# Symmetry projection of the rovibrational functions of methane

O. Álvarez-Bajo *, R. Lemus †, M. Carvajal * and F. Pérez-Bernal *

* *Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain.*
† *Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Apartado Postal 70-543, 04510 México, DF, México.*

**Abstract.** In this work we propose a symmetry projection approach to build a rovibrational basis for methane. In our method, symmetry adapted functions are obtained by simultaneous diagonalization of a set of commuting operators, whose representation is given in terms of direct products of Wigner's *D* functions and vibrational matrix representations provided by a local scheme. The proposed approach is general and permits to obtain in a systematic fashion an orthonormal set of symmetry-projected functions, with good total angular momentum, and carrying the irreducible representations of the molecular symmetry group.

**Keywords:** Methane, symmetry projection, rovibrational functions
**PACS:** 02.20.-a, 33.15.Mt, 33.20.Vq:

## 1. INTRODUCTION

With the advent of new spectroscopic techniques leading to significant advances in high resolution molecular spectroscopy, it has been possible to identify the existence of multiple minima associated with nonrigid molecules [1, 2]. Basically there are two possible approaches when dealing with non rigid molecules: the permutation inversion group (molecular symmetry group), which has its origins in the works of *H.C.Longuet-Higgins* [3] and *J.T.Hougen* [4, 5], and the Schrödinger supergroup formalism proposed by *S. Altmann* [6, 7]. Both have pros and cons when dealing with nonrigid systems but, beyond their differences, the importance of the molecular symmetry (MS) group lies on two facts. On one hand, semirigid molecules are embedded in the formalism and, on the other hand rovibronic and nuclear spin degrees of freedom may be treated in a unified and clear fashion [8, 9, 10]. A remarkable feature of the molecular symmetry group elements is that they can be factorized into three mutually commuting operators, affecting the vibronic, rotational, and nuclear spin coordinates, respectively. This property facilitates the construction of symmetry adapted functions. The present article focus in the symmetry-projection of the basis for rovibrational degrees of freedom.

## 2. MATRIX ELEMENTS OF THE EQUIVALENT ROTATIONS

The symmetry group of semirigid molecules is identified with the molecular point group, while for nonrigid molecules the MS group represents an appropriate approach to describe the symmetry of the system, with the advantage that the semirigid case is

CP1323, *Symmetries in Nature – Symposium in Memoriam of Marcos Moshinsky*
edited by L. Benet, P. O. Hess, J. M. Torres, and K. B. Wolf

embedded in the formalism [8]. The MS group is the subgroup of the complete nuclear permutation-inversion (CNPI) group obtained after the removal of unfeasible operations. Its elements, $p$, can be written as [8, 9]

$$p = v(p)\ \varphi(p)\ s(p), \tag{1}$$

where $v(p)$ is an operation that acts upon coordinates change caused by $p$, $\varphi(p)$ is an operation that affects rotational coordinates, and $s(p)$ is an operation that generates a nuclear spin permutation. Since the operations $v(p)$, $\varphi(p)$, and $s(p)$ act upon different subspaces, they commute with each other. For semirigid molecules a convenient basis to carry out the ro-vibrational description is the direct product

$$|\Psi_{rvs}\rangle = |\Phi_{vib}\rangle \otimes |\Phi_{rot}\rangle \otimes |\Phi_{ns}\rangle. \tag{2}$$

The functions $|\Phi_{ns}\rangle$ correspond to nuclear spin degrees of freedom, that are not addressed in the present paper. The vibrational functions $|\Phi_{vib}\rangle$ may be expressed in a local or a normal scheme. For nonrigid molecules, involving internal rotations for instance, additional functions should be added in order to incorporate the large amplitude degrees of freedom. With regard to rotations, the ket $|\Phi_{rot}\rangle$ corresponds to symmetric top eigenfunctions [11]

$$\Phi^{(rot)}_{Jkm}(\phi,\theta,\chi) = \langle \phi,\theta,\chi|J,k,m\rangle = \sqrt{\frac{(2J+1)}{8\pi^2}}\, D^{(J)*}_{mk}(\phi,\theta,\chi). \tag{3}$$

Hence, for semirigid molecules, a representation $\Delta^{(red)}(p)$ (in general reducible) is given in terms of the direct product

$$\Delta^{(red)}(p) = \Delta^{(red)}[v(p)] \otimes \Delta^{(red)}[\varphi(p)] \otimes \Delta^{(red)}[s(p)]. \tag{4}$$

