in the exact HC calculation by Karlický *et al.* [10]. The potential energy surface used in the calculation is formed by a semiempirical Ar-Ar potential [21] and a newly developed *ab initio* potential [10] to describe 3B interactions.

4.1 The vibrational case: $J = 0$

We start by calculating the vibrational spectrum for the Ar_3 cluster. The predictions for the energy levels at $J = 0$ obtained with the DGF method are compared in Table 1 with the exact result from the HC calculation. The comparison has been made for the three possible irreducible representations for a zero total angular momentum: A'_1 , E' and A'_2 . The agreement between the DGF and HC results is remarkably good. It is thus possible to associate the values of the (v_1, v_2^ℓ) numbers with the labels employed in the DGF scheme to classify the vibrational states. In particular, we can now assign the ℓ quantum number to the different k states: $k = 1, 4, 5, 10$ and 13 correspond to $\ell = 0$; $k = 2-3, 8-9$ and $11-12$ have $\ell = 1$; $k = 6-7$ correspond to $\ell = 2$ and $k = 14$ is assigned to $\ell = 3$. With those values of ℓ and the unique possibility for Ω at $J = 0$, $\Omega = 0$, we have that $n = 2\ell$. The first step is the identification *via* the precise values of n , of the rovibrational symmetry character of the $(k; \Omega = 0)$ states. According with the discussion of Section 3 we can conclude that: (i) states with $\ell = 0$ exhibit $\Gamma_v^{\Omega\ell} = A_1$; (ii) states with $\ell = 1$ and 2 , and therefore, with n not multiple of 3 , lead to $\Gamma_v^{\Omega\ell} = E$ and (iii) the only case with $\ell = 3$, the $(k = 14; \Omega = 0)$ state presents $\Gamma_v^{\Omega\ell}$ as a linear combination of A_1 or A_2 .

These results for $\Gamma_v^{\Omega\ell}$ are included in Table 1.

In order to assign the full symmetry, we must remind from Section 3, that the only possibility for Γ_R for the present case, $J = 0, \Omega = 0$, is A'_1 , which yields $\Gamma = \Gamma_v^{\Omega\ell} \times A'_1 = \Gamma_v^{\Omega\ell}$ and therefore: $\Gamma = A'_1$ for the $\ell = 0$ case and $\Gamma = E'$ for $\ell = 1, 2$. The symmetry assignment for the case of $\ell = 3$ is, in principle, not as straightforward as the preceding situations. The uncertainty for $\Gamma_v^{\Omega\ell}$ is translated to the full symmetry and thus, Γ can also be either A'_1 or A'_2 . There are additional circumstances however that enable us to discriminate the precise symmetry character to which the ($k = 14; \Omega = 0$) state belongs to. Interestingly this is the only vibrational state, within the energy range we are considering here ($\lesssim -185 \text{ cm}^{-1}$), that can be obtained exclusively with the basis set given in Eq. (2), suitable for a three non-identical particles system. The ($k = 1, 4, 5, 10, 13; \Omega = 0$), on the contrary, are the sole levels in the spectrum obtained by using a basis set in which the three particles are treated as identical, with permutations in the corresponding three pairwise distances (see Eq. (13) in Ref. [6]). This is therefore consistent with the assignment to the A'_1 block concluded here by means of the analysis of the corresponding values of n and ℓ . When alternatively the basis employed in the DGF calculation corresponds to a 3B system with two identical particles (see Eq. (14) of Ref. [6]), the spectrum is completed, besides the above mentioned fully symmetric states, with the ($k = 2, 6, 8, 11; \Omega = 0$) bound states. The fact that the ($k = 14; \Omega = 0$) level is exceptionally obtained with the basis set of Eq. (2) supports, in our opinion, the final assignment to the A'_2 irreducible representation performed here. Given that $\Omega_R = A'_1$, $\Gamma_v^{\Omega\ell}$ is then forced to be A_2 .

