

Article

Symmetry Adaptation of the Rotation-Vibration Theory for Linear Molecules

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Abstract: A numerical application of linear-molecule symmetry properties, described by the $D_{\infty h}$ point group, is formulated in terms of lower-order symmetry groups D_{nh} with finite n . Character tables and irreducible representation transformation matrices are presented for D_{nh} groups with arbitrary n -values. These groups can subsequently be used in the construction of symmetry-adapted ro-vibrational basis functions for solving the Schrödinger equations of linear molecules. Their implementation into the symmetrisation procedure based on a set of “reduced” vibrational eigenvalue problems with simplified Hamiltonians is used as a practical example. It is shown how the solutions of these eigenvalue problems can also be extended to include the classification of basis-set functions using ℓ , the eigenvalue (in units of \hbar) of the vibrational angular momentum operator \hat{L}_z . This facilitates the symmetry adaptation of the basis set functions in terms of the irreducible representations of D_{nh} . $^{12}\text{C}_2\text{H}_2$ is used as an example of a linear molecule of $D_{\infty h}$ point group symmetry to illustrate the symmetrisation procedure of the variational nuclear motion program Theoretical ROVibrational Energies (TROVE).

Keywords: ro-vibrational; linear molecule; point groups; molecular symmetry groups; acetylene

1. Introduction

The geometrical symmetry of a centrosymmetric linear molecule in its equilibrium geometry is described by the $D_{\infty h}$ point group (see Table 1). While the molecular vibrational states (assuming a totally symmetric singlet electronic state) span the representations of this point group of infinite order, the symmetry properties of the combined rotation-vibration states must satisfy the nuclear-statistics requirements and transform according to the irreducible representations (irreps) of the finite molecular symmetry group

$$D_{\infty h}(\text{M}) = \{E, (p), E^*, (p)^*\} \quad (1)$$

where, for the centrosymmetric linear molecule A–B–C–...–C–B–A, the permutation operation (p) is the simultaneous interchange of the two A nuclei, the two B nuclei, the two C nuclei, etc., E is the identity operation, E^* is the spatial inversion operation, which inverts the positions of all particles through the molecular centre of mass, and $(p)^* = (p)E^*$ is the permutation-inversion operation [1]. The irreps of $D_{\infty h}(\text{M})$ are given in Table 2 (see also Table A-18 of Ref. [1]). Table 2 presents several alternative notations for the irreducible representations. These alternative notations and multiple names for the same concept are perhaps not quite in agreement with time-honored principles such as Occam’s Razor, but they represent a nice example of the development of spectroscopic notation. We note already here that $D_{\infty h}(\text{M})$ is isomorphic (and, for a triatomic linear molecule A–B–A like CO_2 ,

identical) to the group customarily called $C_{2v}(M)$ (Table A-5 of Ref. [1]), the molecular symmetry group of, for example, the H_2O molecule, whose equilibrium structure is bent. The molecular symmetry (MS) groups $D_{\infty h}(M)$ and $C_{2v}(M)$ are determined by applying the principle of feasibility first introduced by Longuet-Higgins [2] (see also Ref. [1]), and one obviously obtains isomorphic MS groups for all chain molecules $A-B-C-\dots-C-B-A$, irrespective of these molecules having linear or bent equilibrium structures. Longuet-Higgins [2] (see also Ref. [1]) further showed that for a so-called rigid non-linear molecule (in this context, a rigid molecule is defined as one whose vibration can be described as oscillations around a single potential energy minimum), the MS group is isomorphic to the point group describing the geometrical symmetry at the equilibrium geometry. H_2O is a rigid non-linear molecule, whose geometrical symmetry at equilibrium is described by the C_{2v} point group which is indeed isomorphic to the MS group $C_{2v}(M)$. For the rigid linear molecule CO_2 , however, as already mentioned, the geometrical symmetry at equilibrium is described by the infinite-order point group $D_{\infty h}$ which obviously is not isomorphic to the MS group $D_{\infty h}(M) = C_{2v}(M)$ of order four.

Table 1. Common character table for the point group $D_{\infty h}$ and the Extended Molecular Symmetry (EMS) group $D_{\infty h}(EM)$ ^a.

