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Limitations of a Theoretical Method to Calculate the Rovibrational Spectrum of Trimers: H_3^+

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Abstract A method proposed to assign the symmetry character of the rovibrational spectrum of trimers has been applied to the case of H_3^+ . This system, much lighter than previously investigated rare gas three body molecules such as Ar_3 or Ne_3 , constitutes a challenging example to test the possible limitations of this approach. Calculation of the corresponding rovibrational spectra for $J = 1$ and rotational constants and the corresponding comparison with results from hyperspherical coordinates methods reveals that distortion Coriolis coupling terms, not accounted for in the original method, play a significant role for some specific symmetry representations.

1 Introduction

An approximative method based in the use of distributed Gaussian functions (DGF) to describe the interparticle distances was proposed some time ago to characterize the symmetry of the rovibrational spectrum of trimers [1]. Besides the original application to the Ar_3 system [1,2], a recent investigation shows the capabilities of the method for some other examples such as Ne_3 [3]. In this work we extend the study for a much more demanding system, H_3^+ , for which the lighter mass in comparison with those rare gas trimers is expected to play some role in the structure of the rovibrational levels. Protonated hydrogen is one of the most important species in Astrophysics [4–6] and many investigations have been focussed on its rotation–vibration spectrum [7–11]. The absence of low energy stable excited electronic states and a permanent dipolar moment due to the equilateral triangle minimum energy geometry makes that the trimer has not allowed rotational transitions. Since the ν_1 vibrational stretching mode is totally symmetric, the only nonzero transition dipole moment corresponds to the other mode ν_2 associated with a doubly degenerated bending–stretching movement. The only possible experimental detection consists then in the vibration–rotation infrared spectrum produced by changes in the quantum number ν_2 for such ν_2 vibration.

A detailed description of the H_3^+ spectrum is out of the scope of this work, where we will instead test the capabilities of the above mentioned DGF approach to assign the symmetry character to the rovibrational energy levels. We will also perform calculations by means of the same hyperspherical coordinate (HC) method employed in our previous investigation on Ar_3 [2] for a proper comparison of the corresponding $J > 0$ states.

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2 Theory

A modified version of the method proposed in Refs. [1,2] has been employed here for the study of the rovibrational spectrum of H_3^+ . We suggest the interested reader to consult those references for the general theory and we will restrict here to highlight the novel details with respect to the originally reported approach. The overall strategy consists on separating the total Hamiltonian in the sum of the vibrational and rotational components: $H_{\text{tot}} = H_{\text{vib}} + H_{\text{rot}}$. The vibrational Hamiltonian for the present case of homonuclear trimers, after transformations of the total wave function [12, 13], is expressed in terms of the interparticle distances as:

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

m_i being the mass of each atom and $U(\mathbf{R})$ the potential energy operator. On the other hand, the T_{ijk} operator, with $i \neq j \neq k$, of Eq. (1), contains all crossed kinetic terms as follows:

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

For the rotational Hamiltonian the general case of an asymmetric top [14–16] is chosen:

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

where $\kappa = (2B - A - C)/(A - C)$ is Ray's asymmetry parameter [17] and A , B and C are rotational constants.

This H_{tot} is solved by means of a total basis set constructed by means of the eigenstates of the vibrational $J = 0$ case and standard rotational basis functions in terms of J and its projections on the z axis of the body-fixed (Ω) and space-fixed (M) frames, $|k; JM\Omega\rangle$. In order to describe the vibrational eigenstates we initially construct a basis set by means of the product of $\varphi_p(R_i)$ Gaussian functions for each coordinate R_i with center at the value R_p as:

$$\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) = \varphi_{l_1}(R_1)\varphi_{l_2}(R_2)\varphi_{l_3}(R_3). \quad (4)$$

Total symmetry of homonuclear three-particle systems corresponds to the D_{3h} group, but in order to define symmetry-adapted basis sets for the $J = 0$ case, we choose 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} . Their action on the functions from Eq. (4) (see Table 1) leads to:

$$\begin{aligned} \phi_j(\mathbf{R}) = \frac{1}{\sqrt{6}} \left\{ \chi(E)\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) + \chi(C_3) \left[\mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R}) \right] \right. \\ \left. + \chi(\sigma_v) \left[\mathcal{G}_{l_1 l_2 l_3}^{213}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{132}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{321}(\mathbf{R}) \right] \right\} \quad (5) \end{aligned}$$