The correspondence between the spectra obtained for $J = 0$ by means of the DGF and HC calculations shown in Table 1 is also consistent in the case of those states belonging to the E' representation. In the DGF results, the bound states $k = 2 - 3, 6 - 7, 8 - 9$ and 11-12 appear as almost completely degenerate pairs respectively. As explained before, it is found that one of the states of these degenerate states is obtained in the calculation performed with the basis set in which two particles of the systems are treated as identical. By employing the present basis functions (those from Eq. (2)) one obtains the expected degeneration for states belonging to the E' symmetry case.

4.2 The rotating system: $J = 1$ and 6

Once the ℓ quantum number has been assigned to the bound states for a zero total angular momentum, we proceed to the calculation of the rovibrational spectra for $J = 1$ and 6. For these two cases we will test the method proposed in Section 3 to assign the symmetry character of the DGF rotational states.

Thus the obtained energy levels and the assigned symmetry will be compared with the result from the exact HC calculation, in which the different symmetry blocks are treated separately.

The result of the calculation for $J = 1$ is shown in Table 2. The assignment of the total symmetry is the result of the application of the rules for the rovibrational symmetry discussed above for the two only possible values of Ω for $J = 1$ in combination with the fact that, for such total angular momentum, $\Gamma_R = A_2$ for $\Omega = 0$ and $\Gamma_R = A_1, A_2$ for $\Omega = 1$. Let us describe with some detail, as an illustrative example, the overall procedure case by case. As in the purely vibrational problem, we start by calculating the values of n for the different bound states.

Firstly we consider $\Omega = 0$. For this case, $\Gamma_R = A'_2$ which, depending on the value of ℓ , yields the following possibilities:

- (i) $\ell = 0$ leads to $n = 0$ and $\Gamma_v^{\Omega\ell} = A_1$. Therefore we have $\Gamma = A_1 \times A'_2 = A'_2$. This is the case of the ($k = 1, 4, 5, 10, 13; \Omega = 0$) states;
- (ii) $\ell = 1, 2$ lead to $n = 2$ and $n = 4$ respectively, which means that in both cases, $\Gamma_v^{\Omega\ell} = E$. Hence $\Gamma = E \times A'_2 = E'$. This is the assignment for the ($k = 2 - 3, 8 - 9, 11 - 12; \Omega = 0$) and ($k = 6 - 7; \Omega = 0$) states respectively;
- (iii) $\ell = 3$, which corresponds to ($k = 14; \Omega = 0$), leads to $n = 6$. As discussed in the $J = 0$ case, the ambiguity regarding the rovibrational symmetry is solved by choosing $\Gamma_v^{\Omega\ell} = A_2$ and therefore $\Gamma = A_2 \times A'_2 = A'_1$.

Secondly we treat the case in which $\Omega = 1$. As discussed in Section 3, for $J = 1, \Omega = 1$, we find $\Gamma_R = A''_1, A''_2$. Then, depending on the values of ℓ the total symmetry is identified as follows:

- (i) $\ell = 0$ leads to $n = 1$ and then $\Gamma_v^{\Omega\ell} = E$ which forces $\Gamma = E''$. Thus a degenerate pair belonging to this symmetry is expected for the ($k = 1, 4, 5, 10, 13; \Omega = 1$) rovibrational states;
- (ii) $\ell = 1$ leads to two possibilities: $n = 1$, which corresponds to the immediately preceding case, and $n = 3$. For the former value of n , the uncertainty observed on Γ_R is also found for $\Gamma_v^{\Omega\ell}$ which can be either A_1 or A_2 . In essence, the possible combinations $\Gamma_v^{\Omega\ell} \times \Gamma_R$ produce both a state with $\Gamma = A''_1$ and a degenerate partner belonging to $\Gamma = A''_2$. The way to identify which energy corresponds to the $A''_1 - A''_2$ degenerate pair ($n = 3$) and which energy to the level belonging to E'' ($n = 1$) for the ($k = 2 - 3, 8 - 9, 11 - 12; \Omega = 1$) states is to invoke the rule mentioned in Section 3 which establishes that the lower value of n (in this case $n = 1$) corresponds to the more negative energy.
- (iii) $\ell = 2$, which is found only for the ($k = 6 - 7; \Omega = 1$) states, leads to $n = 3$ and $n = 5$. As in the case of $\ell = 1$, the former value of n produces a degenerate pair of bound states of the A''_1 and A''_2 symmetry respectively.

