Review

Theoretical methods for the rotation-vibration spectra of triatomic molecules: Distributed Gaussian functions compared with hyperspherical coordinates

Maykel Márquez-Mijares^a, Octavio Roncero^b, Pablo Villarreal^b and Tomás González-Lezana^{b*}

^a*Instituto Superior de Tecnologías y Ciencias Aplicadas InsTec, Havana University, Ave. Salvador Allende n. 1110, Quinta de los Molinos, Havana 10400, Cuba;*

^b*Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas IFF-CSIC, Serrano 123, 28006 Madrid, Spain*

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An approximate variational method based in the use of distributed Gaussian functions (DGF) and bond-length coordinates has been applied to study the rotation-vibration spectra of different triatomic molecules. In addition, an approach which employs hyperspherical coordinates (HC) and a basis set of hyperspherical harmonics constitutes a valid benchmark to test its capabilities. This work describes the technical details of both methods to provide the energies and symmetry of the corresponding rovibrational states and reviews their application to three different systems: For Ar₃ and Ne₃ the DGF technique exhibits a particularly good performance, but some limitations are observed for a more demanding scenario such as the H₃⁺ ion. The possible origin of these deficiencies are also discussed in detail.

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*Email: t.gonzalez.lezana@csic.es

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1. Introduction

Over the last past decades the rotational-vibrational (RV) spectrum of polyatomic molecules has been the subject of numerous investigations (see for example previous reviews on this matter [1–8]). In parallel to the successive improvement of experimental techniques to acquire highly resolved and detailed molecular spectra, different rigorous quantum mechanical approaches have been developed. There exists a vast literature containing possible RV Hamiltonians starting in the late 30s [9–12]. Pioneering developments proposed the use of the Eckart-Watson Hamiltonian [1, 13] as an efficient approach to calculating low-lying RV energy levels and successive improvements to describe large amplitude internal nuclear motions far from the equilibrium molecular geometry at high energies were incorporated [14, 15]. In a series of papers, Tennyson and collaborators tried compact and useful expressions for the triatomic Hamiltonian in a body-fixed (BF) reference system including attempts of approximate solutions of the resulting eigenvalue problem when the potential functions was expanded in a series of Legendre polynomials [16–19]. This kind of approaches for atom-diatom systems were based in the assumption that the high frequency vibrational modes of the diatom can be separated from the low frequency modes of the complex [14, 20]. Subsequent alternatives such as the Sutcliffe-Tennyson rovibrational Hamiltonian were also of common application [21, 22].

One of the issues discussed over the years deals with the effect of the coupling between rotation and vibration [23–26], a feature which also depends on the choice of molecule-fixed axis system [3]. Under the Eckart frame conditions [27], for instance, the ro-vibrational Coriolis coupling is reduced to zero at the equilibrium geometry. Besides its original expression in normal modes, procedures to derive triatomic Eckart frames in some other different coordinates have been developed [28–31].

Helicity decoupling approximations [32–36] have been tried as computationally cheap numerical alternatives to investigate bound states for large values of the total angular momentum. These approaches lead to the actual separation between vibration and rotation by assuming that the Coriolis coupling between distinct helicity quantum numbers can be neglected. The Hamiltonian is then independently solved in uncoupled blocks with different values of the total angular momentum J and its projection on the BF z -axis, Ω . However the approximation can fail for certain molecular systems. HO_2 , for example, is one of those cases in which the comparison [37–39] between some of these decoupling schemes and calculations performed with methods such as the ScallT program developed by Poirier and collaborators [40, 41] or the Chebyshev filter diagonalization method employed by Zhang and Smith [42–45] reveals the necessity of a proper account for the Coriolis coupling terms.

The description of three-body (3B) systems in terms of hyperspherical coordinates (HC) [46–49] has led to the development of accurate methods [50–52] employed in the

analysis of the RV spectra. Applications of such techniques can be found, for instance, in the detailed study of H_3^+ over the years [53–58]. Similar examples using generalized internal coordinates [59], symmetry-adapted Jacobi coordinates [60], discrete variable representation (DVR) [61, 62], Lanczos-based methods [63] or in combination with finite element methods (FEM) [64] complete a long list of possibilities to treat rotating trimers.

Among the possible strategies to tackle the calculation of the rovibrational energy levels of polyatomic molecule spectra, one can separate the purely vibrational part of the Hamiltonian, that corresponding to a zero total angular momentum, $J = 0$, from that part containing $J > 0$ operators [65]. The basis set employed to solve the full VR problem is then build from the rotationless part completed with standard rotational basis functions [9, 11, 12, 16, 18, 23, 66–68]. For the case of triatomic molecules, this was the procedure employed to study the spectra of molecules such as H_2O [67], H_2Ne [16] or KCN [16]. In their investigation of H_2D^+ , Tennyson and Sutcliffe [18] obtained the vibrational basis set from the eigenstates of a Hamiltonian constructed with the vibrational part and the diagonal elements of the RV Hamiltonian.

Following a similar procedure we tried in the past several possibilities to deal with the $J > 0$ problem for trimers. In particular we started by employing the vibrational basis sets obtained by means of a variational method based on the use of distributed Gaussian functions (DGFs) to describe the interparticle distances in a 3B system [69–71]. The capabilities of this DGF technique to investigate the energies and geometries of the vibrational bound states of molecular trimers have been successfully tested on a large list of different systems such as He_3 [69, 70], Ar_3 [70, 72], Ne_3 [70, 72], LiHe_2 [73, 74], He_2H^- [75] or Ne_2H^- [76]. After preliminary attempts to provide some indications of rotational constants calculated for each vibrational state [76, 77] in the same spirit as discussed in Ref. [38] or to elucidate the possible existence of bound rotational states for elusive systems such as He_3 [78], a method considering the Ar trimer as an asymmetric rotor was applied to study the RV spectrum of the system for values of the total angular momentum up to $J = 20$ [79, 80]. Besides the actual calculation, the procedure includes a recipe for a proper assignment of the energy levels to their corresponding symmetry irreducible representation.

A similar extension from a vibration-only approach employing a generalized finite basis representation [81] to a more general technique to determine the full VR eigen-spectrum of triatomic molecules was reported by Czako *et al.* [82]. In particular the authors proposed a nondirect-product scheme to treat the singularities present in the triatomic RV kinetic energy operator of the Sutcliffe-Tennyson Hamiltonian when Jacobi coordinates are used. The method was applied to H_3^+ in its ground electronic state and RV energy levels above the corresponding barrier to linearity were calculated [82]. Bačić and Light also extended a method designed to obtain the vibrational spectrum of floppy triatomic molecules with a combined application of DVR and a distributed Gaussian basis description [83–86] to a more general approach capable to solve $J > 0$ cases. One of the first applications of this method consisted in the characterization of the rovibrational states of HCN/HNC [62].

In this work we review two different strategies employed during these almost twenty past years in our group in the study of the rovibrational spectra of three identical

atoms systems. On the one hand, an exact method based in HC and, on the other hand, an approximate approach which employs a DGF-based description of the inter-particle distances within the trimer. In some cases, both techniques were combined in an attempt to test the capabilities and possible limitations of the latter, using the HC results as the valid benchmark. Thus, systems such as Ar_3 , Ne_3 and H_3^+ were investigated.

The structure of this work is the following: In Section 2 we give details of the theoretical basis of the two methods. Then in Sections 3.1, 4 and 5 the applications on Ar_3 , Ne_3 and H_3^+ are discussed. Finally in Section 6 we present the conclusions.

2. Theoretical methods

2.1. The hyperspherical coordinates method

2.1.1. Coordinates and hamiltonian

A careful choice of coordinates leads to a convenient treatment of the permutation symmetry of three identical atoms to reduce the number of basis functions required to obtain converged results in the calculation of rovibrational states and spectra. After the separation of the center of mass, the remaining six coordinates can be separated in three Euler angles and three internal coordinates. The Euler angles define the transformation between the space-fixed (SF) and the BF frames, and should be chosen to avoid bias on any of the three atoms and thus guarantee that they are all treated on an equal footing. One common choice is to use as BF frame that defined by the principal inertia axes. For triatomic systems, the largest moment is along the axis perpendicular to the plane defined by the three particles. The polar angles of this axis define two of the Euler angles. In order to calculate bound states, a good choice is to set this axis perpendicular to the plane of the molecule as the z -axis; this allows a simple way to express permutation symmetry as described below. On the contrary, for collisions or fragmentations, it is better to choose the axis parallel along the fragmentation coordinate, because the Coriolis term vanishes at long distances.

The third Euler angle can be defined according to the pseudo-vector defined by Johnson [87]. First we define three sets of Jacobi vectors $\mathbf{r}_\tau$ and $\mathbf{R}_\tau$ as those shown in Fig. 1, in a cyclic way, such as τ runs over the atoms in the order $\tau = \text{A}, \text{B}, \text{C}$. The mass-scaled Jacobi vectors are defined as $\mathbf{s}_\tau = d_\tau^{-1} \mathbf{r}_\tau$ and $\mathbf{S}_\tau = d_\tau \mathbf{R}_\tau$, where

Figure 1. The three sets of Jacobi vectors for a three particle system.

$d_\tau = \sqrt{\frac{2}{\sqrt{3}}}$ for three identical nuclei of mass m . The kinetic part of the Hamiltonian

can be expressed in Cartesian components of these coordinates as follows:

$$T_\tau = -\frac{\hbar^2}{2\mu} \left\{ \frac{\partial^2}{\partial S_x^{(\tau)^2}} + \frac{\partial^2}{\partial S_y^{(\tau)^2}} + \frac{\partial^2}{\partial S_z^{(\tau)^2}} + \frac{\partial^2}{\partial s_x^{(\tau)^2}} + \frac{\partial^2}{\partial s_y^{(\tau)^2}} + \frac{\partial^2}{\partial s_z^{(\tau)^2}} \right\} \quad (1)$$

where $\mu = m/\sqrt{3}$ is the reduced mass. The vector perpendicular to the plane of the molecule is then expressed as $\vec{A} = \mathbf{s}_\tau \times \mathbf{S}_\tau$, with polar angles, α, β . The mass-scaled Jacobi vectors can be rotated according to

$$\mathbf{s}_{\tau'} = \mathcal{R}(\alpha, \beta, 0) \mathbf{s}_\tau = \begin{pmatrix} s_{x'}^{(\tau)} \\ s_{y'}^{(\tau)} \\ 0 \end{pmatrix} \quad (2)$$

$$\mathbf{S}_{\tau'} = \mathcal{R}(\alpha, \beta, 0) \mathbf{S}_\tau = \begin{pmatrix} S_{x'}^{(\tau)} \\ S_{y'}^{(\tau)} \\ 0 \end{pmatrix}. \quad (3)$$

where the rotation $\mathcal{R}(\alpha, \beta, 0)$ is defined as follows [88]:

$$\mathcal{R}(\alpha, \beta, 0) = \begin{pmatrix} \cos \alpha \cos \beta & \sin \alpha \cos \beta & -\sin \beta \\ -\sin \alpha & \cos \alpha & 0 \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & -\cos \beta \end{pmatrix}. \quad (4)$$