We first discuss the representation obtained considering the rotational subspace, and its reduction to MS group irreps. The reducible representation

$$\Delta^{(red)}[\varphi(p)] = ||\langle \Phi^{(rot)}_{Jk'm}|\hat{\varphi}(p)|\Phi^{(rot)}_{Jkm}\rangle||, \tag{5}$$

is obtained with the action of equivalent rotations on the basis (3). Let $R(\alpha,\beta,\gamma)$ be an equivalent rotation characterized by Euler angles $(\alpha,\beta,\gamma)$, referred to the molecule-fixed $(x,y,z)$ system, with origin at the nuclear center of mass. The effect of this rotation over rotational functions (3) is given by

$$\hat{R}(\alpha,\beta,\gamma)|Jkm\rangle = \sum_{k'=-J}^{J} D^{(J)}_{k,k'}(\alpha,\beta,\gamma)\ |Jk'm\rangle, \tag{6}$$

The expression (6) has important consequences in the relation between the product of permutations and the corresponding product of equivalent rotations, as the following theorem establishes [12]

*Theorem. The molecular symmetry group is anti-isomorphic to the group of equivalent rotations*

$$\varphi(p_1p_2) = \varphi(p_3) = \varphi(p_2)\varphi(p_1). \tag{7}$$

## 3. PROJECTION OF METHANE ROTATIONAL FUNCTIONS

In this section we establish an approach to carry out the projection of the rotational basis (3) to irreps of the MS group $\mathscr{T}_d(M)$. To achieve this goal we follow the eigenfunction approach combined with an orthogonalization procedure when necessary.

According to the eigenfunction method [13], the first step consists in establishing an operator which is able to distinguish irreps of the MS group. This operator may be easily identified by constructing a $\lambda$'s table using the formula [13]

$$\lambda_i^{\nu} = \frac{|K_i|\chi_i^{(\nu)*}}{n_\nu}, \tag{8}$$

where $|K_i|$ stands for the number of elements belonging to the $i$-th class, $n_\nu$ corresponds to the dimension of the $\nu$-th irrep, while $\chi_i^{(\nu)}$ is its character. We can label irreps using $\nu$, which is the eigenvalue of the type I Complete Set or Commuting Operators (CSCO-I), as explained below. Hence, from the character table of the $\mathscr{T}_d(M)$ group, we construct a table displaying $\lambda_i^{(\nu)}$ values, with the following equivalence classes

$$\begin{aligned}
K_1 &= \{e\}, && (9)\\
K_2 &= \{(123),(132),(243),(234),(134),(143),(142),(124)\}, && (10)\\
K_3 &= \{(12)(34),(13)(24),(14)(23)\}, && (11)\\
K_4 &= \{(1342)^*,(1243)^*,(1324)^*,(1423)^*,(1432)^*,(1234)^*\}, && (12)\\
K_5 &= \{(12)^*,(13)^*,(14)^*,(23)^*,(24)^*,(34)^*\}. && (13)
\end{aligned}$$

We note that the class $K_5$ distinguishes all the irreps. Consequently the diagonalization of the operator

$$\hat{C} \equiv K_5 = (12)^* + (13)^* + (14)^* + (23)^* + (24)^* + (34)^*, \tag{14}$$

in any representation space, provides eigenvectors $\psi_i^{(\nu)}$ carrying irreps of the MS group:

$$\hat{C}\psi_i^{(\nu)} = \nu\,\psi_i^{(\nu)}; \quad i = 1,\ldots,g_\nu, \tag{15}$$

where $\nu = \lambda_5^{\nu}$, $g_\nu$ is the degeneracy of the irrep, and $g_\nu = n_\nu$ if there is no multiplicity of irreps.

It is clear that the operator (14) does not constitute a complete set of commuting operators, for instance, it does not distinguish between components of the irreps. Hence it is necessary to propose a canonical chain of groups to build a second operator. We may choose the chain

$$\mathscr{T}_d(M) \supset \mathscr{C}_{2v}, \tag{16}$$

where

$$\mathscr{C}_{2v} = \{e,(14)(23),(14)^*,(23)^*\}. \tag{17}$$

The subduction ${}^{\nu}\mathscr{T}_d(M) \downarrow \mathscr{C}_{2v}$ shows the canonical property. In order to distinguish irreps of the subgroup $\mathscr{C}_{2v}$ two classes are needed. Indeed, the operator $\hat{C}(s)$ defined as

$$\hat{C}(s) = (14)^* + 3\,(23)^*, \tag{18}$$

when diagonalized, provides eigenvectors satisfying

$$\hat{C}(s)\ \phi_j^{(\mu)} = \mu\ \phi_j^{(\mu)}; \qquad j = 1, \ldots, g_j, \tag{19}$$

where $\mu$ labels the irreps of the $\mathscr{C}_{2v}$ subgroup. The simultaneous diagonalization of the set of operators

$$\hat{C}_{II} = \{\hat{C}, \hat{C}(s)\} \tag{20}$$

provides eigenvectors carrying irreps of $\mathscr{T}_d(M)$ and $\mathscr{C}_{2v}$:

$$\begin{pmatrix} \hat{C} \\ \hat{C}(s) \end{pmatrix}\ {}_{\kappa}\psi_{\mu}^{(\nu)} = \begin{pmatrix} \nu \\ \mu \end{pmatrix}\ {}_{\kappa}\psi_{\mu}^{(\nu)}, \tag{21}$$

where $\kappa$ is a multiplicity label that takes into account that the same irrep of the MS group could appear several times. In practice, the simultaneous diagonalization (21) may be substituted by the diagonalization of the linear combination

$$\hat{C}_{II} = \hat{C} + 3\ \hat{C}(s), \tag{22}$$

All the $C_{II}$ eigenvalues are different and, consequently, the operator

$$\hat{C}_{II} = (12)^* + (13)^* + 4(14)^* + 10(23)^* + (24)^* + (34)^*, \tag{23}$$

constitutes a CSCO-II, with eigensystem [12]

$$\hat{C}_{II}\ {}_{\kappa}\psi_{\mu}^{\nu} = \zeta\ {}_{\kappa}\psi_{\mu}^{\nu}; \qquad \zeta = \nu + 3\mu. \tag{24}$$

The degeneracy manifested by the multiplicity index $\kappa$ is still present.

Let us now turn our attention back to the rotational space of functions (3). Each permutation-inversion element of the $\mathscr{T}_d(M)$ group has an associated equivalent rotation [12]. Taking into account Eq. (6) and the equivalent rotations associated with the symmetry elements in Eq. (23), we obtain the matrix representation of the $\hat{C}_{II}$ operator:

$$\begin{aligned} \langle Jk'm|\hat{C}_{II}|Jkm\rangle &= D^{(J)}_{kk'}\big(0,\frac{\pi}{2},\pi\big) + D^{(J)}_{kk'}\big(\frac{\pi}{2},\frac{\pi}{2},\frac{\pi}{2}\big) + 4D^{(J)}_{kk'}\big(0,\pi,\frac{\pi}{2}\big) \\ &+ 10D^{(J)}_{kk'}\big(\pi,\pi,\frac{\pi}{2}\big) + D^{(J)}_{kk'}\big(\frac{3\pi}{2},\frac{\pi}{2},\frac{3\pi}{2}\big) + D^{(J)}_{kk'}\big(\pi,\frac{\pi}{2},0\big), \end{aligned} \tag{25}$$

where we stress the difference between the indices of Wigner's D matrices and the representation itself. The diagonalization of this matrix representation of the $\hat{C}_{II}$ operator provides symmetry-adapted functions. The matrix elements of equivalent rotations in the symmetry-adapted basis

$$|\psi_{\gamma}^{J:\Gamma}\rangle = \sum_{k=-J}^{J} s^{J}_{k;\Gamma,\gamma}|Jkm\rangle \tag{26}$$

are given by

$$\langle\psi_{\gamma'}^{J:\Gamma}|\varphi(p)|\psi_{\gamma}^{J:\Gamma}\rangle = M^{(J:\Gamma)}_{\gamma',\gamma}[\varphi(p)] \tag{27}$$

for $p \in \mathscr{T}_d(M)$. Because of the anti-isomorphism (7), the transpose of the matrices (27)

$$\mathbf{D}^{(J;\Gamma)}[\varphi(p)] \equiv \tilde{\mathbf{M}}^{(J;\Gamma)}[\varphi(p)] \tag{28}$$

forms a representation. When the same irrep is generated from functions with different $J$ values the resulting matrices are either equal or complex conjugate. In the latter case they turn out to be equivalent.

Following this approach we are able to obtain symmetry adapted basis generating the same representation. As it is well known, for $J \geq 5$ a multiplicity index appears; some irreps appear more than once. For instance, for $J = 5$ the following reduction is given

$$\mathbf{D}^{(5)}(\varphi(p)) \rightarrow E \oplus 2F_1 \oplus F_2. \tag{29}$$

As expected, degenerate eigenvectors are not in general orthogonal. In order to obtain an orthonormal set of functions generating the same representation we shall proceed as follows. We start considering the set of functions belonging to the first component of the representation, for instance, $\{{}_1\psi_{A_2}^{(5,F_1)}, {}_2\psi_{A_2}^{(5,F_1)}\}$. Since this set is not expected to be orthogonal we should proceed to apply a Gramm-Schmidt orthonormalization approach. In our example they turn out to be orthogonal and this step is not necessary. We thus have

$$\langle {}_1\psi_{A_2}^{(5,F_1)} | {}_2\psi_{A_2}^{(5,F_1)} \rangle = 0. \tag{30}$$