For $n = 5$, $\Gamma_v^{\Omega\ell} = E$ and therefore we have another degeneration in a pair of bound states belonging to $\Gamma = E''$. In this case, however, the associated energy is larger than for the pair with $n = 3$;

- (iv) $\ell = 3$ leads to $n = 5$ and $n = 7$ which means that the $(k = 14; \Omega = 1)$ states belong to the $\Gamma = E''$ symmetry.

This is the analysis of the symmetry properties of the rovibrational states found for $J = 1$ which are shown in Table 2. The Table includes the $\Omega = 0$ and $\Omega = 1$ cases for all the k vibrational states shown in Table 1 for $J = 0$. The highest energies presented in Table 2 are $\sim -187 \text{ cm}^{-1}$, corresponding to the $(k = 14; \Omega = 0)$ and $(k = 14; \Omega = 1)$ rovibrational states. The former being the first state which belongs to the A'_1 symmetry block.

The agreement found between the exact calculation and the predictions estimated with the DGF approach is remarkable. Besides the capability of the method to discriminate the symmetry of the rovibrational states, the comparison with the precise values of the exact energies reveals that the treatment based in the use of the $J = 0$ vibrational states to calculate the spectrum at $J = 1$ yields fairly good results.

The last case investigated here corresponds to $J = 6$, which is the largest value of the total angular momentum analysed in Ref. [10]. Theoretical spectra for this case obtained with the HC and DGF calculations are shown in Tables 3 and 4. In order to avoid excessive information, the number of rovibrational states in each symmetry block has been limited to those levels with $(k \leq 4; \Omega)$. We have preferred to extend however the list of energy levels for the case of the physically acceptable A'_1 and A''_1 blocks, shown in Table 3, which contain the only reported states in the study by Karlický *et al.* [10].

The assignment to the different irreducible representations has been done according with the same procedure as in the case of $J = 1$ discussed above. Bound states belonging to the E' and E'' total symmetry blocks, shown in Table 4, are those whose rovibrational characters were also E , in accord with our findings for $J = 1$. The A_1 irreducible representations are composed by states with an almost quasi-degenerate counterpart in the corresponding A_2 blocks, presented in Table 4, with the only exception of those levels with $\Omega = 0$. The close proximity in energy observed among the $k = 5$ and $k = 6 - 7$ states for a zero total angular momentum is manifested at $J = 6$. Thus, for example, in the A'_1 representation, levels corresponding to the $k = 6 - 7$ vibrational states exhibit deeper energy than some of the rovibrational levels from the $k = 5$ state (see the case of the $(k = 6 - 7; \Omega = 4)$ and $(k = 5; \Omega = 0)$ states in Table 3). In this more congested region of the $J = 6$ spectrum, around $\sim -207 \text{ cm}^{-1}$, the list of levels sorted according with their corresponding rovibrational energy predicted by the DGF method presents some alterations with respect to the HC result: In contrast with the exact result, in the A'_1 block (see Table 3), the

($k = 6 - 7; \Omega = 2$) state is found to be more bound than the ($k = 5; \Omega = 0$) state; an analogous situation is observed for the ($k = 6 - 7; \Omega = 5$) and ($k = 5; \Omega = 3$) states which belong to the A_1' representation, also in Table 3. But despite these slight shifts in energy, the actual differences with respect to the HC rovibrational energies are certainly small, not more than 0.4 cm^{-1} for these cases mentioned above. In fact the largest difference observed in the bound states listed in Tables 3 and 4 is found to be about 0.7 cm^{-1} , which is in our opinion, a quite remarkable result to add to the noticeable reduction in computational time in comparison with the exact HC calculation.