In the primed intermediate frame, the in-plane inertia tensor components are expressed as:

$$I_{x'x'} = \mu \left[\left[S_{y'}^{(\tau)} \right]^2 + \left[s_{y'}^{(\tau)} \right]^2 \right] \quad (5)$$

$$I_{y'y'} = \mu \left[\left[S_{x'}^{(\tau)} \right]^2 + \left[s_{x'}^{(\tau)} \right]^2 \right] \quad (6)$$

$$I_{x'y'} = -\mu \left[S_{x'}^{(\tau)} S_{y'}^{(\tau)} + s_{x'}^{(\tau)} s_{y'}^{(\tau)} \right] \quad (7)$$

$$I_{x'z'} = I_{y'z'} = 0 \quad (8)$$

$$I_{z'z'} = I_{y'y'} + I_{x'x'} \quad (9)$$

This tensor is diagonalized by a rotation γ around the intermediate z' -axis of the vectors $\mathbf{s}'_\tau$ and $\mathbf{S}'_\tau$. In order to find the angle γ , Johnson proposed to define a pseudo vector σ of components [87]:

$$\sigma_{x'} = (I_{y'y'} - I_{x'x'})/\mu \quad (10)$$

$$\sigma_{y'} = -2I_{x'y'}, \quad (11)$$

so that a rotation around z' that makes the y' component zero would automatically diagonalize the inertia tensor. Thus, the third Euler rotation becomes

$$\cos 2\gamma = \frac{\sigma_{x'}}{\sqrt{\sigma_{x'}^2 + \sigma_{y'}^2}} \quad (12)$$

$$\sin 2\gamma = \frac{\sigma_{y'}}{\sqrt{\sigma_{x'}^2 + \sigma_{y'}^2}}. \quad (13)$$

This angle is defined in the interval $0 \leq \gamma \leq \pi$, *i.e.* half of the range of an usual azimuthal angle.

The (α, β, γ) Euler angles define the inertia moment BF frame, in which the mass-scaled vectors are in the xy -plane under the restriction:

$$S_x^{(\tau)} S_y^{(\tau)} - s_x^{(\tau)} s_y^{(\tau)} = 0. \quad (14)$$

These components have to be expressed in internal coordinates that treat all atoms under equal footing, what is not the case of Jacobi coordinates. The condition of Eq. (14) can be imposed in terms of three independent variables. Here we choose the HC, consisting in one hyperradius, ρ , and two other angles, θ and ϕ_τ .

Among the many possible choices of the angles for symmetric HC [47, 89–95], in this work we shall use the HC of Pack and Parker [96]. These coordinates, usually denoted by APHJ, are closely related to those described by Smith [47, 89] and Johnson [97, 98], and are defined as:

$$\rho = \sqrt{\mathbf{s}_\tau^2 + \mathbf{S}_\tau^2} \quad (15)$$

$$\cos \theta = 2\mathbf{s}_\tau \cdot \mathbf{S}_\tau / \rho^2 \quad (16)$$

$$\sin 2\phi_\tau = 2\mathbf{s}_\tau \cdot \mathbf{S}_\tau / \sqrt{(s_\tau^2 + S_\tau^2)^2 - 4(\mathbf{s}_\tau \times \mathbf{S}_\tau)^2}, \quad (17)$$

where the norm of the mass-scaled vectors, s_τ and S_τ , and the angle ϑ_τ between $\mathbf{s}_\tau$ and $\mathbf{S}_\tau$ are defined by:

$$s_\tau = \rho \sqrt{1 + \sin \theta \cos 2\phi_\tau} / \sqrt{2} \quad (18)$$

$$S_\tau = \rho \sqrt{1 - \sin \theta \cos 2\phi_\tau} / \sqrt{2} \quad (19)$$

$$\cos \vartheta_\tau = \rho^2 \sin 2\phi_\tau \sin \theta / (2s_\tau S_\tau). \quad (20)$$

The mass-scaled Jacobi vectors in the SF frame are obtained according to:

$$\begin{pmatrix} s_x^{(\tau)} \\ s_y^{(\tau)} \\ s_z^{(\tau)} \end{pmatrix} = \mathcal{R}(\alpha, \beta, \gamma) \frac{\rho}{2} \begin{pmatrix} (\cos \theta/2 + \sin \theta/2) (\cos \phi_\tau/2 + \sin \phi_\tau/2) \\ (\sin \theta/2 - \cos \theta/2) (\cos \phi_\tau/2 - \sin \phi_\tau/2) \\ 0 \end{pmatrix} \quad (21)$$

$$\begin{pmatrix} S_x^{(\tau)} \\ S_y^{(\tau)} \\ S_z^{(\tau)} \end{pmatrix} = \mathcal{R}(\alpha, \beta, \gamma) \frac{\rho}{2} \begin{pmatrix} (\cos \theta/2 + \sin \theta/2) (\cos \phi_\tau/2 - \sin \phi_\tau/2) \\ (\cos \theta/2 - \sin \theta/2) (\cos \phi_\tau/2 + \sin \phi_\tau/2) \\ 0 \end{pmatrix} \quad (22)$$

These HC are defined in the intervals: $0 \leq \alpha \leq 2\pi$; $0 \leq \beta \leq \pi$; $0 \leq \gamma \leq 2\pi$; $0 \leq \rho \leq \infty$; $0 \leq \theta \leq \pi/2$ and $0 \leq \phi_\tau \leq 2\pi$. The total wave function must fulfill that $\Psi(\gamma + \pi, \phi_\tau + \pi) = \Psi(\gamma, \phi_\tau)$, to avoid two values in the same point of the space.

In these coordinates the volume element has the form:

$$dV = \frac{1}{8} \rho^5 \sin \theta \cos \theta \sin \beta d\rho d\theta d\phi_\tau d\alpha d\beta d\gamma, \quad (23)$$

and the kinetic part of the Hamiltonian can be expressed as follows:

$$T = -\frac{\hbar^2}{2\mu} \frac{1}{\rho^5} \frac{\partial}{\partial \rho} \rho^5 \frac{\partial}{\partial \rho} + \frac{\hbar^2}{2\mu \rho^2} \hat{\Lambda}^2, \quad (24)$$

where $\hat{\Lambda}^2$ is the grand-angular momentum operator given by:

$$\begin{aligned} \hat{\Lambda}^2 = & \frac{4}{\sin 2\theta} \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi_\tau^2} \\ & + \frac{2i \cos \theta}{\sin^2 \theta} J_z \frac{\partial}{\partial \phi_\tau} + 2 \left\{ \frac{J_x^2}{1 - \sin \theta} + \frac{J_y^2}{1 + \sin \theta} + \frac{J_z^2}{2 \sin^2 \theta} \right\}, \end{aligned} \quad (25)$$

with J_x , J_y and J_z being the components of the total angular momentum in the BF frame

$$\begin{aligned} \mathbf{J} = & \mathbf{u}_x^{\text{BF}} \frac{1}{i} \left\{ \cos \gamma \cot \beta \frac{\partial}{\partial \gamma} - \cos \gamma \csc \beta \frac{\partial}{\partial \alpha} + \sin \gamma \frac{\partial}{\partial \beta} \right\} \\ & + \mathbf{u}_y^{\text{BF}} \frac{1}{i} \left\{ -\cot \beta \sin \gamma \frac{\partial}{\partial \gamma} + \csc \beta \sin \gamma \frac{\partial}{\partial \alpha} + \cos \gamma \frac{\partial}{\partial \beta} \right\} \\ & + \mathbf{u}_z^{\text{BF}} \frac{1}{i} \left\{ \frac{\partial}{\partial \gamma} \right\}. \end{aligned} \quad (26)$$

The grand-angular momentum operator of Eq. (25) presents the so-called Eckart singularities at those configurations at which at least two components of the inertia tensor are equal, *i.e.* $\theta = 0, \pi/2$ and π . For three identical particles, this occurs at equilateral triangular and linear configurations. Because of this, it should be imposed that the wave function has to be regular at the singularities. This is done by using hyperspherical harmonics (HH) [99, 100] or approximate HH as described below.

2.1.2. Basis functions

The HH employed to avoid the singularities of the grand-angular momentum operator in Eq. (25) are linear combinations of several helicities Ω , the projection of the total angular momentum on the BF frame [99, 100]. However, the potential does not depend on Ω , and therefore it is better to use approximate HH diagonal in this helicity quantum number, so that the number of potential matrix elements is considerably reduced. The approximate HH are defined in the present treatment as [54, 101]:

$$W_{\Omega,n,k}^{JM}(\alpha, \beta, \gamma, \theta, \phi_\tau) = \sqrt{\frac{2J+1}{8\pi^2}} D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \frac{e^{in\phi_\tau}}{\sqrt{2\pi}} F_k^{J,\Omega,n}(\theta). \quad (27)$$

Since each point of the configuration space is considered several times, to avoid multivalued functions, the basis function should fulfill the condition that $n + \Omega = \text{even}$.

In Eq. (27) $D_{M\Omega}^{J*}$ are Wigner rotation matrix elements [88] and

$$F_k^{J,\Omega,n}(\theta) = \sqrt{\frac{(1+y)^a (1-y)^b (2k+a+b+1) [\Gamma(2k+a+b+1)]^2}{2k! \Gamma(k+a+c+1) \Gamma(k+a+1) \Gamma(k+b+1)}} P_k^{(b,a)}(y) \quad (28)$$

where $P_k^{(b,a)}$ are Jacobi polynomials[102] with $y = 1 - 2 \cos^2 \theta$, $a = |n + \Omega|/2$ and $b = \sqrt{[J(J+1) - \Omega^2]}/2$. These $F_k^{J,\Omega,n}(\theta)$ functions satisfy:

$$\left\{ \frac{-4}{\sin 2\theta} \frac{d}{d\theta} \sin 2\theta \frac{d}{d\theta} + \frac{n^2 + 2n\Omega + \Omega^2}{\sin^2 \theta} + \frac{2J(J+1) - 2\Omega^2}{\cos^2 \theta} - \mathcal{K}(\mathcal{K} + 4) \right\} F_k^{J,\Omega,n}(\theta) = 0 \quad (29)$$

with $\mathcal{K} = 4k + 2a + 2b$.

In this basis set, the angular matrix elements of the Hamiltonian become

$$\begin{aligned}
 \left\langle W_{\Omega nk}^{JM} | H | W_{\Omega' n' k'}^{JM} \right\rangle &= \delta_{\Omega \Omega'} \delta_{nn'} \delta_{kk'} \left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + \frac{\hbar^2}{2\mu\rho^2} \left[\frac{15}{4} + \mathcal{K}(\mathcal{K} + 4) \right] \right\} \\
 &+ \delta_{\Omega \Omega'} \delta_{nn'} \frac{\hbar^2}{2\mu\rho^2} \left\langle F_k^{J, \Omega, n} \left| \frac{\cos \theta - 1}{\sin^2 \theta} \right| F_{k'}^{J, \Omega, n} \right\rangle 2n\Omega \\
 &+ \delta_{\Omega \Omega' \pm 2} \delta_{nn'} \frac{\hbar^2}{2\mu\rho^2} \left\langle F_k^{J, \Omega, n} \left| \frac{\sin \theta}{\cos^2 \theta} \right| F_{k'}^{J, \Omega, n} \right\rangle \\
 &\times \sqrt{J(J+1) - \Omega'(\Omega' \pm 1)} \sqrt{J(J+1) - (\Omega' \pm 1)\Omega} \\
 &+ \delta_{\Omega \Omega'} \delta_{n' - n, \lambda} \left\langle F_k^{J, \Omega, n} | V_\lambda(\rho, \theta) | F_{k'}^{J, \Omega, n'} \right\rangle. \quad (30)
 \end{aligned}$$

The $\left\langle F_k^{J, \Omega, n} | \mathcal{O} | F_{k'}^{J, \Omega, n'} \right\rangle$ matrix elements in Eq. (30) are evaluated numerically by means of a Gaussian quadrature [103].