After using the character table [14] for the C_{3v} symmetry group for $\chi(E)$, $\chi(C_3)$ and $\chi(\sigma_v)$, Eq. (5) leads to the following expressions for each irreducible representation:

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

$$\begin{aligned} \phi_j^{A_2}(\mathbf{R}) = \frac{1}{\sqrt{6}} \left[\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) + \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R}) \right. \\ \left. - \mathcal{G}_{l_1 l_2 l_3}^{213}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{132}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{321}(\mathbf{R}) \right] \quad (7) \end{aligned}$$

$$\phi_j^E(\mathbf{R}) = \frac{1}{\sqrt{6}} \left[2\mathcal{G}_{l_1 l_2 l_3}^{123}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{231}(\mathbf{R}) - \mathcal{G}_{l_1 l_2 l_3}^{312}(\mathbf{R}) \right] \quad (8)$$

Table 1 Action of the symmetry operations of the C_{3v} group (in the first column) on the vibrational functions of Eq. (4) (\mathcal{G}^{123} in second column) and the rotational functions ($D_{M\Omega}^J$ in third column) of Eq. (9)

\mathcal{O}	$\mathcal{O} \mathcal{G}^{123}$	$\mathcal{O} D_{M\Omega}^J$
E	\mathcal{G}^{123}	$D_{M\Omega}^{J*}$
\mathcal{P}_{12}	\mathcal{G}^{213}	$D_{M-\Omega}^{J*}$
\mathcal{P}_{23}	\mathcal{G}^{132}	$(-1)^{J-\Omega} D_{M-\Omega}^{J*}$
\mathcal{P}_{13}	\mathcal{G}^{321}	$(-1)^{J-\Omega} D_{M-\Omega}^{J*}$
\mathcal{P}_{123}	\mathcal{G}^{231}	$D_{M\Omega}^{J*}$
\mathcal{P}_{123}^{-1}	\mathcal{G}^{312}	$D_{M\Omega}^{J*}$

The symmetry of the total wave function for the bound states is assumed to be the result of the product $\Gamma = \Gamma_{\text{vib}}^{\Omega\ell} \times \Gamma_{\text{rot}}$ between the symmetry for a strictly rotational part, Γ_{rot} , and a rovibrational part, $\Gamma_{\text{vib}}^{\Omega\ell}$, where ℓ refers to the vibrational angular momentum number [14].

The rotational functions expressed as a linear combination of rotation Wigner matrices:

$$\mathcal{D}_{M\Omega}^J(\alpha, \beta, \gamma) = A_{M\Omega}^J D_{M\Omega}^{J*}(\alpha, \beta, \gamma) + B_{M\Omega}^J D_{M-\Omega}^{J*}(\alpha, \beta, \gamma) \quad (9)$$

where $\Omega \geq 0$ and the Euler angles α, β, γ relate main inertia axis with the SF system, can also be symmetry adapted by means of the permutation operators in Table 1. The possible values of the coefficients of Eq. (9) becomes: (i) $A_{M\Omega}^J = \chi(E) + 2\chi(C_3)$ and $B_{M\Omega}^J = 3(-1)^{J-\Omega}\chi(\sigma_v)$ if $\Omega \neq 0$ and (ii) $A_{M\Omega}^J = \chi(E) + 2\chi(C_3) + 3(-1)^J\chi(\sigma_v)$ and $B_{M\Omega}^J = 0$ if $\Omega = 0$. As discussed in Ref. [1], these expressions are used to design a recipe to assign the symmetry to the rovibrational spectrum. If $\Omega = 0$, Γ_{rot} is equal to A_1 (A_2) for even (odd) values of J , and can be either A_1 or A_2 for $\Omega \neq 0$. On the other hand, for the rovibrational part, a simple rule in terms of the number η , defined as $\eta = |\pm 2\ell - \Omega|$, with $\ell, \Omega \geq 0$, consists on: (i) $\Gamma_{\text{vib}}^{\Omega\ell} = A_1$ for $\eta = 0$; (ii) $\Gamma_{\text{vib}}^{\Omega\ell} = A_1, A_2$ for η multiple of 3; and (iii) $\Gamma_{\text{vib}}^{\Omega\ell} = E$ if η is not multiple of 3. Finally, given that the symmetry operations employed to adapt the basis function do not correspond to D_{3h} but the C_{3v} group, we distinguish the ' or '' character of the total symmetry Γ depending on whether Ω is even or odd, respectively.