The spectra shown in this work for the cases of $J = 1$ and $J = 6$ reveal that, as suggested in Section 3, the rovibrational symmetry $\Gamma_v^{\Omega\ell}$ of the ($k; \Omega$) states depends on the precise values of Ω . It is thus easy to verify that the $\Gamma_v^{\Omega\ell}$ character seen for the ($k; \Omega = 0$) bound states at the $J = 0$ case shown in Table 1, actual seeds for the spectra of the $J > 0$ situations, differs when Ω increases. As a particular example, whereas the ($k = 1; \Omega = 0$) state exhibits $\Gamma_v^{\Omega\ell} = A_1$, the ($k = 1; \Omega = 1, 2, 4, 5$) cases correspond to $\Gamma_v^{\Omega\ell} = E$ and the ($k = 1; \Omega = 3, 6$) states may be either $\Gamma_v^{\Omega\ell} = A_1$ or A_2 . A physical explanation for this dependence of the “vibrational” symmetry on the rotational part may be that the C_2 symmetry operator for the permutation of two identical particles affects rotational and vibrational coordinates simultaneously [19]. The ℓ quantum number nevertheless seems to remain as a valid label to identify the vibrational states as J increases.

5 Conclusions

In this study we have proposed an approximate method to calculate the spectra of rotating trimers and to identify, in a reliable manner, the symmetry of the corresponding rovibrational levels. The method, which is based on the use of distributed Gaussian functions (DGFs) to describe the interparticle distances, constitutes a generalisation of a widely used approach to treat purely vibrating three-body systems. The application to a rotating trimer reveals that energy levels are in good agreement with results from an exact hyperspherical coordinates calculation for $J = 1$ and for a larger value of the total angular momentum as $J = 6$, to prove the efficiency of the procedure. In addition, the assignment of the symmetry character of the obtained rotational levels has been found to be correct, not only for the totally symmetric cases A_1 , but for the rest of possible irreducible representations for the trimer under consideration, that is E and A_2 . The method, developed in the basis of the ℓ and Ω quantum numbers, should be however perfectly applicable to more general cases in which, as for the DGF technique, the assignment of the symmetry character of rovibrational energy levels is needed. Present results show that the only requirement is the assignment of the ℓ quantum number to the purely

vibrational ($J = 0$) spectrum. Our intention is to extend the study to much larger values of the total angular momenta for which the exact calculation becomes numerically too demanding. Two more issues to analyse would be certainly of interest in order to complete the test reported in this letter. On one hand, one might wonder about the possibilities of the proposed method in the calculation of rotational constants. On the other hand, and according with the present results, we plan to investigate if those scenarios in which the rovibrational levels are highly congested constitute or not a possible limit to the validity of the approximate method. Given that the main goal of the present communication was nevertheless to test the procedure to assign the symmetry of the predicted spectra, those above mentioned aspects will be the scope of forthcoming work.

6 Acknowledgments

This work has been funded by the Spanish MEC and CSIC under Grants FIS2007-62006, CTQ2007-62898 and 200650I134. We would like to sincerely thank authors of Ref. [10] for sending us the subroutine for their potential energy surface. Useful discussions with Prof. B. Lepetit and Prof. J. M. Hutson are also acknowledged.

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Table 1

Bound state energies given in cm^{-1} for the Ar_3 cluster at zero angular momentum, $J = 0$, obtained by means of the HC and DGF calculations for the A'_1 , E' and A'_2 symmetry blocks. The HC states are labelled by the (v_1, v_2^ℓ) , with Ω (not shown here) identical to the corresponding value in the DGF calculation. k index and Ω quantum number for the DGF states are in fourth and fifth columns. The corresponding rovibrational, $\Gamma_v^{\Omega\ell}$, and rotational, Γ_R , symmetries are given in sixth and seventh columns respectively. (* Assignment of the rovibrational symmetry $\Gamma_v^{\Omega\ell}$ for this case is discussed in the text).

Γ	HC		DGF				
	(v_1, v_2^ℓ)	$E(cm^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E(cm^{-1})$
A'_1	$(0,0^0)$	-252.23	1	0	A_1	A_1	-252.23
	$(1,0^0)$	-221.79	4	0	A_1	A_1	-221.79
	$(0,2^0)$	-209.48	5	0	A_1	A_1	-209.48
	$(2,0^0)$	-195.97	10	0	A_1	A_1	-195.98
	$(2,1^0)$	-191.29	13	0	A_1	A_1	-191.28
E'	$(0,1^1)$	-229.78	2,3	0	E	A_1	-229.79
	$(0,2^2)$	-209.32	6,7	0	E	A_1	-209.33
	$(1,1^1)$	-202.58	8,9	0	E	A_1	-202.58
	$(0,3^1)$	-193.21	11,12	0	E	A_1	-193.22
A'_2	$(0,3^3)$	-187.76	14	0	A_1, A_2^*	A_1	-187.76

Table 2

Same as Table 1 for $J = 1$. (* The rovibrational symmetry for this state was assigned in the case of $J = 0$; see text for further details. ‡ For this state $\Omega = -1$).