For the hyperradius ρ , we employ $\varphi_v(\rho)$ functions obtained numerically in a equidistant grid of points solving the monodimensional radial Schrödinger equation with a mono-dimensional potential corresponding to a reference nuclear configuration:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} + V(\rho, \theta = 0, \phi_\tau = 0) - E_v \right] \varphi_v(\rho) = 0. \quad (31)$$

When the number of functions of a single reference potential is too low, several reference configurations are used and the radial functions are orthonormalized numerically with the Schmidt method [104]. These $\varphi_v(\rho)$ functions are also employed to evaluate the corresponding matrix elements by numerical integration of the dependence on ρ of Eq. (30).

2.1.3. Symmetry

The symmetry operators for a system containing three identical atoms are the $\mathcal{P}_{AB}$, $\mathcal{P}_{BC}$ and $\mathcal{P}_{AC}$ permutations of two particles and the cyclic three atoms permutations $\mathcal{P}_{ABC}$ and $\mathcal{P}_{ABC}^{-1}$. These operators together with the identity, E , form the S_3 permutation group, which is isomorphic with the C_{3h} point group. The total permutation-inversion is obtained combining the permutation group with the inversion of all spatial coordinates of the atoms, leading to the D_{3h} group. The total Hamiltonian is invariant under any of these symmetry operations, and the basis set functions belonging to different irreducible representations, Γ , are not coupled. The construction of symmetry adapted basis functions allows block-diagonalization of the total Hamiltonian matrix and to classification of the resulting eigenfunctions according to their symmetry.

In order to symmetry adapt the basis functions we have to analyze the effect of the corresponding operators in both the HC and the basis functions. The transformation of the vector $\vec{A} = \mathbf{s}_\alpha \times \mathbf{S}_\alpha$ affects the α, β Euler angles. We employ Eqs. (21) and (22) to see how the HC are affected by the symmetry operators, as summarized in Table 1.

By using the symmetry properties of the Wigner functions [88], the symmetry operators either leave the basis functions unchanged or change the signs of Ω and

Table 1. Action of the symmetry operations of the permutation-inversion group on the HC and basis functions[54, 101]. ρ and θ are invariant under all symmetry operations.

Symmetry Operator $\mathcal{P}$	Transformed coordinate $\mathcal{P}(\alpha, \beta, \gamma, \phi_\tau)$	Transformed basis function $\mathcal{P}W_{\Omega nk}^{JM}$
E	$\alpha, \beta, \gamma, \phi_\tau$	$W_{\Omega nk}^{JM}$
$\mathcal{P}_{AB}$	$\alpha + \pi, \pi - \beta, \pi - \gamma, 4\pi/3 - \phi_\tau$	$(-1)^{J-\Omega+n} e^{i4n\pi/3} W_{-\Omega-nk}^{JM}$
$\mathcal{P}_{BC}$	$\alpha + \pi, \pi - \beta, \pi - \gamma, -\phi_\tau$	$(-1)^{J-\Omega+n} W_{-\Omega-nk}^{JM}$
$\mathcal{P}_{CA}$	$\alpha + \pi, \pi - \beta, \pi - \gamma, -4\pi/3 - \phi_\tau$	$(-1)^{J-\Omega+n} e^{-i4n\pi/3} W_{-\Omega-nk}^{JM}$
$\mathcal{P}_{ABC}$	$\alpha, \beta, \gamma, \phi_\tau + 4\pi/3$	$e^{i4n\pi/3} W_{\Omega nk}^{JM}$
$\mathcal{P}_{ABC}^{-1}$	$\alpha, \beta, \gamma, \phi_\tau - 4\pi/3$	$e^{-i4n\pi/3} W_{\Omega nk}^{JM}$
E^*	$\alpha, \beta, \gamma + \pi, \phi_\tau$	$(-1)^\Omega W_{\Omega nk}^{JM}$

n simultaneously, as summarized in Table 1. The symmetry adapted angular basis functions are then expressed as

$$\mathcal{W}_{\Omega nk}^{JM\Gamma} = A_{\Omega n}^{\Gamma} W_{\Omega nk}^{JM} + B_{\Omega n}^{\Gamma} W_{-\Omega-nk}^{JM} \quad (32)$$

where the $A_{\Omega n}^{\Gamma}$ and $B_{\Omega n}^{\Gamma}$ coefficients are obtained through the application of the projection operators on each irreducible representation Γ , and can take the possible values:

(1) For $\Omega \neq 0$ or $n \neq 0$:

$$\begin{aligned} A_{\Omega n}^{\Gamma} &= \left\{ \chi^{\Gamma}(E) + \chi^{\Gamma}(E^*)(-1)^{\Omega} + \left[\chi^{\Gamma}(C_3) + \chi^{\Gamma}(S_3)(-1)^{\Omega} \right] 2 \cos(4n\pi/3) \right\} \\ B_{\Omega n}^{\Gamma} &= [1 + 2 \cos(4n\pi/3)] \left\{ \chi^{\Gamma}(C_2)(-1)^{J+\Omega+n} + \chi^{\Gamma}(\sigma_v)(-1)^{J+n} \right\} \end{aligned} \quad (33)$$

(2) For $\Omega = n = 0$:

$$\begin{aligned} A_{\Omega n}^{\Gamma} &= \chi^{\Gamma}(E) + \chi^{\Gamma}(E^*) + \left[\chi^{\Gamma}(C_2) + \chi^{\Gamma}(\sigma_v) \right] (-1)^J [1 + 2 \cos(4n\pi/3)] \\ &\quad + \left[\chi^{\Gamma}(C_3) + \chi^{\Gamma}(S_3) \right] 2 \cos(4n\pi/3) \\ B_{\Omega n}^{\Gamma} &= 0 \end{aligned} \quad (34)$$

where $\chi^{\Gamma}(\mathcal{C})$ is the character of the symmetry class $\mathcal{C}$ of the irreducible representation Γ of the D_{3h} group. $\Gamma = A', A'', B', B'', E'$ and E'' and therefore the Hamiltonian matrix factorizes in 6 blocks.

2.1.4. Eigenstates and assignment

The rovibrational states, $\Psi_i^{J\Gamma}$ can be expressed in terms of the basis functions described in the previous sections as follows:

$$\Psi_i^{J\Gamma}(\rho, \theta, \phi_\tau) = 4\rho^{-5/2} \sum_{\Omega, n, k, v} C_{\Omega, n, k, v}^{J\Gamma i} \varphi_v(\rho) \mathcal{W}_{\Omega n k}^{J\Gamma}(\alpha, \beta, \gamma, \theta, \phi_\tau), \quad (35)$$

where the $C_{\Omega, n, k, v}^{J\Gamma i}$ coefficients and corresponding $E_i^{J\Gamma}$ eigenvalues are obtained by diagonalization of the Hamiltonian matrix for particular values of J and Γ . The Hamiltonian matrix size increases very rapidly with J and it is therefore impossible to apply a variational method for large J 's. Instead, we use an iterative procedure based on the Lanczos algorithm [105] in two steps. The eigenvalues are obtained with a non-orthogonal Lanczos procedure following the method of Cullum and Willoughby [106]. The eigenstates are then obtained iteratively using the conjugate gradient method [107, 108].

The only good quantum numbers associated with each eigenstate are the total angular momentum, J , and the symmetry, characterized by the Γ irreducible representation of the D_{3h} group. Traditionally, for the classification of the eigenstates the (v_1, v_2^ℓ) and G and U approximated quantum numbers are used [109]. v_1 and v_2 correspond to the symmetric and antisymmetric vibrations and ℓ labels the vibrational angular momentum. They can be obtained as follows:

- (1) v_1 corresponds to the v with the largest contribution in the expansion of Eq. (35), since the $\varphi_v(\rho)$ functions correspond to a prediagonalization of the symmetric stretch at the equilibrium values of θ and ϕ_τ . v_1 is calculated directly counting the number of nodes of these $\varphi_v(\rho)$ basis functions.
- (2) The antisymmetric stretch, v_2 , is associated with the θ coordinate. It is obtained by comparing the full eigenstate with the monodimensional solutions of the problem for the equilibrium values of ρ , ϕ_τ and $J=0$.
- (3) ℓ is connected to the ϕ_τ variable and is obtained as $\ell = |\Omega_{\max} + n_{\max}|/2$ where $n_{\max}$ and $\Omega_{\max}$ are the values of those n and Ω , respectively, with a major contribution in the expansion of Eq. (35). Since those numbers are defined in the basis functions their contribution to the total wave function is easily obtained by inspection of its square modulus for their possible values.
- (4) G is also obtained from $n_{\max}$ and $\Omega_{\max}$ as $G = |n_{\max} + 3\Omega_{\max}|/2$.
- (5) Finally, U is equal, in absolute value, to ℓ , and its sign allows to distinguish between the A_1 and A_2 components. Since we are using symmetry adapted functions, this latter number is not required to specify the character of the states, and in what follows we shall label the states by (v_1, v_2^ℓ) , J , G and Γ .

2.2. The distributed Gaussian functions method

There exist previous reports of Hamiltonians written in pair coordinates ($R_i, i = 1, 2, 3$) to treat the vibrational-rotational problem of triatomic molecules in the literature [110, 111]. We have developed however an alternative approximative approach based on these internal coordinates which approximates the total Hamiltonian as the sum of a vibrational and a rotational component: $H_{\text{tot}} = H_{\text{vib}} + H_{\text{rot}}$. In a first step the rotationless $J = 0$ problem is solved, as explained below in Section 2.2.1, and

the corresponding eigenstates $|k\rangle$ are used in an extended basis with the standard rotational functions to solve the $J > 0$ part, as will be shown in Section 2.2.2.

2.2.1. The purely vibrational problem: $J = 0$

The vibrational Hamiltonian can be expressed in internal coordinates R_1, R_2 and R_3 as [69, 71, 77]:

$$H_{\text{vib}} = \sum_{i=1}^3 \left[-\frac{\hbar^2}{m_i} \left(\frac{\partial^2}{\partial R_i^2} + \frac{1}{R_i} + \frac{\partial}{\partial R_i} - \frac{1}{4R_i^2} + T_{ijk} \right) \right] + U(\mathbf{R}). \quad (36)$$

m_i being the mass of each atom and $U(\mathbf{R})$ the potential energy operator, with $\mathbf{R} = (R_1, R_2, R_3)$. The T_{ijk} operator, with $i \neq j \neq k$, of Equation (36), contains all crossed kinetic terms with derivatives in each R_i coordinate:

$$T_{ijk} = \frac{R_j^2 + R_k^2 - R_i^2}{2R_j R_k} \left(\frac{\partial^2}{\partial R_j \partial R_k} - \frac{1}{2R_j} \frac{\partial}{\partial R_k} - \frac{1}{2R_k} \frac{\partial}{\partial R_j} + \frac{1}{4R_j R_k} \right). \quad (37)$$

We can consider the following products:

$$\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) = \varphi_{l_1}(R_1) \varphi_{l_2}(R_2) \varphi_{l_3}(R_3), \quad (38)$$

where the $\varphi_{l_j}(R_i)$ functions are DGFs for the coordinates R_i with centers in the values R_j as basis functions to express the vibrational eigenstates. Each of this product $\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R})$ can be interpreted as a triangle in which the three particles are separated for the distances $R_1 = R_{l_1}$, $R_2 = R_{l_2}$ and $R_3 = R_{l_3}$. In the case of three identical particles, the permutation of the identical particles produces six possible triangles as shown in Figure 2.