$D_{\infty h}(EM)$:	E_0	E_ε	\dots	∞E_ε^*	$(12)\pi^*$	$(12)_{\pi+\varepsilon}^*$	\dots	$\infty(12)_\varepsilon$
	1	2	\dots	∞	1	2	\dots	∞
$D_{\infty h}$:	E	$2C_\infty^\varepsilon$	\dots	$\infty\sigma_v^{(\varepsilon/2)}$	i	$2S_\infty^{\pi+\varepsilon}$	\dots	$\infty C_2^{(\varepsilon/2)}$
Σ_g^+, A_{1g} :	1	1	\dots	1	1	1	\dots	1
Σ_u^+, A_{2u} :	1	1	\dots	1	-1	-1	\dots	-1
Σ_g^-, A_{2g} :	1	1	\dots	-1	1	1	\dots	-1
Σ_u^-, A_{1u} :	1	1	\dots	-1	-1	-1	\dots	1
Π_g, E_{1g} :	2	$2\cos\varepsilon$	\dots	0	2	$2\cos\varepsilon$	\dots	0
Π_u, E_{1u} :	2	$2\cos\varepsilon$	\dots	0	-2	$-2\cos\varepsilon$	\dots	0
Δ_g, E_{2g} :	2	$2\cos 2\varepsilon$	\dots	0	2	$2\cos 2\varepsilon$	\dots	0
Δ_u, E_{2u} :	2	$2\cos 2\varepsilon$	\dots	0	-2	$-2\cos 2\varepsilon$	\dots	0
Φ_g, E_{3g} :	2	$2\cos 3\varepsilon$	\dots	0	2	$2\cos 3\varepsilon$	\dots	0
Φ_u, E_{3u} :	2	$2\cos 3\varepsilon$	\dots	0	-2	$-2\cos 3\varepsilon$	\dots	0
\vdots	\vdots	\vdots	\dots	\vdots	\vdots	\vdots	\dots	\vdots

^a The elements of $D_{\infty h}$ are defined as follows: C_∞^ε is a rotation by ε about the molecular axis, $\sigma_v^{(\varepsilon/2)}$ is a reflection in a plane containing the molecular axis, i is the point group inversion operation, $S_\infty^{\pi+\varepsilon}$ is an improper rotation by $\pi + \varepsilon$ about the molecular axis, and $C_2^{(\varepsilon/2)}$ is a rotation by π about an axis perpendicular to the molecular axis (see also Ref. [1]). Here, $\varepsilon = 0 \cdot \dots \cdot 2\pi$. See the text for the definitions of the $D_{\infty h}(EM)$ operations.

One can argue that the MS group as defined by Longuet-Higgins [2] (see also Ref. [1]) provides the simplest symmetry description of a molecule required for understanding its energy level pattern and the properties deriving from this pattern. For rigid non-linear molecules, this symmetry description is identical to that arising from the molecular point group at equilibrium, and this explains the many successful, traditional applications of point group symmetry, especially in chemical contexts. For a rigid linear molecule, the infinite-order point group obviously provides a much more detailed symmetry description than the finite MS group. Again, one can argue that the MS group provides the symmetry operations relevant for describing the ‘fully coupled’ rovibronic (rotation-vibration-electronic) wavefunctions of a molecule and that the additional point group symmetry is redundant and unnecessary. In practice, however, the point group symmetry gives rise to useful information, in particular for the electronic, vibrational, and rotational basis functions used to express the fully coupled wavefunctions, and so it is advantageous to also employ the point group

symmetry. The particular problems associated with the symmetry description of linear molecules were described early on by Hougen [3], and by Bunker and Papoušek [4]. The latter authors introduced the so-called Extended Molecular Symmetry (EMS) Group which, for a centrosymmetric linear molecule, is isomorphic to the $D_{\infty h}$ point group. We discuss the EMS group in more detail below.

Table 2. Character table for the $D_{\infty h}(M)$ Molecular Symmetry (MS) group ^a.