Γ	HC		DGF				
	(v_1, v_2^ℓ)	$E(\text{cm}^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E(\text{cm}^{-1})$
A'_1	$(0, 3^3)$	-187.65	14	0	A_2^*	A_2	-187.65
A''_1	$(0, 1^1)$	-229.64	2,3	1	A_1, A_2	A_1, A_2	-229.70
	$(0, 2^2)$	-209.30	6,7	1	A_1, A_2	A_1, A_2	-209.26
	$(1, 1^1)$	-202.49	8,9	1	A_1, A_2	A_1, A_2	-202.49
	$(0, 3^1)$	-193.11	11,12	1	A_1, A_2	A_1, A_2	-193.13
E'	$(0, 1^1)$	-229.66	2,3	0	E	A_2	-229.67
	$(0, 2^2)$	-209.21	6,7	0	E	A_2	-209.22
	$(1, 1^1)$	-202.47	8,9	0	E	A_2	-202.47
	$(0, 3^1)$	-193.10	11,12	0	E	A_2	-193.11
E''	$(0, 0^0)$	-252.15	1	1	E	A_1, A_2	-252.15
	$(0, 1^1)^\ddagger$	-229.74	2,3	1	E	A_1, A_2	-229.71
	$(1, 0^0)$	-221.71	4	1	E	A_1, A_2	-221.71
	$(0, 2^0)$	-209.39	5	1	E	A_1, A_2	-209.39
	$(0, 2^2)$	-209.18	6,7	1	E	A_1, A_2	-209.26
	$(1, 1^1)$	-202.51	8,9	1	E	A_1, A_2	-202.50
	$(2, 0^0)$	-195.89	10	1	E	A_1, A_2	-195.89
	$(0, 3^1)$	-193.04	11,12	1	E	A_1, A_2	-193.15
	$(2, 1^0)$	-191.21	13	1	E	A_1, A_2	-191.21
$(0, 3^3)$	-187.68	14	1	E	A_1, A_2	-187.68	
A'_2	$(0, 0^0)$	-252.12	1	0	A_1	A_2	-252.12
	$(1, 0^0)$	-221.68	4	0	A_1	A_2	-221.68
	$(0, 2^0)$	-209.36	5	0	A_1	A_2	-209.37
	$(2, 0^0)$	-195.87	10	0	A_1	A_2	-195.87
	$(2, 1^0)$	-191.18	13	0	A_1	A_2	-191.17
A''_2	$(0, 1^1)$	-229.64	2,3	1	A_1, A_2	A_2, A_1	-229.70
	$(0, 2^2)$	-209.31	6,7	1	A_1, A_2	A_2, A_1	-209.25
	$(1, 1^1)$	-202.49	8,9	1	A_1, A_2	A_2, A_1	-202.49
	$(0, 3^1)$	-193.13	11,12	1	A_1, A_2	A_2, A_1	-193.13

Table 3

Same as Tables 1 and 2 for the A_1 irreducible representations for $J = 6$.