The expression of the DGFs is the following:

$$\varphi_p(R_i) = \sqrt[4]{\frac{2\alpha_p}{\pi}} e^{-\alpha_p(R_i - R_p)^2}, \quad (39)$$

with $\alpha_p = 4\beta/(R_{p+1} - R_{p-1})^2$ and the β optimization parameter is chosen close to 1 controlling the overlap between adjacent functions. The centers of the Gaussian functions must satisfy the triangular condition: $|R_{l_1} - R_{l_2}| \leq R_{l_3} \leq R_{l_1} + R_{l_2}$. The use of such a non-orthogonal basis introduces an overlap matrix in the standard Schrödinger equation as explained in Ref. [71]. The corresponding pseudo-eigenvalue problem has to be transformed to an usual eigenvalue problem by means of a method developed by Löwdin [112] which requires the diagonalization of the overlap matrix.

For homonuclear three-particle systems total symmetry corresponds to the D_{3h} group, but we construct symmetry-adapted basis for the $J = 0$ case from Eq. (38) taking into consideration the permutation operators of the C_{3v} symmetry group: E , $\mathcal{P}_{12}$, $\mathcal{P}_{23}$, $\mathcal{P}_{13}$, $\mathcal{P}_{123}$, and $\mathcal{P}_{123}^{-1}$. Under the action of these operators, the $\mathcal{G}^{123}(\mathbf{R})$ functions are transformed to $\mathcal{G}^{123}(\mathbf{R})$, $\mathcal{G}^{213}(\mathbf{R})$, $\mathcal{G}^{132}(\mathbf{R})$, $\mathcal{G}^{321}(\mathbf{R})$, $\mathcal{G}^{231}(\mathbf{R})$ and $\mathcal{G}^{312}(\mathbf{R})$, respectively, and therefore we can consider basis functions expressed as:

Figure 2. Graphical scheme for the basis functions employed in the method. Each $\mathcal{G}_{lmn}^{123}(\mathbf{R})$ function of Eq. (38) comprises a DGF for the R_1, R_2 and R_3 coordinates with centers in R_l, R_m and R_n , respectively. Those centers can be interpreted as the sides of a triangle as shown in the Figure. Permutation of those values yields, for homonuclear trimers, the six triangular arrangements at the bottom.

$$\begin{aligned} \phi_{l_1 l_2 l_3}^{\Gamma}(\mathbf{R}) = \frac{1}{\sqrt{6}} \{ & \chi(E) \mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) + \chi(C_3) [\mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R})] \\ & + \chi(\sigma_v) [\mathcal{G}_{l_1 l_2 l_3}^{213}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{132}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{321}(\mathbf{R})] \}. \end{aligned} \quad (40)$$

The substitution of the $\chi(E)$, $\chi(C_3)$ and $\chi(\sigma_v)$ characters [23] leads to the following expressions for each irreducible representation:

$$\begin{aligned} \phi_{l_1 l_2 l_3}^{A_1}(\mathbf{R}) = & \frac{1}{\sqrt{6}} [\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R}) \\ & + \mathcal{G}_{l_1 l_2 l_3}^{213}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{132}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{321}(\mathbf{R})], \end{aligned} \quad (41)$$

$$\begin{aligned} \phi_{l_1 l_2 l_3}^{A_2}(\mathbf{R}) = & \frac{1}{\sqrt{6}} [\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R}) \\ & - \mathcal{G}_{l_1 l_2 l_3}^{213}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{132}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{321}(\mathbf{R})], \end{aligned} \quad (42)$$

$$\phi_{l_1 l_2 l_3}^E(\mathbf{R}) = \frac{1}{\sqrt{6}} [2\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R})]. \quad (43)$$

Thus, if we denote (l_1, l_2, l_3) with a general index j , the vibrational eigenstate can be written as:

$$\Phi_k^\Gamma(\mathbf{R}) = \sum_j a_j^{(k)} N_j \phi_j^\Gamma(\mathbf{R}), \quad (44)$$

where N_j are normalization constants.

2.2.2. The rovibrational case: $J > 0$

The solution of the $J > 0$ case requires first the actual calculation of the rovibrational energy levels and then the assignment of the corresponding symmetry character. This last step is performed following a procedure proposed previously [79] which we will include here briefly.

The rotational Hamiltonian is chosen from the general case of an asymmetric top [23, 66, 113]:

$$H_{\text{rot}} = \frac{1}{2}(A + C)\mathbf{J}^2 + \frac{1}{2}(A - C)(J_A^2 + \kappa J_B^2 - J_C^2) \quad (45)$$

where $\kappa = (2B - A - C)/(A - C)$ is Ray's asymmetry parameter [114] and A , B and C are rotational constants.

The vibrational eigenstates obtained in Eq. (44) are employed in an extended basis $|k; J\Omega M\rangle$, where, besides the total angular momentum, J , its projection in the BF and SF z -axis, Ω and M , respectively, are included. In this vibration-rotation basis the matrix for the above H_{rot} for each Γ symmetry representation, shown in Eq. (45) is expressed as:

$$\langle k\Gamma; J\Omega M | H_{\text{rot}} | k'\Gamma; J'\Omega' M' \rangle = \sum_{jj'} a_j^{(k)} a_{j'}^{(k')} N_j N_{j'} \langle \phi_j^\Gamma; J\Omega M | H_{\text{rot}} | \phi_{j'}^\Gamma; J'\Omega' M' \rangle \quad (46)$$

The matrix elements in Eq. (46) are calculated by evaluation of the rotational Hamiltonian in the centers $R_i^\dagger$ of the DGFs obtained as the product of the corresponding $\varphi_l(R_i)$ and $\varphi_{l'}(R_i)$ functions for each R_i . A graphical scheme of that product Gaussian function with a center $R_i^\dagger$ (intermediate between R_l and $R_{l'}$) and width depending of those from the other DGFs, is shown in Figure 3.

The rotational matrix of Eq. (46) is diagonal in both J and M but not in Ω , which is then not a good quantum number. Like in HC calculations, the assignment of Ω if

Figure 3. Scheme of the Gaussian function (in blue) obtained as the product of the $\varphi_p(R)$ (red solid line) and $\varphi_{p'}(R)$ (green dotted line). The center $R_i^\dagger$ of this product Gaussian function is employed to evaluate matrix elements of H_{rot} . See text for details.

necessary, is made considering the corresponding dominant values. The corresponding elements of the above expression can be then further expanded as [23, 66, 113]:

$$\begin{aligned} \langle J\Omega M \mid H_{\text{rot}}(R_1^\dagger, R_2^\dagger, R_3^\dagger) \mid J\Omega' M \rangle &= \frac{A^\dagger - C^\dagger}{2} \mathcal{H}^\dagger \sqrt{f(J, \Omega \pm 1)} \delta_{\Omega \pm 2, \Omega'} \\ &+ \left[\frac{A^\dagger + C^\dagger}{2} J(J+1) + \frac{A^\dagger - C^\dagger}{2} \left[\mathcal{F}^\dagger J(J+1) + (\mathcal{G}^\dagger - \mathcal{F}^\dagger) \Omega^2 \right] \right] \delta_{\Omega, \Omega'} \end{aligned} \quad (47)$$

with

$$f(J, \Omega \pm 1) = \frac{1}{4} [J(J+1) - \Omega(\Omega \pm 1)] [J(J+1) - (\Omega \pm 1)(\Omega \pm 2)]. \quad (48)$$

In our calculations, a near oblate basis has been considered, and therefore: $\mathcal{F} = (\kappa+1)/2$, $\mathcal{G} = -1$ and $\mathcal{H} = (\kappa-1)/2$ [23, 113]. The † symbols in Eq. (47) indicate that, as explained above, the different quantities have been evaluated at the corresponding $R_i^\dagger$ values.

The rotational constants A , B , C which appear, both explicitly and in various of the quantities in Eq. (46), are calculated considering the BF frame formed by the instantaneous principal axes of inertia for each triangle with sides $R_1^\dagger$, $R_2^\dagger$ and $R_3^\dagger$. The use of a reference system satisfying the Eckart conditions [27, 30] produces similar results for both C and the average value $\bar{B} = (A+B)/2$. Previous comparative applications of these two possible reference systems for Ar_3 [115] revealed that the

only difference concerns the values of A and B : whereas those rotational constants are almost identical, $A \sim B$, within the Eckart scheme, a description based in principal axes of inertia distinguishes between both constants.

2.2.3. The symmetry assignment

The total symmetry Γ of the energy levels of the spectrum obtained following the procedure explained in the previous section can be expressed as the product of a strictly rotational component, Γ_{rot} , and a rovibrational part, $\Gamma_{\text{vib}}^{\Omega\ell}$, as $\Gamma = \Gamma_{\text{rot}} \times \Gamma_{\text{vib}}^{\Omega\ell}$, where ℓ , understood before in the section for HC as a number associated with ϕ_τ (see Section (2.1.4)) is here properly defined as the quantum number for the vibrational angular momentum [23].

The rotational functions indicated at the beginning of Section (2.2.2) simply as $|J\Omega M\rangle$ can be expressed as a linear combination of rotation Wigner matrices in a similar way as done in the HC calculation shown in Eq. (32):

$$\mathcal{D}_{M\Omega}^J(\alpha, \beta, \gamma) = A_{M\Omega}^J D_{M\Omega}^{J*}(\alpha, \beta, \gamma) + B_{M\Omega}^J D_{M-\Omega}^{J*}(\alpha, \beta, \gamma) \quad (49)$$

where $\Omega \geq 0$ and the Euler angles α, β, γ relate the main inertia axis with the SF system.

These functions can be also symmetry adapted by means of the permutation operators for the C_{3v} symmetry group as shown in Table 1. As a result of the action of these operations on the above rotational functions, the possible values of the coefficients of Eq. (49) depending on Ω are:

- (1) $A_{M\Omega}^J = \chi(E) + 2\chi(C_3)$ and $B_{M\Omega}^J = 3(-1)^{J-\Omega}\chi(\sigma_v)$ if $\Omega \neq 0$,
- (2) $A_{M\Omega}^J = \chi(E) + 2\chi(C_3) + 3(-1)^J\chi(\sigma_v)$ and $B_{M\Omega}^J = 0$ if $\Omega = 0$.

These conditions enable us to develop the following recipe to characterize the symmetry of the rotational energy levels [79]:

- (1) If $\Omega = 0$, Γ_{rot} corresponds to A_1 (A_2) for even (odd) values of J ,
- (2) If $\Omega \neq 0$, Γ_{rot} can be either A_1 or A_2 .