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	E	(p)	E^*	$(p)^*$
Σ_g^+	$+s$	A_1	A^+	A_g	A_{1g}	1	1	1	1
Σ_u^+	$+a$	B_2	B^+	B_u	A_{2u}	1	−1	1	−1
Σ_g^-	$-a$	B_1	B^-	B_g	A_{2g}	1	−1	−1	1
Σ_u^-	$-s$	A_2	A^-	A_u	A_{1u}	1	1	−1	−1

^a Γ_1 – Γ_6 are several alternative notations for the irreducible representations of $D_{\infty h}(M)$. Γ_3 is customarily used for $C_{2v}(M)$ and Γ_5 is for $C_{2h}(M)$ (Table A-8 of Ref. [1]). g and u stand for the German gerade (even) and ungerade (odd), related to the permutation-inversion operation $(p)^*$.

The aim of the present work is to illustrate how $D_{\infty h}$ symmetry can be implemented into general nuclear-motion programs. As an example we use TROVE [5,6], a numerical variational method to solve for the ro-vibrational (rotational-vibrational) spectra of (small to medium) general polyatomic molecules, which has been used to simulate the hot spectra of various polyatomic molecules [7–19] as part of the ExoMol project [20,21], a database of *ab initio* spectra of molecules of astrophysical importance. Since calculations of this type are based on electronic properties of the molecule, primarily the potential energy and dipole moment surfaces, obtained by solving the electronic Schrödinger equation, one can claim that such calculations are also rovibronic. However, as the calculations are directly concerned with the rotation and vibration, we characterize them as ro-vibrational. The use of molecular symmetry has applications in diverse fields, including molecular spectroscopy and the construction of molecular wavefunctions, ligand-field theory, material science, and electronic structure calculations [1,22–25]. While the use of a symmetry-adapted basis set has been shown to make calculations of ro-vibrational energies far more efficient by reducing the size of the Hamiltonian matrix blocks to be diagonalized [22], it is not strictly necessary. This is in contrast to intensity calculations, which would hardly be practicable without knowledge about the symmetry of the ro-vibrational states, mainly due to the selection rules imposed by the nuclear spin statistics associated with different irreducible representations [17,22]. A symmetry-free intensity calculation would involve the actual numerical computation of a colossal number of vanishing intensities for transitions that do not satisfy the symmetry selection rules. In this context, it is also important that some energy levels have zero weights and do not exist in nature. Without knowledge of how the eigenvectors transform under the symmetry operations, it is therefore impossible—or at least immensely complicated—to describe the molecular spectrum correctly. We show how a symmetrization procedure similar to that of TROVE can be extended to enable symmetry classification, in particular of vibrational basis functions, in the $D_{\infty h}$ point group and thereby introduce the possibility of labelling these basis functions by the value of the vibrational angular momentum quantum number ℓ (see, for example, Ref. [26]). In practice, it turns out that the infinitely many elements in $D_{\infty h}$ represent a problem in numerical calculations; we circumvent this by employing, instead of $D_{\infty h}$, one of its subgroups D_{nh} with a finite value of n . We discuss below how to choose an adequate n -value.

In numerical calculations, the vibrational and rotational basis functions are initially symmetry classified before they are combined to form the ro-vibrational basis. For a linear molecule, only combinations with $k = \ell$ are physically meaningful, where k is the z-axis-projection of the rotational angular momentum quantum number and ℓ is the vibrational angular momentum quantum number (see, for example, Refs. [1,18,26–28]). With the extended symmetrization procedure of the present work, the vibrational basis functions can be labelled by their ℓ -values and it becomes straightforward to construct the meaningful combinations. In a given ro-vibrational calculation, the required extent of the rotational excitation is defined by the maximum value J_{\max} of the angular

momentum quantum number J . The maximum values of $|k|$ and $|\ell|$, K_{\max} and L_{\max} , respectively, are then $K_{\max} = L_{\max} = J_{\max}$. However, in practise the numerical calculations are computationally limited by the total number of quanta representing vibrational bending modes, which controls the maximum value for $|\ell|$, and thus $|k|$. We find that the group D_{nh} suitable for symmetry classification in numerical calculations has an n -value determined by $K_{\max} = L_{\max}$.