Γ	HC		DGF				
	(v_1, v_2^ℓ)	$E(cm^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E(cm^{-1})$
A_1'	(0,0 ⁰)	-250.85	1	6	A_1, A_2	A_1, A_2	-250.85
	(0,0 ⁰)	-249.80	1	0	A_1	A_1	-249.80
	(0,1 ¹)	-227.68	2,3	4	A_1, A_2	A_1, A_2	-227.86
	(0,1 ¹)	-227.56	2,3	2	A_1	A_1, A_2	-227.54
	(1,0 ⁰)	-220.46	4	6	A_1, A_2	A_1, A_2	-220.46
	(1,0 ⁰)	-219.43	4	0	A_1	A_1	-219.40
	(0,2 ⁰)	-208.17	5	6	A_1, A_2	A_1, A_2	-208.17
	(0,2 ²)	-207.69	6,7	4	A_1, A_2	A_1, A_2	-207.48
	(0,2 ⁰)	-207.22	5	0	A_1	A_1	-206.94
	(0,2 ²)	-206.84	6,7	2	A_1, A_2	A_1, A_2	-207.05
A_1''	(0,0 ⁰)	-250.06	1	3	A_1, A_2	A_1, A_2	-250.06
	(0,1 ¹)	-228.35	2,3	5	A_1, A_2	A_1, A_2	-228.12
	(0,1 ¹)	-227.43	2,3	1	A_1, A_2	A_1, A_2	-227.36
	(1,0 ⁰)	-219.68	4	3	A_1, A_2	A_1, A_2	-219.69
	(0,2 ⁰)	-207.48	5	3	A_1, A_2	A_1, A_2	-207.48
	(0,2 ²)	-207.33	6,7	5	A_1, A_2	A_1, A_2	-207.72
	(0,2 ²)	-207.09	6,7	1	A_1, A_2	A_1, A_2	-207.05
	(1,1 ¹)	-201.00	8,9	5	A_1, A_2	A_1, A_2	-200.97
	(1,1 ¹)	-200.28	8,9	1	A_1, A_2	A_1, A_2	-200.14
	(2,0 ⁰)	-193.93	10	3	A_1, A_2	A_1, A_2	-193.95

Table 4

Same as Table 4 for the A_2 and E irreducible representations for $J = 6$. (* For these states, Ω takes the $-\Omega$ value given in fifth column.)

Γ	HC		DGF				
	(v_1, v_2^ℓ)	$E(cm^{-1})$	k	Ω	$\Gamma_v^{\Omega\ell}$	Γ_R	$E(cm^{-1})$
A_2'	(0,0 ⁰)	-250.85	1	6	A_1, A_2	A_2, A_1	-250.85
	(0,1 ¹)	-227.68	2,3	4	A_1, A_2	A_2, A_1	-227.86
	(0,1 ¹)	-227.56	2,3	2	A_1, A_2	A_2, A_1	-227.54
	(1,0 ⁰)	-220.46	4	6	A_1, A_2	A_2, A_1	-220.46
A_2''	(0,0 ⁰)	-250.06	1	3	A_1, A_2	A_2, A_1	-250.06
	(0,1 ¹)	-228.35	2,3	5	A_1, A_2	A_2, A_1	-228.12
	(0,1 ¹)	-227.29	2,3	1	A_1, A_2	A_2, A_1	-227.36
	(1,0 ⁰)	-219.68	4	3	A_1, A_2	A_2, A_1	-219.69
E'	(0,0 ⁰)	-250.26	1	4	E	A_1, A_2	-250.27
	(0,0 ⁰)	-249.91	1	2	E	A_1, A_2	-249.92
	(0,1 ¹)	-228.13	2,3	6	E	A_1, A_2	-228.44
	(0,1 ¹)	-228.03	2,3	4	E	A_1, A_2	-227.86
	(0,1 ¹)	-227.46	2,3	2	E	A_1, A_2	-227.50
	(0,1 ¹)	-227.32	2,3	0	E	A_1	-227.36
E''	(0,0 ⁰)	-250.53	1	5	E	A_1, A_2	-250.53
	(0,0 ⁰)	-249.83	1	1	E	A_1, A_2	-249.83
	(0,1 ¹)	-227.88	2,3	5	E	A_1, A_2	-228.12
	(0,1 ¹)	-227.77	2,3	3	E	A_1, A_2	-227.66
	(0,1 ¹)*	-227.54	2,3	3	E	A_1, A_2	-227.66
	(0,1 ¹)*	-227.41	2,3	1	E	A_1, A_2	-227.46
	(1,0 ⁰)*	-220.14	4	5	E	A_1, A_2	-220.14
	(1,0 ⁰)	-219.46	4	1	E	A_1, A_2	-219.49