A similar procedure can be followed for the rovibrational part, establishing the character of $\Gamma_{\text{vib}}^{\Omega\ell}$ as a function of the number η , defined as $\eta = |\pm 2\ell - \Omega|$ with $\ell, \Omega \geq 0$. Conditions on the values of this η factor are obtained via the symmetry adapted functions:

$$f_{\eta}^{\Gamma_v^{\Omega\ell}}(\phi_\tau) = A_{\eta}^{\Gamma_v^{\Omega\ell}} e^{-i\eta\phi_\tau} + B_{\eta}^{\Gamma_v^{\Omega\ell}} e^{i\eta\phi_\tau}, \quad (50)$$

where ϕ_τ is one of the hyperangles employed in the HC formalism [54, 101] as shown in Section 2.1. Again, the application of the C_{3v} symmetry operators shown in Table 1 on the above Eq. (50) yields the following expression for the $A_{\eta}^{\Gamma_v^{\Omega\ell}}$ and $B_{\eta}^{\Gamma_v^{\Omega\ell}}$ coefficients:

$$A_{\eta}^{\Gamma_v^{\Omega\ell}} = \chi^{\Gamma_v^{\Omega\ell}}(E) + \chi^{\Gamma_v^{\Omega\ell}}(C_3) 2 \cos \frac{4\pi}{3} \eta \quad (51)$$

$$B_{\eta}^{\Gamma_v^{\Omega\ell}} = \chi^{\Gamma_v^{\Omega\ell}}(\sigma_v) \left(1 + 2 \cos \frac{2\pi}{3} \eta \right). \quad (52)$$

Table 2. $J = 0$ vibrational bound state energies, in cm^{-1} , for the Ar_3 cluster obtained by means of HC (second column) and DGF (fourth column) methods. The HC states are identified with the (v_1, v_2^ℓ) quantum numbers (first column) and DGF states with k (third column). Results from Ref. [79].

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

The substitution of the corresponding values for the $\chi^{\Gamma_{\Omega\ell}}_v$ characters in the above Eq. (51) leads to the following considerations:

- (1) $\Gamma_{\text{vib}}^{\Omega\ell} = A_1$ for $\eta = 0$;
- (2) $\Gamma_{\text{vib}}^{\Omega\ell} = A_1, A_2$ for η multiple of 3;
- (3) $\Gamma_{\text{vib}}^{\Omega\ell} = E$ if η is not multiple of 3.

Finally we distinguish the ' or '' character of the total symmetry Γ depending on whether Ω is even or odd, respectively. This final consideration arises from the choice of the C_{3v} group instead of D_{3h} to adapt the basis function in the calculation.

The use of ℓ , a quantum number not included in the DGF formalism described here, and also the functions of Eq. (50), oblige to find additional support from the HC calculation to link the values of this label to the corresponding $J = 0$ vibrational states. Once this connection is established the assignment of the symmetry character for the rest of the $J > 0$ rovibrational spectra by means of the above discussed indications is straightforward.

3. Applications to homonuclear trimers

3.1. Ar_3 : A nearly rigid example

Ar_3 has been the subject of a long list of theoretical investigations. Several approaches were applied to calculate the bound states of the rotationless $J = 0$ problem [70, 116–126]. Heavier than other rare gas trimers and so showing a more localized behaviour compared with He_3 or Ne_3 [70, 123], the contribution of 3B terms to the overall potential energy surface (PES) of the Ar trimer has been found to be of certain relevance [117, 119, 120, 126–128]. Thus for example, the Axilrod-Teller term is responsible for differences observed in the average geometrical structure of some of the Ar_3 vibrational bound states [126]. *Ab initio* calculations were also performed to calculate 3B

Table 3. Rotational constants, in cm^{-1} , for Ar_3 calculated with the DGF approach [80] (from first to third columns) in comparison with values reported by Karlický *et al.* [130] (from fourth to last columns).

k	DGF [80]		(v_1, v_2^ℓ)	Ref. [130]	
	$\bar{B}$	C		B	C
1	1739.21	861.32	(0, 0 ⁰)	1738.35	863.32
2-3	1713.20	837.77	(0, 1 ¹)	1697.59	785.88
4	1692.48	831.62	(1, 0 ⁰)	1691.92	834.58
5	1688.57	812.15	(0, 2 ⁰)	1596.78	809.92
6-7	1687.46	809.40	(0, 2 ²)	1694.31	627.73
8-9	1669.44	806.15	(1, 1 ¹)	1630.11	644.37
10	1666.43	782.32	(2, 0 ⁰)	1653.20	782.53

interactions for this cluster [127, 129, 130]. Nothing can be said experimentally since the argon trimer does not have permanent dipole moment and deviations from the equilateral geometry induce only a small transient dipole which makes far-infrared absorption investigations of the system an extremely complicated task [119, 131].

Attempts to study the rovibrational spectrum of Ar_3 have been focussed on the calculation of the rotational constants corresponding to the first vibrational bound states [119, 132]. Karlický *et al.* [130] carried out a HC calculation of the energy levels up to $J = 6$ using an *ab initio* pairwise two-body (2B) potential. Rotational constants were extracted from the calculated rovibrational spectra by means of least-squares fits to an analytical formula for the approximate bound state energies. The method discussed in Section 2 was originally tested to study the Ar_3 rotational structure [79] up to the same value of the total angular momentum as Ref. [130], but calculations were extended up to $J = 20$ in another study [80].

The PES employed in the DGF calculations for the Ar_3 system included the HF-DID1 semiempirical Ar-Ar potential by Aziz [133] and the *ab initio* 3B potential from Ref. [130]. The basis was constructed with 23 Gaussian functions, where the first one is located at $6.21 a_0$, separated by equidistant steps of $0.23 a_0$, which generates about 12,167 triangular ϕ_j functions.

3.1.1. The rovibrational spectrum

As explained in the previous sections, we start by calculating the bound states for the rotationless problem, $J = 0$. Results are shown in Table 2 in comparison with a HC calculation. The original test of the method [79, 80] was made without the symmetry-adapted basis shown in Eqs. (41)-(43), so the only index we employ in this first calculation to label the DGF energy levels is simply k . Besides the good accord between energies obtained with both methods, Table 2 enables to establish the connection between k and ℓ .

Authors of the HC calculation of Ref. [130] also reported values of the rotational constants for the Ar trimer. Since the Ar_3 molecule was assumed as a symmetric top in that study, a direct comparison with present DGF results requires to consider $\bar{B} = (A + B)/2$, the average value, instead of the separate rotational constants.

The comparison with those obtained by means of the DGF approach [80], shown in Table 3, shows that, in general, the accord between results calculated by means of the two theoretical methods is reasonably good, especially for those states with $\ell = 0$. It is worth mentioning than those cases with $\ell > 0$ and $v_2 > 0$ led to the largest standard deviations in the least-square fitting performed in Ref. [130], thus suggesting that perhaps, the origin of the discrepancies observed with respect to the DGF calculations may be in the uncertainty of some of the rotational constants reported by Karlický *et al.*

One of the non zero total angular momenta investigated with the presently discussed DGF method was $J = 6$ [79]. Table 4 presents the rovibrational states for that case corresponding, not only to the physically acceptable A'_1 and A''_1 irreducible representations (those fully symmetric states with respect to Ar permutations given the spin-zero statistics of the system) reported by Karlický *et al.* [130], but also for A''_2 , A'_2 , E' and E'' in an attempt to test completely the capabilities of the investigated method.

The symmetry character of the rovibrational energy levels for $J = 6$ shown in Table 4 is assigned according to the recipes discussed above. For instance, given the even value of the total angular momentum under consideration, those states with $\Omega = 0$ (which means that they will correspond to ' states for the total symmetry) have $\Gamma_{\text{rot}} = A_1$. This is the case of a $k = 1$ level of energy -249.80 cm^{-1} and other with $k = 2, 3$ of energy -227.36 cm^{-1} . The values of ℓ for those states are 0 and 1, respectively, and therefore $\eta = 0$ for the former and $\eta = 2$ for the latter. Following the procedure detailed in the previous section, that leads to $\Gamma_{\text{vib}}^{\Omega\ell} = A_1$ and $\Gamma_{\text{vib}}^{\Omega\ell} = E$, respectively. The product of thus obtained Γ_{rot} and $\Gamma_{\text{vib}}^{\Omega\ell}$ yields the final assignment to the A'_1 and E' representations for the two levels of Table 4 under consideration.

Analogously, there are four states in Table 4 with $\Omega = 1$, which means that both A_1 and A_2 representations are possible for Γ_{rot} with " total symmetry. These are two degenerate levels associated with $k = 2, 3$ at -227.36 cm^{-1} with $\ell = 1$; other at -227.46 cm^{-1} ($k = 2, 3$; $\ell = 1$), and the last one at -249.83 ($k = 1$; $\ell = 0$). These pairs of Ω and ℓ values make either $\eta = 1$ (twice), then producing $\Gamma_{\text{vib}}^{\Omega\ell} = E$, or $\eta = 3$ which leads to $\Gamma_{\text{vib}}^{\Omega\ell} = A_1$ or A_2 . The degenerate pair splits into $\Gamma = A''_1$ and $\Gamma = A''_2$, whereas the two other remaining states, for which $\eta = 1$, correspond to the E'' representation.

We end the analysis of the $J = 6$ spectrum shown in Table 4 with the $\Omega = 6$ case. The rotational part is then given by $\Gamma_{\text{rot}} = A_1, A_2$ and Γ has ' symmetry. The levels are: (i) A degenerate pair ($k = 1$; $\ell = 0$; $\eta = 6$) at -250.85 cm^{-1} which produce states with $\Gamma_{\text{vib}}^{\Omega\ell} = A_1, A_2$ and therefore splits to $\Gamma = A'_1$ and A'_2 ; (ii) ($k = 2, 3$; $\ell = 1$; $\eta = 4, 8$) states at -228.44 cm^{-1} which both generates $\Gamma_{\text{vib}}^{\Omega\ell} = E$ cases and thus $\Gamma = E'$.

The calculation of the rovibrational spectrum for larger values of the total angular momentum also allows to test the efficiency of the method in comparison with some other approaches. Thus, in Table 5 we present the rovibrational energy levels for $J = 20$ calculated by means of a HC and the present DGF method for the A'_1 and A''_1 irreducible representations. The comparison includes up to $k = 4$ states from the vibrational basis function in the latter approach. What makes the remarkably good agreement between energies obtained by means of both approaches even more inter-

Table 4. $J = 6$ rovibrational bound state energies, in cm^{-1} , for the Ar_3 cluster obtained by means of HC (third column) and DGF (eight column) methods. The HC states are identified with the (v_1, v_2^ℓ) quantum numbers (second column) and DGF states with k (fourth column). Total symmetry Γ (first column), rovibrational symmetry $\Gamma_{\text{vib}}^{\Omega\ell}$ (sixth column) and rotational symmetry Γ_{rot} (seventh column) are also shown. Results from Ref. [79].