We now generate the rest of the components by means of the equation [14]

$$\sum_{R \in G} D_{\beta\alpha}^{(\Gamma)*}(R) \hat{\mathscr{O}}_R \, {}_\kappa\psi_\alpha^{(J,\Gamma)} = \frac{|G|}{n_\Gamma} {}_\kappa\psi_\beta^{(J,\Gamma)}. \tag{31}$$

Applying this relation to generate the rest of the components $\beta$, with $\beta \neq \alpha$, we are able to obtain orthogonal sets of functions, as the following theorem establishes [12]

*Theorem. In case of irrep multiplicity, given the set* $\{{}_{\kappa_1}\psi_\alpha^{(J,\Gamma)}, {}_{\kappa_2}\psi_\alpha^{(J,\Gamma)}\}$ *composed by the* $\alpha$*-th component of the same irrep* $\Gamma$ *with* $\kappa_1 \neq \kappa 2$ *and the property* $\langle {}_{\kappa_1}\psi_\alpha^{(J,\Gamma)} | {}_{\kappa_2}\psi_\alpha^{(J,\Gamma)} \rangle = 0$*, the sets* $\{{}_{\kappa_1}\psi_\beta^{(J,\Gamma)}, {}_{\kappa_2}\psi_\beta^{(J,\Gamma)};\ \ \beta \neq \alpha\}$ *associated with the rest of the components and generated through Eq. (31), satisfy* $\langle {}_{\kappa_1}\psi_\beta^{(J,\Gamma)} | {}_{\kappa_2}\psi_\beta^{(J,\Gamma)} \rangle = 0$ *for* $\beta \neq \alpha$.

The approach presented is useful if we intend to obtain the rovibrational functions by means of a coupling procedure using Clebsch-Gordan coefficients, since in this case the rotational and vibrational functions must be built in a consistent way. Another possibility consists in obtaining the rovibrational functions in one step, following the eigenfunction method.

## 4. RO-VIBRATIONAL FUNCTIONS

In this section we shall consider the rovibrational functions symmetrization. In compact form, these functions may be expressed as

$$|\Psi_{rv}^{\Gamma,\gamma}\rangle = [|\Phi_{rot}^{\Gamma_1}\rangle \times |\Phi_{vib}^{\Gamma_2}\rangle]_{\gamma}^{\Gamma}, \tag{32}$$

where the symbol $\times$ stands for coupling of the irreps $\Gamma_1$ and $\Gamma_2$ to $\Gamma$. Hence, we may construct the functions $|\Phi_{rot}^{\Gamma_1,\gamma_1}\rangle$ and $|\Phi_{vib}^{\Gamma_2,\gamma_2}\rangle$ in an independent way to thereafter carry out the coupling. The rotational functions can be symmetry-projected using the approach presented in the previous sections. In the case of the vibrational functions, we may use a local or a normal scheme to construct the projected functions [15]. In any case, for the sake of consistency, both projections have to be carried out using the same explicit for of the MS group irreps.

In the vibrational space, although the normal basis has the advantage of getting rid of spurious states in a straightforward way, a local scheme is a better option, even though the molecule is intended to be described in a normal basis. The advantages of the local scheme are the following [15]: a) it allows yo easily generalize the vibrational description to any molecular system with a minimum input, b) the normal mode scheme is included as a particular case, c) the symmetry-adapted basis may be used with two possible interpretations: local harmonic or anharmonic (associated with Morse or Pöschl-Teller potentials) functions, and, finally, d) is the appropriate scheme to take advantage of the eigenfunction method of projection [15].

In the local scheme the vibrational basis of methane is given by

$$|V;\mathbf{v}\rangle \equiv |V;v_1,v_2,v_3,v_4,v_5,v_6,v_7,v_8,v_9,v_{10}\rangle, \tag{33}$$

where $v_i$ is the number of quanta for the $i$-th oscillator, and $V = V_s + V_b$ is the total number of quanta, $V = \sum_i v_i$. The first four are associated with the stretching (C-H) and the last six with the bending (HCH) degrees of freedom. We could proceed to project the local functions (33) to obtain

$$|V;\Phi_{vib}^{p,\Gamma_2,\gamma_2}\rangle = \sum_{\mathbf{v}} D_{\mathbf{v}}^{p,\Gamma_2,\gamma_2} |V;\mathbf{v}\rangle_p \tag{34}$$

where $p$ stands for the partition [15]. This set of functions, however, contains a bending spurious mode. We can build approximate vibrational normal functions $|v_0;v_1v_2v_3^{\ell_3}v_4^{\ell_4}\rangle$ [16] introducing the change of basis [15]

$$|V;v_0v_1v_2v_3^{\ell_3}v_4^{\ell_4}\rangle_{\gamma}^{\Gamma} = \sum_{p} A^{V,p}_{v_0,v_1,v_2,v_3^{\ell_3},v_4^{\ell_4}} |V;\Phi_{vib}^{p,\Gamma,\gamma}\rangle. \tag{35}$$

The $A$ coefficients in (35) are obtained diagonalizing the matrix representation of the number operators defined bellow and the vibrational angular momentum in the symmetry-adapted basis of Eq. (34) [15]. The label $v_0$ corresponds to the $A_1$ spurious bending mode. Hence the physical space is identified by setting $v_0 = 0$ in (35) [17].