The diagonalization in separate blocks corresponding to the A_1, A_2 and E representations allows a better and faster description of the different rovibrational levels, using a larger number of DGF basis in Eq. (4) for each symmetry group. In particular, for the present case of H_3^+ , a set of 45 DGFs with equally spaced centers from 0.31 Å with intervals of 0.04 Å were employed. A total number of 11,465; 9801 and 42,442 ϕ_j functions were generated according with Eqs. (6)–(8) for the A_1, A_2 and E representations, respectively. Each radial basis function of Eq. (4) defines a triangle with values for each side given by the center of the DGF employed in each R_i coordinate. Rotational constants are calculated in the reference system of main inertia axis with the z axis perpendicular to the molecule plane. As in previous applications of the method [1,2] the integration in the R_i coordinates in all Hamiltonian matrix elements between these basis functions was solved by invoking a mean-value like approach with the corresponding DGF centers. Since it is not a good quantum number the H_{rot} matrix contains non-diagonal term connecting Ω and $\Omega \pm 2$ values. In this study we have used the potential energy surface by Aguado et al. [18].

3 Results

The first step is to solve the $J = 0$ vibrational problem. The results of the DGF calculation for the A_1', E' and A_2' are shown in Table 2, where energy levels reported in Ref. [18] are also included for comparison. The differences between the energies obtained with the two methods, E_{HC} and E_{DGF} , remain below the $\approx 4 \text{ cm}^{-1}$ cases, thus yielding an error always smaller than 0.03%. The comparison with the HC results also allows the correspondence of the ℓ number to the different v^{Γ} states in the DGF spectrum, a requirement for the symmetry assignment discussed in the previous section for the rovibrational spectrum for the $J > 0$ cases.

Rotational constants have been calculated for the first states of the A_1 and E representations by means of the DGF approach. The corresponding values in cm^{-1} are shown in Table 3 besides those from the *ab initio* calculation by Carney and Porter [7]. It is worth mentioning that a proper comparison with results of Ref. [7] requires dividing matrix elements for the rotational coefficients shown in Table I of that work by 2, since the actual expression of the Hamiltonian employed by those authors includes a $\frac{1}{2}$ factor in the coefficients for the

Table 2 Vibrational states for $J = 0$ of H_3^+

Γ	(v_1, v_2^{ℓ})	E_{HC}	v^{Γ}	E_{DGF}
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)	10,593.59	10	10,590.47
	(0, 5 ³)	10,920.06	11	10,917.27
	(1, 4 ⁰)	11,813.23	12	11,809.39
	E'	(0, 1 ¹)	2521.08	1
(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)		10,645.36	10	10,642.13
(1, 4 ²)		10,859.62	11	10,856.68
(3, 1 ¹)		11,324.39	12	11,321.36
(1, 4 ²)		11,656.24	13	11,652.49
A'_2	(0, 3 ³)	7492.44	1	7489.65
	(1, 3 ³)	10,209.54	2	10,206.09
	(0, 5 ³)	11,527.62	3	11,523.51

HC levels (third column) are taken from Ref. [18] and DGF results (fifth column) are from this work. Energies are in cm^{-1} and referred to the ground state. The symmetry group Γ is in first column, the (v_1, v_2^{ℓ}) numbers in the HC calculation are in the second column and the v^{Γ} number of the DGF calculation is in the fourth column

Table 3 Rotational constants in cm^{-1} for some of the bound states of H_3^+ obtained with the present DGF values (last two columns) in comparison with constants from Ref. [7] (from second to fifth columns) divided by 2 (see text for details)

k	A'	B'	\bar{B}	C'	v^{Γ}	\bar{B}_{DGF}	C_{DGF}
1	43.22	43.23	43.22	20.61	1^{A_1}	43.49	20.37
2	41.37	46.32	43.84	19.74	1^E	44.08	19.18
3	46.25	41.42	43.84	19.74	1^E	44.08	19.18
4	42.14	42.19	42.17	19.99	2^{A_1}	42.45	19.77