Γ	HC		k	Ω	DGF		$E \text{ (cm}^{-1}\text{)}$
	(v_1, v_2^ℓ)	$E(\text{cm}^{-1})$			$\Gamma_{\text{vib}}^{\Omega\ell}$	Γ_{rot}	
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
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
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
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
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

esting is the low computational cost of the DGF calculation. For the case of systems such as the argon trimer it constitutes a reliable alternative to computationally more expensive exact calculation such as the HC employed here. As an example of the different numerical cost between both methods, it is worth mentioning that the comparison with the DGF results revealed that several levels were originally missing in preliminary HC calculations for $J = 20$, thus forcing us to substantially increase the number of iterations in the diagonalization scheme employed by the exact approach.

3.1.2. Behaviour as a function of temperature

An interesting application of the method, such as the presently reviewed DGF approach, to calculate the rovibrational spectra of a triatomic molecule up to reasonably large values of J was reported in Pérez de Tudela *et al.* [134]. In that work a path integral Monte Carlo (PIMC) method [135, 136] was employed to study the behaviour of the energy, average structure and heat capacity as a function of the temperature T . As T increases the system starts to explore different structural geometries, passing from rigid equilateral triangles to floppier arrangements once the barrier to linearity is overcome. The use of a variable confining volume revealed how this transition

Table 5. Same as Table 4 for $J = 20$. HC results are in second column and the DGF energies are in the fifth column. Only the total symmetry Γ (last column) is specified. Results from Ref. [80].

(v_1, v_2^ℓ)	HC		k	Ω	DGF		Γ
	$E(\text{cm}^{-1})$				$E(\text{cm}^{-1})$		
(0,0 ⁰)	-237.36		1	18	-237.39		A_1'
(0,0 ⁰)	-234.50		1	15	-234.51		A_1''
(0,0 ⁰)	-232.17		1	12	-232.15		A_1'
(0,0 ⁰)	-230.36		1	9	-230.32		A_1''
(0,0 ⁰)	-229.08		1	6	-229.01		A_1'
(0,0 ⁰)	-228.31		1	3	-228.22		A_1''
(0,0 ⁰)	-228.05		1	0	-227.95		A_1'
(0,1 ¹)	-218.43		2,3	20	-217.49		A_1'
(0,1 ¹)	-215.44		2,3	19	-216.36		A_1''
(0,1 ¹)	-215.00		2,3	17	-214.27		A_1''
(0,1 ¹)	-212.73		2,3	16	-213.32		A_1'
(0,1 ¹)	-212.02		2,3	14	-211.58		A_1'
(0,1 ¹)	-210.55		2,3	13	-210.80		A_1''
(0,1 ¹)	-209.59		2,3	11	-209.42		A_1''
(0,1 ¹)	-208.87		2,3	10	-208.81		A_1'
(0,1 ¹)	-207.71		2,3	8	-207.78		A_1'
(0,1 ¹)	-207.68		2,3	7	-207.36		A_1''
(1,0 ⁰)	-207.38		4	18	-207.42		A_1'
(0,1 ¹)	-206.99		2,3	2	-206.52		A_1'
(0,1 ¹)	-206.73		2,3	1	-206.35		A_1''
(0,1 ¹)	-206.36		2,3	5	-206.60		A_1''
(0,1 ¹)	-205.60		2,3	4	-206.35		A_1'
(1,0 ⁰)	-204.56		4	15	-204.60		A_1''
(1,0 ⁰)	-200.50		4	9	-200.51		A_1''
(1,0 ⁰)	-199.23		4	6	-199.24		A_1'
(1,0 ⁰)	-198.48		4	3	-198.46		A_1''

observed for the overall structure of the trimer is possible when the Ar atoms are allowed to move freely occupying more delocalized positions. As a consequence, the internal energy exhibits a sudden increase beyond certain temperature.

A possible way to obtain a dependence of the energy with the temperature consists of performing a Boltzmann average of the rovibrational energy calculated as explained in the previous sections [137]:

$$\langle E(T) \rangle = \left[\sum_{J=0}^{J_{\max}} \sum_l (2J+1) E_l^J e^{-\beta E_l^J} \right] \cdot \left[\sum_{J=0}^{J_{\max}} \sum_l (2J+1) e^{-\beta E_l^J} \right]^{-1}, \quad (53)$$

where $\beta = 1/k_B T$, and l stands for the corresponding rovibrational states which belong to the physically acceptable symmetry irreducible representation A_1 for each value of J [79, 130]. The sum is extended to the value of the total angular momentum $J_{\max}$ at which convergence is ensured. For the largest value of the temperature analysed there, $T = 40$ K, $J_{\max} = 80$ was found to be sufficient.

The comparison of the thermally averaged energy as explained in Eq. (53) and PIMC results [134] is shown in Figure 4 up to $T = 40$ K. The different behaviour of the PIMC energies (in black dashed lines) depending on the values of the confinement

radius (2.6 Å, 4 Å and 10 Å) used to restrict the movements of the Ar atoms is clear: when the system is free to explore more delocalized structures, the energy exhibits a sudden increase beyond $T \sim 20$ K. The DGF result is in good agreement with the PIMC calculation performed under the most limiting confinement in which the Ar trimer hardly abandon the minimum energy equilateral geometries. Usually the passage from the nearly rigid equilateral triangles associated with situations close to the ground and low energy bound states to floppier collinear geometries is interpreted as indicative of internal mode softening of the system [138]. The vibrational basis set employed in the average of Eq. (53) contains bound states which are far from the more delocalized linear structures [125, 126].

Figure 4. Average energy for the Ar trimer calculated by means of a PIMC approach with different values of the confinement radius (black dashed lines); two models considering the discrete spectra of Morse potentials adapted to equilateral triangles (Morse A) and collinear geometries (Morse B) (red and blue solid lines); models including the total fragmentation Ar+Ar+Ar continuum (green lines) and the Boltzmann averaged approach of Eq. (53). See text for further details.

A further investigation on this sense was carried out by considering a model based in a two Morse potentials which allows to include both a larger number of analytically obtained energy levels from the bound discrete spectrum and even the contribution from the corresponding continuum [134]. In particular the model was developed considering a potential (Morse A) describing short-amplitude motions in combination with another potential (Morse B) which allows softer large-amplitude modes. The different behaviour of the corresponding thermally averaged energies reveals the con-

Table 6. Vibrational ($J = 0$) energy levels for Ne_3 obtained with a HC calculation [142] (third column), the FEM from Ref. [139] (fifth column) and the DGF approach [142] (last column). The symmetry group is in first column; the ℓ quantum number from the HC calculation is in second column; in fourth column is the index v of the states of the FEM calculation and in sixth column is the index number for each irreducible representation, v^Γ .

Γ	HC			FEM		DGF
	ℓ	$E \text{ (cm}^{-1}\text{)}$	v	$E \text{ (cm}^{-1}\text{)}$	v^Γ	$E \text{ (cm}^{-1}\text{)}$
A'_1	0	-51.51	0	-51.50	1	-51.51
	0	-36.44	2	-36.43	2	-36.44
	3	-34.22	4	-34.22	3	-34.35
	0	-31.64	6	-31.63	4	-31.85
	0	-28.04	8	-28.04	5	-28.22
	0	-24.09	10	-24.08	6	-24.14
	0	-22.46	12	-22.45	7	-22.46
	0	-21.91	14	-21.90	8	-22.06
	0	-19.22	18	-19.21	9	-19.17
E'	1	-38.76	1	-38.75	1	-38.76
	1	-34.63	3	-34.63	2	-34.71
	2	-32.42	5	-32.42	3	-32.63
	2	-28.65	7	-28.64	4	-28.87
	1	-24.55	9	-24.54	5	-24.57
	1	-23.46	11	-23.45	6	-23.48
	1	-22.36	13	-22.34	7	-22.44
	1	-20.23	15	-20.23	8	-20.26
	1	-19.65	17	-19.65	9	-19.62
A'_2	3	-20.06	16	-20.05	1	-20.06
	3	-18.50	19	-18.49	2	-18.60

tribution of each type of geometries (see red and blue lines in Figure 4). It is also clear that in order to reproduce the abrupt change experienced by the energy curve obtained with the least limiting confinement in the PIMC calculation when the temperature is sufficiently increased, the dissociative continua of the $\text{Ar}_2 + \text{Ar}$ and total fragmentation $\text{Ar} + \text{Ar} + \text{Ar}$ cases have to be taken into account within this two-Morse-potential model [134].

4. Ne_3 : A lighter system

The Ne trimer has been also subject of different investigations. In some cases it was chosen as an intermediate example between the heavier Ar_3 system and the comparatively much lighter helium trimer [70, 123]. This has been reflected in the still rigidlike features exhibited by its structural properties in comparison with the diffuse nature of He_3 . A complete description of the rotationless spectrum was reported years ago by means of the DGF approach explained in Section 2.2.1 [72]. Structural properties and energy levels were studied by means of different pairwise 2B interaction potentials. Previous investigations employed DVR methods [118], a symmetry-adapted Lanczos approach with Pekeris coordinates [125] and quasirandom DGF [124]. One of the attempts in the past to analyze the rotational spectrum of the system was made by

Table 7. Comparison between the rovibrational energy levels for Ne_3 at $J = 3$ obtained with the FEM from Ref. [139] (second column) and the DGF approach [142] (last column). Ω , ℓ and the index v^Γ of the corresponding vibrational state in each irreducible representation (see Eqs. (41-43)) are given in the first, third and fourth columns, respectively. The rovibrational $\Gamma_{\text{vib}}^{\Omega\ell}$ (fifth column), rotational Γ_{rot} (sixth column) and total Γ (seventh column) symmetries are also indicated.

Ω	$E(\text{cm}^{-1})$	ℓ	v^Γ	$\Gamma_{\text{vib}}^{\Omega\ell}$	Γ_{rot}	Γ	$E(\text{cm}^{-1})$
3	-50.33	0	1^{A_1}	A_1/A_2	A_1/A_2	A_1''	-50.35
3	-50.33	0	1^{A_1}	A_1/A_2	A_1/A_2	A_2''	-50.35
0	-49.61	0	1^{A_1}	A_1	A_2	A_2'	-49.62
2	-37.44	1	1^E	A_1	A_1/A_2	A_1'	-37.44
2	-37.39	1	1^E	A_1	A_1/A_2	A_1''	-37.29
1	-37.20	1	1^E	A_1/A_2	A_1/A_2	A_1''	-37.21
1	-36.67	1	1^E	A_1/A_2	A_1/A_2	A_2''	-36.81
3	-35.38	0	2^{A_1}	A_1/A_2	A_1/A_2	A_1''	-35.29
0	-34.53	0	2^{A_1}	A_1	A_2	A_2'	-34.35
2	-49.93	0	1^{A_1}	E	A_1/A_2	E'	-49.94
1	-49.69	0	1^{A_1}	E	A_1/A_2	E'	-49.70
3	-37.91	1	1^E	E	A_1/A_2	E''	-37.65
3	-37.53	1	1^E	E	A_1/A_2	E''	-37.63
2	-37.27	1	1^E	E	A_1/A_2	E'	-37.25
1	-37.02	1	1^E	E	A_1/A_2	E''	-37.01
0	-36.75	1	1^E	E	A_1/A_2	E'	-36.85
2	-34.86	0	2^{A_1}	E	A_1/A_2	E'	-34.84
1	-34.66	0	2^{A_1}	E	A_1/A_2	E''	-34.58

Salci *et al.* [139] in which energy levels up to $J = 3$ were calculated by means of a FEM assuming that the molecule was an oblate symmetric top. Among other things, the authors found: (i) differences with respect to analytical expressions for the energies of a symmetric planar trimer when the vibrational excitation was increased and (ii) a significant contribution from the Coriolis coupling terms. Using the same 2B pairwise potential, Suno [140] performed a HC calculation to obtain the rotational energies up to $J = 6$. A more extended investigation covering the rotational spectrum between $J = 0$ and 18 was reported by Yang *et al.* [141] who analyzed energy levels and wave functions of the corresponding Ne_3 bound states in a quantum dynamical calculation.