The TROVE symmetrization approach makes use of a set of simplified, ‘reduced’ vibrational Hamiltonians, each one describing one vibrational mode of the molecule. The symmetrization is achieved by utilizing the fact that each of these Hamiltonian operators commutes with the operations in the symmetry group of the molecule in question [22], so that eigenfunctions of a reduced vibrational Hamiltonian generate irreducible representations of the symmetry group. Consequently, we obtain a symmetry-adapted ro-vibrational basis set numerically by solving the eigenvalue problems for the reduced Hamiltonians; the vibrational basis functions are products of the eigenfunctions thus obtained. In the course of the present work, we have implemented in TROVE a general subroutine to generate automatically all transformation matrices associated with the irreducible representations of a given symmetry group D_{nh} ; this can be applied to general nuclear motion routines. The matrices are chosen to describe the transformation of vibrational basis functions that are eigenfunctions of the operator \hat{L}_z (with eigenvalues $\ell\hbar$) representing the vibrational angular momentum.

To the best of our knowledge, no general transformation matrices for $D_{\infty h}$ have been reported in the literature although the corresponding character tables have been published many times (see, for example [29]). Hegelund et al. [30] have described the transformation properties of the customary rigid-rotor/harmonic-oscillator basis functions (see, for example, Refs. [1,26,31]) for D_{nh} point groups with arbitrary $n \geq 3$ (see also Section 12.4 of Ref. [1]). The basis functions span the irreducible representations of D_{nh} and the coefficients obtained, defining the transformation properties, can straightforwardly be organized as transformation matrices. The present paper aims at providing the missing information for $D_{\infty h}$. As an illustration, we present how this symmetry information is implemented in TROVE as part of the automatic symmetry adaptation technique [22].

The paper is structured as follows. Section 2 gives an overview of the rotational and vibrational symmetry classifications and groups for a centrosymmetric linear molecule, and Section 3 presents the corresponding irreducible-representation transformation matrices and character tables. The symmetrization approach implemented in TROVE is outlined in Section 4, followed by some numerical examples in Section 5. Our conclusions are given in Section 6.

2. Rotational and Vibrational Symmetry

2.1. The Groups $D_{\infty h}(M)$, $D_{\infty h}(EM)$, and $D_{\infty h}$

Our general aim is to construct a symmetry adapted basis set for centrosymmetric linear molecules (such as, for example, CO_2 or C_2H_2) to be used in variational solutions of the ro-vibrational Schrödinger equation [22]. We employ basis functions that are products of rotational and vibrational factor functions:

$$\Phi_{J,k,v,\ell} = \Phi_{J,k}^{\text{rot}} \Phi_{v,\ell}^{\text{vib}}, \quad (2)$$

where J is the rotational angular momentum quantum number, k is the projection of the angular momentum on the molecule-fixed z axis, v is a generic vibrational quantum number and ℓ is the vibrational angular momentum quantum number. We use the physically meaningful basis functions having $k = \ell$ [1,26]. A common choice for the rotational basis functions are the rigid-symmetric-rotor functions [1,26] $\Phi_{J,k}^{\text{rot}} = |J, k, m\rangle$, from which we will omit the rotational quantum number m (the projection of the rotational angular momentum on the space-fixed z -axis) from $\Phi_{J,k}^{\text{rot}}$ since nothing depends on it in the situation of no external electric or magnetic fields, as considered here.

The complete internal wavefunction Φ_{int} (see Chapter 8 of Ref. [1]) is subject to Fermi-Dirac and Bose-Einstein statistics [1]. In the present work, we neglect the dependence of the energy on the nuclear spin, and so we take $\Phi_{\text{int}} = \Phi_{\text{elec}} \Phi_{\text{rv}} \Phi_{\text{ns}}$ where Φ_{elec} is the electronic wavefunction

(which, as mentioned above, we assume to describe a totally symmetric singlet electronic state), Φ_{rv} is the rotation-vibration wavefunction represented in the variational calculation by a linear combination of the basis functions in Equation (2), and Φ_{ns} is a nuclear-spin wavefunction. Nuclear spin statistics requires Φ_{int} to change sign under the operation (p) in Equation (1) if (p) involves an odd number of odd permutations of fermions [1], and to be invariant under (p) in all other cases. If (p) $\Phi_{int} = +\Phi_{int}(-\Phi_{int})$, Φ_{int} has Σ_g^+ or Σ_u^- (Σ_u^+ or Σ_g^-) symmetry in the group $D_{\infty h}(M)$ of Equation (1) (Table 2), depending on whether the parity p is $+1(-1)$. The parity is the character under E^* : $E^* \Phi_{int} = p \Phi_{int}$.