Let us now turn our attention to the projection of the rovibrational space. To this end we shall consider the simplified operator

$$p = \varphi(p)v(p), \tag{36}$$

where the spin permutation is not incorporated yet. The present approach is general, but in order to illustrate the procedure followed to eliminate spurious states, we consider as an example the rovibrational space composed by rotational functions and vibrational states with one quantum in the bending modes $V = V_b = 1$.

In general our starting point is the basis

$$\{|Jkm\rangle \otimes |V;\mathbf{v}\rangle\}, \tag{37}$$

which in the considered particular case

$$\{|Jkm\rangle \otimes |1;v_5v_6v_7v_8v_9v_{10}\rangle\}. \tag{38}$$

For the sake of brevity we introduce the following notation for the vibrational subspace

$$|i\rangle = |1;0\ldots v_i\ldots 0\rangle; \quad v_i = 1 \tag{39}$$

The action of a permutation operator $p$ on the direct product

$$|Jkm\rangle \otimes |i\rangle \ ; \ \ i = 5,\ldots,10, \tag{40}$$

is given by

$$\hat{p}\{|Jkm\rangle \otimes |i\rangle\} = \sum_{k',j} \Delta^{(red)}_{k'j;ki}(p)\{|Jk'm\rangle \otimes |j\rangle\}, \tag{41}$$

where

$$\Delta^{(red)}_{k'j;ki}(p) = D^{(J)}_{kk'}[\varphi(p)]\ \Delta^{(vib)}_{ji}[v(p)]. \tag{42}$$

Therefore, the matrix representation of an element $p \in \mathscr{T}_d(M)$ is given by the direct product

$$\Delta^{(red)}(p) = \tilde{D}^{(J)}[\varphi(p)]\ \otimes \Delta^{(vib)}[v(p)]. \tag{43}$$

This result implies that the representation of the operator defined in Eq. (22) is obtained in terms of a sum of direct products. For $J = 1$ the dimension of the space (40) is 18, with reduction

$$\Delta^{(red)}(p) \quad \rightarrow \quad A_2 \oplus E \oplus 3F_1 \oplus 2F_2. \tag{44}$$

The corresponding symmetry adapted functions are provided by the eigenvectors of $\hat{C}_{II}$ in the representation of the basis (40). In (44) several multiplicities appear. In this case, however, the approach followed in §3 to distinguish the eigenvectors is not enough, because in addition to the necessity of obtaining a set of orthogonal function carrying the same irrep, the spurious states must be identified and eliminated.

In order to break the degeneracy in the $\hat{C}_{II}$ eigensystem, we propose to introduce a new set of operators to obtain a complete set of commuting operators. To this end we

define tensors constructed in terms of linear combinations of local bosonic operators $a_i^\dagger$, associated with internal coordinates. For the stretching space we have

$$T_s^{\dagger A_1} = \frac{1}{2}(a_1^\dagger + a_2^\dagger + a_3^\dagger + a_4^\dagger), \quad (45)$$

$$T_s^{\dagger F_2,A_1} = \frac{1}{2}(a_1^\dagger - a_2^\dagger - a_3^\dagger + a_4^\dagger), \quad (46)$$

$$T_s^{\dagger F_2,B_1} = -\frac{1}{\sqrt{2}}(a_2^\dagger - a_3^\dagger), \quad (47)$$

$$T_s^{\dagger F_2,B_2} = -\frac{1}{\sqrt{2}}(a_1^\dagger - a_4^\dagger), \quad (48)$$

where the coefficients are the same used to build symmetry-adapted local coordinates. In a similar way, for the bending space

$$T_b^{\dagger A_1} = \frac{1}{\sqrt{6}}(a_5^\dagger + a_6^\dagger + a_7^\dagger + a_8^\dagger + a_9^\dagger + a_{10}^\dagger), \quad (49)$$

$$T_b^{\dagger E,A_1} = \frac{1}{2\sqrt{3}}(-a_5^\dagger - a_6^\dagger + 2a_7^\dagger - a_8^\dagger - a_9^\dagger + 2a_{10}^\dagger), \quad (50)$$

$$T_b^{\dagger E,A_2} = \frac{1}{2}(a_5^\dagger - a_6^\dagger - a_8^\dagger + a_9^\dagger), \quad (51)$$

$$T_b^{\dagger F_2,A_1} = -\frac{1}{\sqrt{2}}(-a_7^\dagger + a_{10}^\dagger), \quad (52)$$

$$T_b^{\dagger F_2,B_1} = \frac{1}{\sqrt{2}}(-a_5^\dagger - a_6^\dagger + a_8^\dagger + a_9^\dagger), \quad (53)$$

$$T_b^{\dagger F_2,B_2} = \frac{1}{\sqrt{2}}(-a_5^\dagger + a_6^\dagger - a_8^\dagger + a_9^\dagger). \quad (54)$$