The DGF calculation of Ref. [142] was carried out with 50 Gaussian functions $\varphi_i(R)$ with centers starting from 2.38 Å equally spaced with an interval of 0.16 Å. The vibrational problem was solved using symmetry-adapted basis functions: A total number of 19,053 $\phi_j^{A_1}$ functions from Equation (41) for the A_1 representation; 15,877 $\phi_j^{A_2}$ functions from Equation (42) for the representation A_2 and, finally 36,790 ϕ_j^E functions from Equation (43) for E . We employed the HFD-B Ar-Ar pairwise potential by Aziz and Slaman [143].

Table 6 shows the results of the calculations for $J = 0$ by means of the HC and DGF approaches in comparison with those purely vibrational energy levels reported

by Salci *et al.* [139]. In this case the diagonalization of the rotationless Hamiltonian H_{vib} is performed using the symmetry-adapted basis set functions from Eqs. (41)–(43) and the corresponding eigenstates are obtained in separate blocks labelled with v^Γ . This approach therefore differs from our previous calculation for Ar_3 and from the FEM calculation in Ref. [139] where vibrational states are identified with a sole label v . The direct comparison established in Table 6 with the HC states enables the connection between each v^Γ quantum index and ℓ , which is used for the assignment of the rovibrational spectra with $J > 0$.

One example of the application of the present method for the Ne trimer case can be discussed for $J = 3$ [142]. In Table 7 we present the DGF results in comparison with those obtained with the FEM approach of Ref. [139]. The procedure enables to see how, for instance, the vibrational ground state of the A_1 group, $(v^\Gamma, \ell) = (1^{A_1}, 0)$, is responsible for rotational eigenstates for the A_1'' , A_2'' , A_2' and E' groups depending on the value of Ω . Thus, the case with $\Omega = 0$ is the only one with a well defined $\Gamma_{\text{rot}} = A_2$ which, combined with $\Gamma_{\text{rot}} = A_2$, leads to the A_2' state with the lowest energy. The degenerate states with $\Omega = 3$ are, in turn, the origin of the ground states for the A_1'' and A_2'' groups, whereas the values of Ω which yield to non-multiple of 3 values for η produce the first two levels of the E' group.

In conclusion, results shown in Table 6 and those other comparisons [142] with previous works of Refs. [139–141] suggest that the DGF approach is as good for Ne_3 as previously discussed for the heavier system Ar_3 .

5. H_3^+ : The limitations of the approximate method

H_3^+ is a well studied system which plays a relevant role in Astrophysics [144–146]. The molecule in principle does not have allowed rotational transitions due to the absence of: (i) low energy stable electronic states and (ii) a permanent dipole moment because of the equilateral triangle geometry of its minimum energy structure. On the other hand, the ν_1 vibrational stretching mode is totally symmetric and therefore, only the other mode ν_2 associated with a doubly degenerated bending-stretching movement contributes to a nonzero transition dipole moment. Ruling out theoretical suggestions of a yet to be confirmed observable spectrum due to rotation induced distortions [147, 148], the only possibilities for a experimental detection consist then in the vibration-rotation infrared spectrum produced with changes in the quantum number v_2 for such ν_2 vibration. “Forbidden” stretching transitions have been also investigated as an alternative way to explore the system [149, 150]. This has motivated an ample list of works focussed on the characterization of its RV spectrum [151–155]. Carney and Porter reported one of the first *ab initio* predictions of the P , Q and R branches of the RV spectra of both the H_3^+ and D_3^+ ions in their equilateral triangle geometry [153]. Miller and Tennyson carried out an *ab initio* calculation of the vibrational frequencies and rotational constants of H_3^+ and different isotopic variants with substitutions of H atoms by deuterium [151]. These investigations included then different overtone bands [152, 156–159]. The observation of rotation-vibration transitions has been extended more recently to cover the visible regions [160, 161]. Carrington and collaborators [162–165], on the other hand, analyzed in detail the near-dissociation spectra of H_3^+ .

Table 8. Comparison of $J = 0$ vibrational energy levels for H_3^+ obtained with the HC (third column) method [54] and DGF [166] results (fifth column). Energies, in cm^{-1} , are referred to the ground state. The symmetry group Γ (first column), the (v_1, v_2^ℓ) numbers of the HC calculation (second column) and the v^Γ label of the DGF calculation (fourth column) are included.

Γ	(v_1, v_2^ℓ)	HC [54]	v^Γ	DGF [166]
		$E_{\text{HC}}(\text{cm}^{-1})$		$E_{\text{DGF}}(\text{cm}^{-1})$
A_1'	(0, 0 ⁰)	0	1	0
	(1, 0 ⁰)	3179.08	2	3178.38
	(0, 2 ⁰)	4777.61	3	4775.79
	(2, 0 ⁰)	6263.57	4	6262.16
	(0, 3 ³)	7284.47	5	7281.73
	(1, 2 ⁰)	7769.27	6	7766.76
	(0, 4 ⁰)	8999.82	7	8996.52
	(3, 0 ⁰)	9253.95	8	9251.83
	(1, 3 ³)	9967.84	9	9964.50
	(2, 2 ⁰)	10593.59	10	10590.47
	(0, 5 ³)	10920.06	11	10917.27
	(1, 4 ⁰)	11813.23	12	11809.39
E'	(0, 1 ¹)	2521.08	1	2520.10
	(0, 2 ²)	4997.53	2	4995.62
	(1, 1 ¹)	5554.59	3	5552.93
	(0, 3 ¹)	7004.97	4	7002.35
	(1, 2 ²)	7870.02	5	7867.45
	(2, 1 ¹)	8488.87	6	8486.52
	(0, 4 ²)	9111.12	7	9107.77
	(1, 3 ¹)	9652.54	8	9649.12
	(0, 4 ⁴)	9996.95	9	9993.57
	(2, 2 ²)	10645.36	10	10642.13
	(1, 4 ²)	10859.62	11	10856.68
	(3, 1 ¹)	11324.39	12	11321.36
	(1, 4 ²)	11656.24	13	11652.49
A_2'	(0, 3 ³)	7492.44	1	7489.65
	(1, 3 ³)	10209.54	2	10206.09
	(0, 5 ³)	11527.62	3	11523.51

As explained in the Introduction, the H_3^+ molecule has been studied before by means of HC methods. In particular, the present version of this technique was employed to calculate the rovibrational spectra up to $J = 20$ on the ground $1^1A'$ state [54] and the vibrational eigenstates on the lowest triplet excited $^3A'$ state [101]. Similar investigations treated the case of the rovibrational levels and spectra of the isotopic variant D_3^+ on both electronic states [55]. The purpose of considering this trimer in this review is not to provide a complete description of the corresponding rovibrational spectra (see for instance Ref. [155] for a detailed review of the existing literature on this respect). However, H_3^+ constitutes both a fantastic test for the HC method in comparison with previous studies and a limiting case for the approximate DGF approach.

Symmetry-adapted basis sets for each irreducible representation were employed in the DGF calculation of Ref. [166]. 45 equally spaced Gaussian functions with centers

Table 9. Rotational constants (in cm^{-1}) for the lowest H_3^+ bound states. The three first columns correspond to DGF results [166] (the v^Γ label, the average $\bar{B}_{\text{DGF}} = (A + B)/2$ and C_{DGF} constants). Results from the *ab initio* calculation by Carney *et al.* [153] (divided by 2 due to a different notation for the rotational Hamiltonian) are in the remaining columns.

v^Γ	DGF [166]		n	A' [153]	Ref. [153]		
	$\bar{B}_{\text{DGF}}$	C_{DGF}			B' [153]	$\bar{B}$	C' [153]
1^{A_1}	43.49	20.37	1	43.22	43.23	43.22	20.61
1^E	44.08	19.18	2	41.37	46.32	43.84	19.74
1^E	44.08	19.18	3	46.25	41.42	43.84	19.74
2^{A_1}	42.45	19.77	4	42.14	42.19	42.17	19.99

from $0.31 \text{ \AA}$ with intervals of $0.04 \text{ \AA}$ were used, producing 11465, 9801 and 42442 ϕ_j functions for the A_1 , A_2 and E representations, respectively, according to Equations (41)-(43). The PES used in the calculation corresponds to that reported by Aguado *et al.* [54] with 2B contributions from a DIM potential and a non-additive 3B term. The evaluation of the corresponding potential matrix elements are, by far, much more complicate than the corresponding calculations performed for the two other systems under consideration in the present review, Ar_3 and Ne_3 . As explained in Section 2.2.2, the integration of the Hamiltonian elements depending on the internal coordinates is solved by means of the mean-value approximation shown in Eq. (46).

The calculation of the vibrational spectrum of H_3^+ with the DGF approach [166] produces the energy levels shown in Table 8 which also includes the results from the HC calculation from Ref. [54]. Thus we establish the connection between the different v_Γ indexes from the DGF calculation and the values of ℓ from the HC investigation. The differences between energies from both methods are not larger than $\sim 4 \text{ cm}^{-1}$ in any case, that is $\sim 0.03\%$ error. The application of basis adapted to the different symmetry cases Γ optimizes on the other hand the DGF calculation thus ensuring a description of a larger number of levels for each irreducible representation. It is thus possible to obtain some of the A'_2 states, those appearing after the 5^{A_1} and 4^E with a reasonably economical computational effort.

In Table 9 we compare the rotational constants obtained by means of the DGF approach [166] with the *ab initio* results reported by Carney *et al.* [153]. Due to the definition of the rotational Hamiltonian made by those authors, an actual comparison between both set of data requires dividing the *ab initio* constants by two. The agreement between the C and the average values $\bar{B} = (A + B)/2$ is good both for the A_1 state and for the doubly degenerated 1^E state.

HC values for the energies of the H_3^+ rovibrational states for $J = 1$ were compared [166] with the predictions obtained by means of the present DGF approach for various irreducible representations. As shown in Table 10, the agreement found for those levels belonging to A'_2 and E' is certainly good, as those observed previously for the cases of Ar_3 and Ne_3 . However the situation is completely different when we analyse states of the A'_2 and E' representations. Differences between the HC and DGF energy values can be larger than 50 cm^{-1} (see for instance the $(0, 2^2) - 2^E$ and $(1, 2^2) - 5^E$ levels

Table 10. $J = 1$ rovibrational states for H_3^+ from HC (fourth column) and DGF (sixth column) calculations, both from Ref. [166]. As in Table 8, energies in cm^{-1} are referred to the vibrational ground state. Value of Ω (third column), the symmetry group Γ (first column), the (v_1, v_2^ℓ) numbers of the HC calculation (second column) and the v^Γ label of the DGF calculation (fourth column) are included.