The nuclear-spin wavefunction Φ_{ns} does not depend on the spatial coordinates of the nuclei and so it is invariant under the “geometrical” symmetry operations of the point group $D_{\infty h}$. It is also invariant under E^* but it may have its sign changed by (p). Thus, it can have Σ_g^+ or Σ_u^+ symmetry in $D_{\infty h}(M)$ (Table 2).

We note that only the operation (p) $\in D_{\infty h}(M)$ [Equation (1)] is relevant for the discussion of Fermi-Dirac and Bose-Einstein statistics in connection with the complete internal wavefunction Φ_{int} . $E^* \in D_{\infty h}(M)$ is also a “true” symmetry operation, but the operations in the point group $D_{\infty h}$ do not occur naturally in this context. However, as mentioned above it is advantageous also to make use of the $D_{\infty h}$ symmetry, and for this purpose Bunker and Papoušek [4] defined the EMS group $D_{\infty h}(EM)$ which is isomorphic to $D_{\infty h}$. The operations in $D_{\infty h}(EM)$ can be written as (see also Section 17.4.2 of Ref. [1])

$$E(= E_0), E_\varepsilon, (p)_\varepsilon, E_\varepsilon^*, (p)_\varepsilon^* \quad (3)$$

where the angle ε satisfies $0 \leq \varepsilon < 2\pi$ and is chosen independently for the operations in Equation (3). A general element O_ε of the EMS group is defined as follows: (i) The effect of O_ε on the spatial coordinates of the nuclei and electrons in the molecule is the same as that of the element O of the MS group; (ii) The effect of O_ε on the Euler angles [1] θ and ϕ is the same as the effect of O of the MS group; (iii) The effect of O_ε on the Euler angle [1] χ is defined by Eqs. (17-101)–(17-104) of Ref. [1], so as to mimic a rotation by ε about the molecular axis.

The irreducible representations of $D_{\infty h}$ and $D_{\infty h}(EM)$ are listed in Table 1. Four of them are one-dimensional (1D): Σ_g^+ , Σ_g^- , Σ_u^+ , and Σ_u^- and an infinite number are two-dimensional (2D): $\Pi_{g/u}$, $\Delta_{g/u}$, $\Phi_{g/u}$, $\Gamma_{g/u}$, $H_{g/u}$, $I_{g/u}$, \dots . As indicated in the table, an equivalent notation is A_{1g} , A_{2g} , A_{2u} , A_{1u} for 1D irreps and E_{ng} and E_{nu} , where $n = 1, 2, \dots, \infty$ for 2D irreps, see Table 1. The rotational basis functions $\Phi_{J,k}^{rot} = |J, k\rangle$ span the irreducible representations of $D_{\infty h}(EM)$ as given in Table 3.

Table 3. The irreducible representation Γ of $D_{\infty h}(EM)$ spanned by the rotational wavefunction $|J, k\rangle$ of a linear molecule in the absence of external electric and magnetic fields. The irrep depends on k , the z -axis projection in units of \hbar , of the rotational angular momentum.

k	Γ
0	Σ_g^+ Σ_g^-
± 1	Π_g
± 2	Δ_g
± 3	Φ_g
\vdots	\vdots

For a linear centrosymmetric molecule, both the rotational and vibrational basis functions can be classified according to the irreps of the infinite-order $D_{\infty h}(EM)$. This group is defined such that the effect of the operations on the vibronic coordinates are identical to those of the point group $D_{\infty h}$. It follows from the discussion given above, however, that only the operations in the MS group $D_{\infty h}(M)$ (corresponding to $\varepsilon = 0$ for the operations in $D_{\infty h}(EM)$) are relevant for determining the requirements of Fermi-Dirac and Bose-Einstein statistics. $D_{\infty h}(EM)$ operations with $\varepsilon > 0$ are artificial (in the sense

that the complete ro-vibrational Hamiltonian does not commute with them [1]) and therefore the basis function $\Phi_{J,k,v,l}$ from Equation (2) must be invariant to them—we can view this as a “reality check” of $\Phi_{J,k,v,l}$, which turns out to be invariant to the artificial operations for $k = \ell$. It is seen from Table 1 that consequently, $\Phi_{J,k,v,l}$ can only span one of the four irreducible representations Σ_g^+ , Σ_g^- , Σ_u^+ , and Σ_u^- of the EMS group $D_{\infty h}(\text{EM})$. In the Introduction, we already gave examples of the weird and wonderful universe of spectroscopic notation. We now extend this universe by pointing out that according to the labelling scheme of Ref. [32], the four irreps Σ_g^+ , Σ_g^- , Σ_u^+ , and Σ_u^- are also denoted e ortho, e para, f ortho and f para. The correspondence depends on whether J is even or odd and is given in Table 4.