We now proceed to construct the number operators

$$\hat{\tilde{\nu}}_0 = [\hat{T}_b^{\dagger A_1} \times \hat{T}_b^{A_1}]^{A_1} = \frac{1}{6}(\hat{X}_b + \hat{Y}_b + \hat{Z}_b), \quad (55)$$

$$\hat{\tilde{\nu}}_1 = [\hat{T}_s^{\dagger A_1} \times \hat{T}_s^{A_1}]^{A_1} = \frac{1}{4}(\hat{X}_s + \hat{Y}_s), \quad (56)$$

$$\hat{\tilde{\nu}}_2 = \sqrt{2}][\hat{T}_b^{\dagger E} \times \hat{T}_b^{E}]^{A_1} = \frac{1}{3}(\hat{X}_b + \hat{Z}_b) - \frac{1}{6}\hat{Y}_b, \quad (57)$$

$$\hat{\tilde{\nu}}_3 = \sqrt{3}[\hat{T}_s^{\dagger F_2} \times \hat{T}_s^{F_2}]^{A_1} = \frac{1}{4}(3\hat{X}_s - \hat{Y}_s), \quad (58)$$

$$\hat{\tilde{\nu}}_4 = \sqrt{3}[\hat{T}_b^{\dagger F_2} \times \hat{T}_b^{F_2}]^{A_1} = \frac{1}{2}(\hat{X}_b - \hat{Z}_b), \quad (59)$$

where the symbol $\times$ stands for tensorial coupling, and we have introduced the definitions

$$\hat{X}_s = \sum_{i=1}^{4} a_i^\dagger a_i, \quad (60)$$

$$\hat{Y}_s = \sum_{i<j=1}^{4} (a_i^\dagger a_j + a_j^\dagger a_i), \tag{61}$$

$$\hat{X}_b = \sum_{i=5}^{10} a_i^\dagger a_i, \tag{62}$$

$$\begin{aligned}\hat{Y}_b &= (a_5^\dagger a_8 + a_5^\dagger a_6 + a_5^\dagger a_{10} + a_5^\dagger a_7 + a_8^\dagger a_{10} + a_8^\dagger a_7 + a_8^\dagger a_9 + a_6^\dagger a_{10} \\ &+ a_6^\dagger a_7 + a_6^\dagger a_9 + a_{10}^\dagger a_9 + a_7^\dagger a_9 + H.c.),\end{aligned} \tag{63}$$

$$\hat{Z}_b = (a_5^\dagger a_9 + a_6^\dagger a_8 + a_7^\dagger a_{10} + H.c.), \tag{64}$$

where H.c. stands for Hermitian conjugate.

Simultaneous diagonalization of $C_{II}$ and the operators (45-64) breaks the degeneracy in (44), as we proceed to explain. After having diagonalized the CSCO-II, the eigenvectors general form is

$$|_q\Psi_{\Gamma\gamma}^{JmV}\rangle = \sum_{k=-J}^{J} \sum_{\mathbf{v}} s_{k\mathbf{v};q\Gamma\gamma}^{JmV} |Jkm\rangle \otimes |V;\mathbf{v}\rangle, \tag{65}$$

where $\{JmV\}$ characterize the representation space and $q$ is the multiplicity index. The number operators are diagonal in $\Gamma$ and $V$ connecting only states with different multiplicity label $q$ because they are invariant and preserve the number of quanta. Hence, for a number operator $\hat{\nu}_\zeta$ we have

$$\langle_{q'}\Psi_{\Gamma\gamma}^{JmV}|\hat{\nu}_\zeta|_q\Psi_{\Gamma\gamma}^{JmV}\rangle = \sum_{k',\mathbf{v}'} \sum_{k,\mathbf{v}} s_{k'\mathbf{v}';q'\Gamma\gamma}^{JmV*} \langle Jk'm| \otimes \langle V;\mathbf{v}'|\hat{\nu}_\zeta|Jkm\rangle \otimes |V;\mathbf{v}\rangle s_{k\mathbf{v};q\Gamma\gamma}^{JmV}. \tag{66}$$