Γ	(v_1, v_2^ℓ)	HC [166]		v^Γ	DGF [166] $E_{\text{DGF}} (\text{cm}^{-1})$
		Ω	$E_{\text{HC}} (\text{cm}^{-1})$		
A_1'	(0, 0 ⁰)	0	86.97	1 ^{A₁}	86.44
	(1, 0 ⁰)	0	3263.94	2 ^{A₁}	3262.71
	(0, 2 ⁰)	0	4869.57	3 ^{A₁}	4865.84
	(2, 0 ⁰)	0	6346.48	4 ^{A₁}	6344.66
	(0, 3 ³)	0	7379.96	5 ^{A₁}	7375.52
	(1, 2 ⁰)	0	7857.92	6 ^{A₁}	7853.89
A_2''	(0, 1 ¹)	1	2616.35	1 ^E	2583.30
	(0, 2 ²)	1	4994.29	2 ^E	5053.29
	(1, 1 ¹)	1	5645.02	3 ^E	5614.76
	(0, 3 ¹)	1	7081.82	4 ^E	7069.06
	(1, 2 ²)	1	7872.36	5 ^E	7923.68
	(2, 1 ¹)	1	8575.07	6 ^E	8547.18
	(0, 1 ¹)	0	2609.21	1 ^E	2607.12
	(0, 2 ²)	0	5087.09	2 ^E	5083.74
E'	(1, 1 ¹)	0	5640.80	3 ^E	5638.06
	(0, 3 ¹)	0	7101.85	4 ^E	7097.38
	(1, 2 ²)	0	7958.52	5 ^E	7954.52
	(2, 1 ¹)	0	8573.50	6 ^E	8570.20
E''	(0, 0 ⁰)	1	64.13	1 ^{A₁}	63.78
	(0, 1 ¹)	1	2547.83	1 ^E	2581.45
	(1, 0 ⁰)	1	3241.56	2 ^{A₁}	3240.54
	(0, 2 ⁰)	1	4841.81	3 ^{A₁}	4840.43
	(0, 2 ²)	1	5124.75	2 ^E	5062.29
	(1, 1 ¹)	1	5584.53	3 ^E	5612.65
	(2, 0 ⁰)	1	6324.47	4 ^{A₁}	6322.86
	(0, 3 ¹)	1	7045.64	4 ^E	7062.39
	(0, 3 ³)	1	7324.23	5 ^{A₁}	7364.88
	(0, 3 ³)	1	7571.37	1 ^{A₂}	7551.68
	(1, 2 ⁰)	1	7839.99	6 ^{A₁}	7833.36
	(1, 2 ²)	1	7989.16	5 ^E	7933.40
	(2, 1 ¹)	1	8520.62	6 ^E	8544.74

of both symmetry groups). The reason for these apparently selective discrepancies between both methods was suggested [166] to rely on the Coriolis term:

$$H_{\text{Cor}} = -2C\Omega\zeta\ell, \quad (54)$$

with ζ being the Coriolis coupling coefficient between normal coordinates. The above term in Eq. (54) accounts for centrifugal distortion effects in asymmetric rotors [23, 167] and it is not included explicitly within the DGF formalism. The dependence of H_{Cor} on both Ω and ℓ would explain why the failure of the DGF predictions is more relevant for those states with nonzero values of such quantum numbers. Some indications of the magnitude of such coupling effects which split levels with $\Omega \neq 0$

Table 11. H_3^+ rovibrational energy levels for $J = 15$ obtained with the present HC method (fourth column) and those from Ref. [159] (last column). Value of the irreducible representation Γ (first column), the (v_1, v_2^ℓ) (second column) and G (defined in Section 2.1.4) numbers (see text for details) (third column) are included.

Γ	(v_1, v_2^ℓ)	G	E_{HC} [54]	E_{HC} [159]	Γ	(v_1, v_2^ℓ)	G	E_{HC} [54]	E_{HC} [159]
A_2''	$(0, 0^0)$	9	2857.031	2856.729	A_2'	$(0, 0^0)$	6	3726.965	3726.549
	$(0, 0^0)$	3	4215.692	4215.239		$(0, 1^1)$	9	5198.093	5198.463
	$(1, 0^0)$	9	5945.604	5944.843		$(0, 1^1)$	9	5454.533	5454.531
	$(0, 1^1)$	6	6087.613	6087.546		$(0, 1^1)$	3	6539.947	6539.917
	$(0, 1^1)$	6	6412.631	6412.298		$(0, 2^2)$	12	6668.732	6671.817
	$(0, 1^1)$	0	7080.889	7080.385		$(1, 0^0)$	6	6805.430	6804.443
	$(1, 0^0)$	3	7317.489	7316.346		$(0, 1^1)$	3	6959.556	6959.027
	$(0, 2^0)$	9	7506.640	—		$(1, 1^1)$	9	8108.044	8109.734
	$(0, 2^2)$	9	8091.790	—		$(1, 0^0)$	6	8259.400	8259.969
	$(1, 0^0)$	3	8711.558	—		$(1, 1^1)$	9	8445.714	8445.703
	$(0, 2^0)$	9	8932.009	—		$(0, 2^2)$	6	8690.945	—
	$(1, 1^1)$	6	9057.368	9057.019		$(0, 2^2)$	6	9018.069	—
	$(0, 2^2)$	3	9268.058	—		$(0, 2^2)$	0	9317.971	—
	$(1, 1^1)$	6	9347.696	9347.039		$(1, 2^2)$	12	9323.859	—
	$(0, 3^3)$	12	9403.516	—		$(0, 2^2)$	0	9555.461	—
	$(0, 2^2)$	3	9564.750	—		$(1, 2^2)$	12	9590.181	9598.235
	$(1, 1^1)$	0	10006.819	—	E'	$(0, 0^0)$	10	2451.806	2451.609
E''	$(0, 0^0)$	7	3485.172	3484.774		$(0, 0^0)$	8	3197.263	3196.903
	$(0, 0^0)$	5	3926.607	3926.171		$(0, 0^0)$	4	4086.876	4086.428
	$(0, 0^0)$	1	4348.830	4348.363		$(0, 0^0)$	2	4297.085	4296.621
	$(0, 1^1)$	10	5026.132	5026.286		$(0, 1^1)$	11	4539.201	4539.952
	$(0, 1^1)$	8	5555.387	5555.503		$(1, 0^0)$	10	5559.581	5559.156
	$(0, 1^1)$	8	5827.935	5827.729		$(0, 1^1)$	7	5842.711	5842.782
	$(0, 1^1)$	4	6401.167	6401.110		$(0, 1^1)$	7	6145.521	6145.235
	$(1, 0^0)$	7	6580.739	6579.774		$(0, 1^1)$	5	6227.089	6226.789
	$(0, 1^1)$	2	6612.508	6612.443		$(0, 1^1)$	1	6327.096	6326.432
	$(0, 1^1)$	4	6812.204	6811.731		$(0, 1^1)$	5	6628.986	6628.627
	$(1, 0^0)$	5	6968.121	6967.289		$(0, 1^1)$	1	6666.137	6666.069
	$(0, 1^1)$	2	7073.232	7072.408		$(0, 2^0)$	10	7034.521	7036.309
	$(0, 2^2)$	11	7219.669	7220.652		$(0, 1^1)$	1	7055.835	7055.249
	$(1, 0^0)$	1	7430.528	7429.303		$(1, 0^0)$	4	7192.943	7191.838
	$(0, 1^1)$	2	7921.123	—		$(1, 0^0)$	2	7382.916	7381.697
	$(0, 2^0)$	7	8109.035	8109.399		$(1, 1^1)$	11	7474.824	7477.810
	$(1, 1^1)$	8	8379.865	8380.666		$(0, 2^2)$	10	7686.525	7687.224

can be estimated from the F_{nm} terms in the formalism by Carter and Porter [153]. In their *ab initio* calculation the separation of the degenerated $n = 2$ and $n = 3$ states is 37.031 cm^{-1} which compares extremely well with the difference between the HC and DGF calculations of about 33.1 and 33.6 cm^{-1} seen between the $(0, 1^1) - 1^E$ levels of the A_2'' and E'' groups, respectively. Therefore, if we set ζ to a constant value equals to 1, $H_{\text{Cor}}(v_1, v_2^\ell)$ becomes $\sim 37 \text{ cm}^{-1}$ for states with $v_2 = 1$ and $\ell = 1$, which certainly correspond to the difference observed for the DGF energies of those states with respect to the HC calculation. For $v_2 = 2; \ell = 2$ the Coriolis term of Eq. (54) becomes $\sim 70 \text{ cm}^{-1}$, also of the same order of the above mentioned difference between the DGF and HC results, but it gets too large for the cases of $v_2 = 3; \ell = 1$ and $v_2 = 3; \ell = 3$: $\sim 34 \text{ cm}^{-1}$ and $\sim 102 \text{ cm}^{-1}$, respectively.

In Ref. [166] it was shown that more refined *ad hoc* choices for such a parameter manage to bring HC and DGF into a better agreement, thus suggesting the role

played by the $H_{\text{Cor}}(v_1, v_2^\ell)$ term. Attending to the existing relation between the v_2 and ℓ numbers and the degeneration of the corresponding rovibrational states one could choose (besides the already mentioned $\zeta = 1$ for $v_2 = \ell = 1$), $\zeta = 1/2$ when $v_2 = 3, \ell = 1$, the Coriolis term becomes $H_{\text{Cor}}(v_1, 3^1) = 17 \text{ cm}^{-1}$; $\zeta = 2/3$ when $v_2 = \ell = 2$ which leads to $H_{\text{Cor}}(v_1, 2^2) = 47 \text{ cm}^{-1}$ and $\zeta = 1/4$ when $v_2 = \ell = 3$ and then $H_{\text{Cor}}(v_1, 3^3) = 25 \text{ cm}^{-1}$. All these values are consistent with the apparent failure of the DGF approach to account for these centrifugal distortion effects for H_3^+ .

The situation, on the contrary, for the HC approach is much more favourable. Whereas previous studies admitted not well converged rotational eigenstates for high values of the total angular momentum $J > 10$ [159], energies up to $J = 20$ were reported by Aguado *et al* [54]. As an example, a comparison between results from both calculations, that performed in Ref. [54] and the previous investigation by Dinelli *et al.* [159], is shown in Table 11. The missing energy levels of the latter calculation (a number which increases even more when more rotational states are investigated or larger values of the total angular momentum are considered) shows the above mentioned difficulties.

6. Conclusions

In this work we have reviewed two different approaches to calculate the rotation-vibration spectrum of trimers. On the one hand an exact method based in hyperspherical coordinates (HC) and, on the other hand, an approximate method which employs distributed Gaussian functions (DGF) for the pair coordinates. In both cases we discuss the procedure followed to assign the corresponding symmetry character to the energy levels. Examples of combined applications to different systems such as Ar_3 , Ne_3 and H_3^+ , allow us to establish the limitations of the DGF method. In particular, for H_3^+ , it was found that centrifugal distortion effects were not taken into account conveniently and noticeable discrepancies with respect to the exact results obtained with the HC technique indicates the deficiencies of the DGF approach for specific systems.

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