Table 4. Symmetry labels for the ro-vibrational states of a linear molecule such as $^{12}\text{C}_2\text{H}_2$. The e/f labels are defined in Ref. [33] and *ortho/para* define the nuclear-spin state [32,34]. Γ_a , Γ_b and Γ_c are alternative notations for the irreducible representations of $D_{\infty h}(\text{M})$ (see Table 2 for an expanded list).

	Γ_a	Γ_b	Γ_c	e/f	<i>Ortho/Para</i>
J odd:	Σ_g^+	A_{1g}	$+s$	f	<i>para</i>
	Σ_u^-	A_{1u}	$-s$	e	<i>para</i>
	Σ_g^-	A_{2g}	$-a$	e	<i>ortho</i>
	Σ_u^+	A_{2u}	$+a$	f	<i>ortho</i>
J even:	Σ_g^+	A_{1g}	$+s$	e	<i>para</i>
	Σ_u^-	A_{1u}	$-s$	f	<i>para</i>
	Σ_g^-	A_{2g}	$-a$	f	<i>ortho</i>
	Σ_u^+	A_{2u}	$+a$	e	<i>ortho</i>

The rotational and vibrational factor wavefunctions $\Phi_{J,k}^{\text{rot}}$ and $\Phi_{v,\ell}^{\text{vib}}$, respectively, in Equation (2) are symmetry classified in $D_{\infty h}(\text{EM})$ and there are no restrictions as to their possible symmetries. However, the fact that the product function $\Phi_{J,k,v,l}$ must transform according to a 1D irrep introduces restrictions on the possible combinations of $\Phi_{J,k}^{\text{rot}}$ and $\Phi_{v,\ell}^{\text{vib}}$, these restrictions limit the physically useful combinations to those with $k = \ell$. For example, the vibrational state ν_5 (with vibrational basis functions $\Phi_{v_5=1,\ell=\pm 1}^{\text{vib}}$ of Π_u symmetry in $D_{\infty h}(\text{EM})$) of acetylene C_2H_2 can be combined with the $\Phi_{J,k}^{\text{rot}}$ rotational wavefunctions having $(J, k) = (1, \pm 1)$ (and Π_g symmetry) to produce three ro-vibrational combinations with symmetries Σ_u^+ , Σ_u^- and Π_u in $D_{\infty h}(\text{EM})$. However, only the Σ_u^+ and Σ_u^- states can be used in practice and the Π_u state must be discarded.

2.2. The Point Groups D_{nh} and Their Correlation with $D_{\infty h}$

In numerical, variational ro-vibrational calculations, the symmetrization and symmetry classification of rotational and vibrational basis functions facilitate the actual calculations, since the matrix representation of the ro-vibrational Hamiltonian, which is diagonalized numerically in a variational calculation, becomes block diagonal according to the symmetries of the basis functions [1]. In addition, the resulting eigenfunctions are automatically symmetrized and can be labelled by the irrep that they generate. Without this, the calculations would produce redundant energies, there would be no way to determine the appropriate nuclear-spin statistics to be applied to a given state, and it would be impossible to identify the rotation-vibration transitions allowed by symmetry selection rules [1]. In particular, one could not determine the nuclear spin-statistical weight factors g_{ns} entering into intensity calculations (for $^{12}\text{C}_2\text{H}_2$ the spin-statistical weight factors are 1 for Σ_g^+ and Σ_u^- (*para*) ro-vibrational states and 3 for Σ_g^- and Σ_u^+ (*ortho*) states). There are no allowed electric dipole transitions between *ortho* and *para* states [17,32].

$D_{\infty h}$ is the geometrical symmetry group of a (horizontal, say) circular disc whose upper and lower surfaces are equivalent so that one can turn the disc upside-down without any observable change resulting from this. Similarly, D_{nh} is the geometrical symmetry group of a (horizontal, say) regular polygon with n vertices (i.e., a regular n -gon) whose upper and lower surfaces are equivalent.