Average values $\bar{B} = (A + B)/2$ from both calculations are shown in fourth and sixth columns

different components of the total angular momentum (see Equation (1) of Ref. [7]). Despite the difference in the potential energy in each calculation, values of C and the average $\bar{B} = (A + B)/2$ agree reasonably well. Moreover, the corresponding eigenenergies for the pure vibrational elements given in Ref. [7] for the $n = 1-3$ states (2515.99, 2516.17 and 3185.32 cm^{-1}) compare quite well with energies for the doubly-degenerated 1^E and the 2^{A_1} states shown in Table 2: 2520.10, 2510.10 and 3178.38 cm^{-1} , respectively.

The calculation of the rovibrational states for $J = 1$ yields the energy levels shown in Table 4. We have also employed the HC method of Ref. [18] to complete the calculation to the case of $J = 1$, originally not included in the work by Aguado et al. The comparison between both set of results reveals a remarkable finding: whereas the agreement between the HC and DGF levels for the A'_2 and E' representations is as good as the one we have seen for the pure vibration spectrum (see Table 2), noticeable differences are observed for the entire set of states corresponding to the A'_2 block and some cases from the E' group. Discrepancies can be

Table 4 Rovibrational states of H_3^+ for $J = 1$ obtained by means of the HC (fourth column) and DGF methods (sixth column) are from this work

Γ	(v_1, v_2^ℓ)	Ω	E_{HC}	v^Γ	E_{DGF}	$ \Delta E $
A'_1	$(0, 0^0)$	0	86.97	1^{A_1}	86.44	0.5
	$(1, 0^0)$	0	3263.94	2^{A_1}	3262.71	1.2
	$(0, 2^0)$	0	4869.57	3^{A_1}	4865.84	3.7
	$(2, 0^0)$	0	6346.48	4^{A_1}	6344.66	1.8
	$(0, 3^3)$	0	7379.96	5^{A_1}	7375.52	4.4
A''_2	$(1, 2^0)$	0	7857.92	6^{A_1}	7853.89	4.0
	$(0, 1^1)$	1	2616.35	1^E	2583.30	33.1
	$(0, 2^2)$	1	4994.29	2^E	5053.29	59.0
	$(1, 1^1)$	1	5645.02	3^E	5614.76	30.3
	$(0, 3^1)$	1	7081.82	4^E	7069.06	12.8
	$(1, 2^2)$	1	7872.36	5^E	7923.68	51.3
E'	$(2, 1^1)$	1	8575.07	6^E	8547.18	27.9
	$(0, 1^1)$	0	2609.21	1^E	2607.12	2.1
	$(0, 2^2)$	0	5087.09	2^E	5083.74	3.4
	$(1, 1^1)$	0	5640.80	3^E	5638.06	2.7
	$(0, 3^1)$	0	7101.85	4^E	7097.38	4.5
E''	$(1, 2^2)$	0	7958.52	5^E	7954.52	4.0
	$(2, 1^1)$	0	8573.50	6^E	8570.20	3.3
	$(0, 0^0)$	1	64.13	1^{A_1}	63.78	0.4
	$(0, 1^1)$	1	2547.83	1^E	2581.45	33.6
	$(1, 0^0)$	1	3241.56	2^{A_1}	3240.54	1.0
	$(0, 2^0)$	1	4841.81	3^{A_1}	4840.43	1.4
	$(0, 2^2)$	1	5124.75	2^E	5062.29	62.5
	$(1, 1^1)$	1	5584.53	3^E	5612.65	28.1
	$(2, 0^0)$	1	6324.47	4^{A_1}	6322.86	1.6
	$(0, 3^1)$	1	7045.64	4^E	7062.39	16.8
	$(0, 3^3)$	1	7324.23	5^{A_1}	7364.88	22.7
	$(0, 3^3)$	1	7571.37	1^{A_2}	7551.68	19.7
	$(1, 2^0)$	1	7839.99	6^{A_1}	7833.36	6.6
	$(1, 2^2)$	1	7989.16	5^E	7933.40	55.8
$(2, 1^1)$	1	8520.62	6^E	8544.74	24.1	

Energies are in cm^{-1} and referred to the ground vibrational $J = 0$ state. Differences between HC and DGF energies, $|\Delta E|$ are in the last column

larger than 60 cm^{-1} for some states (see for instance $(0, 2^2)$, 2^E of E'' in Table 4) which, despite it accounts for an error of $\approx 1.2\%$, it clearly constitutes a significant deviation with respect to the HC calculation.