If we now use the extension of the operator $\hat{\nu}_\zeta$ given by $\hat{1} \otimes \hat{\nu}_\zeta$, the matrix defined by

$$\mathbf{M} = ||\langle_{q'}\Psi_{\Gamma\gamma}^{JmV}|\hat{\nu}_\zeta|_q\Psi_{\Gamma\gamma}^{JmV}\rangle|| \tag{67}$$

takes the form

$$\mathbf{M} = \mathbf{S}^\dagger\{\mathbf{1}^{(J)} \otimes \mathbf{C}\}\mathbf{S}, \tag{68}$$

where

$$\mathbf{S} = ||s_{k\mathbf{v};q\Gamma\gamma}^{JmV}||; \quad \mathbf{1}^{(J)} = \delta_{k'k}; \quad \mathbf{C} = ||\langle V;\mathbf{v}'|\hat{\nu}_\zeta|V;\mathbf{v}\rangle||. \tag{69}$$

The matrix $\mathbf{1}^{(J)}$ is the $(2J+1)$-dimensional identity matrix.

With the number of quanta labels (eigenvalues of the number operators isomorphic to normal quantum numbers), the spurious states identification is immediate: all states with $\nu_0 \neq 0$ should be eliminated. In this example it was not necessary to diagonalize the square of the vibrational angular momentum operators

$$\begin{aligned}\hat{\ell}_2^{A_2} &= -i\sqrt{2}[\hat{T}_b^{\dagger E} \times \hat{T}_b^E]^{A_2} \\ \hat{\ell}_3^{F_1,\gamma} &= i\sqrt{2}[\hat{T}_s^{\dagger F_2} \times \hat{T}_s^{F_2}]_\gamma^{F_1} \\ \hat{\ell}_4^{F_1,\gamma} &= i\sqrt{2}[\hat{T}_b^{\dagger F_2} \times \hat{T}_b^{F_2}]_\gamma^{F_1},\end{aligned}$$

where $\gamma = A_2, B_1, B_2$. If necessary, they may be incorporated to the set of operators to be diagonalized to distinguish degenerate states.

The rovibrational Hamiltonian commutes, in addition to the elements of $\mathscr{T}_d(M)$, with the components of the angular momentum $\mathbf{R}$, which in our case is given by [18]

$$\hat{\mathbf{R}} = \hat{\mathbf{J}} - (\hat{\ell}_s + \hat{\ell}_b), \tag{70}$$

where $l = l_s + l_b$, corresponds to the sum of the vibrational angular momentum associated with stretching and bending motions. The formula for the coupled wave functions in the case of angular momentum substraction is the same as the addition formula with the exception that the eigenfunctions $\phi_{\ell m}$ of the vector $\ell = (\ell_3 + \ell_4)$ are replaced by their complex conjugate, where $\phi^*_{\ell m} = (-1)^m \phi_{\ell -m}$. The eigenvalues of $\hat{R}^2$ are $R(R+1)$. We should thus consider also the diagonalization of the operator

$$\hat{R}^2 = \hat{J}^2 + \hat{\ell}^2 - 2\hat{\mathbf{J}} \cdot \hat{\ell}, \tag{71}$$

involving functions of the same irrep, angular momentum $J$ and total vibrational angular momentum $\ell$.

In general, we may first proceed to diagonalize the operator

$$\ell^2 = \ell_3^2 + \ell_4^2 + 2\, \ell_3 \cdot \ell_4, \tag{72}$$

and later on continue diagonalizing (71) following an approach similar to the one used to obtain (68). In this case, however, the transformation properties of $J$ are needed. Projecting the operators $\hat{J}_i$, we obtain

$$T^{(1)}_{F_1,A_2} = J_0; \quad T^{(1)}_{F_1,B_1} = \frac{1}{\sqrt{2}}(J_{+1} + iJ_{-1}); \quad T^{(1)}_{F_1,B_2} = \frac{1}{\sqrt{2}}(J_{+1} - iJ_{-1}), \tag{73}$$

which enable us to carry out the dot product with $\ell$:

$$\mathbf{J} \cdot \ell = \sqrt{3}[J \times \ell]^{A_1}, \tag{74}$$

with

$$\hat{J}_{\pm}|Jkm\rangle = \sqrt{(j \pm k)(j \mp k + 1)}|J, k \mp 1, m\rangle. \tag{75}$$

We have thus presented an approach that has the remarkable property that given the matrix elements of number, angular momentum and symmetry operations involved in the CSCO-II in the vibrational space, the symmetrization of the rovibrational functions can be obtained in a relatively simple way through the incorporation of the Wigner's $D$ matrices associated with equivalent rotations.

As mentioned before, the resulting eigenfunctions are given in terms of local functions, which may be translated into anharmonic oscillators, a feature that may be used to take into account anharmonicities from the outset.

## 5. SUMMARY AND CONCLUSIONS

In this work some relations involving the equivalent rotations associated with the permutation-inversion group have been analyzed. In particular, the matrix elements of equivalent rotations were deduced following a novel method. The anti-isomorphism between permutations and equivalent rotations has been also proved, a remarkable property taken into account in the projection of rotational and rovibrational functions.

Rotational functions are projected to irreps of the molecular symmetry group $\mathscr{T}_d(M)$ using the eigenfunction method, which is based on the diagonalization of a complete set of commuting operators (CSCO) in the representation space. The CSCO of type II, which distinguishes irreps as well as their corresponding components, was built in terms of a linear combination of Wigner's D functions. Since in this process degeneracy persists for $J > 4$, an approach to orthogonalize the degenerate functions carrying the same irrep was presented. This is a compulsory task if coupling coefficients are used to construct the rovibrational functions.

The incorporation of the vibrational degrees of freedom has also been presented. It has been shown that the projection of the rovibrational space is given in terms of direct products of Wigner's D functions and representation matrices involving the vibrational space. It has been also established a procedure to eliminate spurious sates that are intrinsic to spherical top molecules when described in terms of internal coordinates. In particular the bending space of one quanta was studied in detail in order to exemplify our approach to eliminate the spurious modes as well as to introduce the invariance under rotational angular momentum. In our method the diagonalization of the Hamiltonian may be viewed as the last step in the accomplishment of establishing the complete set of commuting operators of the system.

The attractive feature of our approach is that the projection of the rovibrational functions is relatively simple, provided that one has a code to deal with the vibrational degrees of freedom. In addition, the projected functions are given in a local scheme, a fact that allows to consider local potentials as anharmonic potentials (Morse, for instance). This fact may represent an interesting alternative to the approaches based on tensorial formalisms where a normal mode basis is used from the beginning [19]. Although this approach has been applied to methane, it should be stressed that the method is general. Besides, this procedure may help to build in a systematic manner the interactions of the molecular Hamiltonian in phenomenological fashion either in the algebraic or phase space.

## ACKNOWLEDGMENTS

This work has partially supported by CONACyT, México. This work has also been partially supported by the Spanish MEC and by European regional development funds (FEDER) under project CPAN-Ingenio (CSD2007-00042), and by the Junta de Andalucía (projects P07-FQM-02962 and P07-FQM-03014).

# REFERENCES


1. H. J. Wörner, X. Qian, and F. Merkt, *J. Chem. Phys.* **126**, 144305 (2007).
2. M. Carvajal, F.W. Willaert, J. Demaison, and I. Kleiner, *J. Mol. Spectrosc.* **246**, 158–166 (2007).
3. H. C. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963).
4. J. T. Hougen *J. Chem. Phys.* **37**, 1433 (1962).
5. J. T. Hougen *J. Chem. Phys.* **39**, 358 (1963).
6. S. Altmann, Proc. Roy. Soc. 1967 *Mol.Phys.*, **A298** 184.
7. S. Altmann, *Induced reprentations in crystals and molecules*, Academic Press, London, 1977.
8. P. R.Bunker, and P. Jensen *Molecular Symmetry and Spectroscopy*, 1998, NRC Research Press, Ottawa, Canada.
9. P. R. Bunker, and P. Jensen *Fundamentals of Molecular Symmetry*, 2005. Institute of Physics. Series in Chemical Physics.
10. D. Papousek, and M. R. Aliev, *Molecular Vibrational-Rotational Spectra*. Elsevier, Amsterdam, 1982.
11. E. P. Wigner, *Group Theory and its applications to the quantum mechanics of atomic spectra*, 1959, Academic Press, New York.
12. O. Álvarez-Bajo, R. Lemus, M. Carvajal, and F. Pérez-Bernal, *Equivalent rotations associated with the permutation inversion group revisited: symmetry projection of the rovibrational functions of methane*. *Molecular Physics*. Submitted.
13. J. Q. Chen, *Group Representation Theory for Physicists*, World Scientific, 1989.
14. M. Hammermesh *Group Theory and its applications to physical problems*, 1962, DoverPublications, Inc., New York.
15. R. Lemus, *Mol. Phys.* **101**, 2511–2528 (2003).
16. G. H. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, Krieger Publishing Company, Malabar, Florida, 1991.
17. A. Frank, R. Lemus, F. Pérez-Bernal, and R. Bijker, *J. Mol. Spectrosc.* **196**, 329–334 (1999).
18. K. T. Hecht, *J. Mol. Spectrosc.* **5**, 355–389 (1960).
19. V. Boudon, *et.al. J. Mol. Spectrosc.* **228**, 620–634 (2004).