A close inspection reveals that these apparent deficiencies in the DGF estimation correspond to cases in which both Ω and ℓ are larger than 0. The reason for such coincidence can be in the existence of a Coriolis term in the general expression of rotational Hamiltonians. Thus, as explained before [14, 19] one of the terms of order \mathbf{J}^4 which accounts for centrifugal distortion effects in asymmetric rotors can be expressed as:

$$H_{\text{Cor}} = -2C\Omega\zeta\ell \quad (10)$$

where ζ is the Coriolis coupling coefficient between normal coordinates. This term appears in investigations of the rotational–vibrational spectrum of molecular species [7, 20–22] and seems to play a role in the case of the H_3^+ system. In an attempt to study the origin of the discrepancies here observed between the DGF and HC energy levels structure for $J = 1$ we have tried to quantify the value of the term in Eq. (10) in our calculation. The first estimate can be calculated by comparison with the results by Carney and Porter [7]. In their *ab initio* prediction of the H_3^+ rotation–vibration spectrum, the value of the F_{nm} terms accounting for the Coriolis coupling that split levels with nonzero Ω for the case of the degenerated $n = 2$ and 3 states of their calculation is 37.031 cm^{-1} . That energy is close to the difference observed between the HC and DGF calculations for the 1^E levels in the A''_2 and E'' representations (33.1 and 33.6 cm^{-1} , respectively), thus suggesting that the absence of such a H_{Cor} term in the Hamiltonian expressed in Eq. (3) can be certainly responsible of the above mentioned discrepancies, at least for these $(0, 1^1)$ states.

By assuming a constant value $\zeta = 1$ in Eq. (3) and calculating the rotational constant C for each vibrational state v^r of Table 2 we can estimate the Coriolis coupling term for some other states, $H_{\text{Cor}}(v_1, v_2^l)$ and compare with the corresponding differences $|\Delta E|$ shown in Table 3. The thus obtained estimates, $H_{\text{Cor}}(v_1, 1^1) \sim 37 \text{ cm}^{-1}$, $H_{\text{Cor}}(v_1, 2^2) \sim 70 \text{ cm}^{-1}$, $H_{\text{Cor}}(v_1, 3^1) \sim 34 \text{ cm}^{-1}$ and $H_{\text{Cor}}(v_1, 3^3) \sim 102 \text{ cm}^{-1}$, are in reasonable agreement with the deviations between the HC and DGF energies for $(v_1, 1^1)$ and $(v_1, 2^2)$, but are probably too large in the $(v_1, 3^1)$ cases.

A possible refinement for these estimations consists on the definition of the ζ coefficient according to the existing relation between the v_2 and ℓ numbers and the degeneration of the corresponding rovibrational states. Thus, letting $\zeta = 1$ for $v_2 = \ell = 1$; $\zeta = 1/2$ for $v_2 = 3, \ell = 1$; $\zeta = 2/3$ for $v_2 = \ell = 2$ and $\zeta = 1/4$ for $v_2 = \ell = 3$, the values of the Coriolis term become $H_{\text{Cor}}(v_1, 2^2) \sim 47 \text{ cm}^{-1}$; $H_{\text{Cor}}(v_1, 3^1) \sim 17 \text{ cm}^{-1}$ and $H_{\text{Cor}}(v_1, 3^3) \sim 25 \text{ cm}^{-1}$, which improves notably the comparison with the corresponding $|\Delta E|$ observed in Table 3 between DGF and HC energies. This therefore seems to confirm the role played by the distortion Coriolis coupling effects. A proper description of the H_3^+ rotation–vibration spectrum would then require its inclusion in the corresponding Hamiltonian. This is not the case in the presently used DGF approach, which among other things, does not explicitly consider the ℓ number. Further work is needed to complete the capabilities of such a method, possibly including these distortion terms although retaining its simplicity.

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