That is, we can think of $D_{\infty h}$ as the limiting case of a progression of D_{nh} groups: $D_{\infty h} = \lim_{n \rightarrow \infty} D_{nh}$. As mentioned above, we aim at implementing $D_{\infty h}$ symmetry for the ro-vibrational basis functions employed in variational calculations. However, owing to the infinitely many operations of $D_{\infty h}$ and the corresponding infinitely many irreps, this is impracticable. Consequently, we resort to the strategy often used in numerical calculations and approximate ∞ by a large, finite number n or, in other words, we approximate $D_{\infty h}$ by D_{nh} with a suitably large n -value. In order to do this, we must discuss the correlation between D_{nh} and $D_{\infty h}$.

In Table 5 we list the symmetry operations in D_{nh} . It is seen that we must distinguish between n even and odd. The difference in group structure—and an accompanying difference in the labelling of the irreps—are caused by the fact that for n even, the point group inversion i (as explained in connection with Equations (4)–(7) of Ref. [1], the point group inversion operation i is *different* from the spatial inversion operation E^* and should be careful to distinguish between the two) is present in D_{nh} , whereas for n odd it is not. Since $i \in D_{\infty h}$, in some sense an even- n D_{nh} is more similar to $D_{\infty h}$ than an odd- n D_{nh} . It could be argued that only even- n D_{nh} groups should be considered in the limit of $n \rightarrow \infty$; this is the approach we have taken in the example calculations of Section 4. However, for completeness we also discuss odd- n D_{nh} groups here. The corresponding information is potentially useful for the treatment of polyatomic molecules with an MS group isomorphic to an odd- n D_{nh} group.

Table 5. Symmetry operations of the D_{nh} groups, for even and odd n . σ_h , σ_v and σ_d represent reflections in planes perpendicular to the molecular axis, containing the molecular axis, and bisecting the angle between a pair of C_2 axes, respectively. An improper rotation S_n^r is a rotation by $r(\frac{2\pi}{n})$ ($r = 1 \dots n - 2$) followed by a reflection in the plane perpendicular to the molecular axis and containing the nuclear center-of-mass. C_n^r represents rotations by $r(\frac{2\pi}{n})$, where $r = 1 \dots n - 1$. See Ref. [1] for further details on these symmetry operations.

Symmetry Operation	Number of Operations	Description
Even n :		
E	1	Identity
C_n^r	$n - 1$	Rotations about the n -fold molecular axis
C_2'/C_2''	n	n rotations by π about axes perpendicular to the molecular axis
i	1	Point group inversion
S_n^r	$n - 2$	Improper rotation (see caption)
σ_h	1	Horizontal reflection (see caption)
σ_v	$n/2$	Vertical reflection (see caption)
σ_d	$n/2$	Diagonal reflection (see caption)
Total:	$4n$	
Odd n :		
E	1	Identity
C_n^r	$n - 1$	Rotations about the n -fold molecular axis
C_2'	n	n rotations by π about axes perpendicular to the molecular axis
S_n^r	$n - 1$	Improper rotation (see caption)
σ_h	1	Horizontal reflection (see caption)
σ_v	n	Vertical reflection (see caption)
Total:	$4n$	

It will be shown (see Sections 4 and 5) that the optimum value for n for the D_{nh} group used in a TROVE calculation to approximate $D_{\infty h}$ depends on the maximum value L_{\max} of the vibrational angular momentum number ℓ required for a given calculation. We have $L_{\max} = K_{\max}$, the maximum value on the z-axis projection of the rotational angular momentum. In practical calculations we are

usually limited by L_{\max} , as determined by the maximum total value of vibrational bending quanta, rather than by K_{\max} , as determined by the maximum quanta of rotational excitation.

The general formulation of the irreducible representations of D_{nh} for arbitrary n is outlined in Section 3 below.

3. General Formulation of the Character Tables and the Irreducible Representation Transformation Matrices of the D_{nh} Groups

3.1. General Structure

Let us consider for a moment the point group C_{3v} . It contains the six operations

$$C_{3v} = \{E, C_3, C_3^2, \sigma^{(xz)}, \sigma^{(2)}, \sigma^{(3)}\}. \quad (4)$$

We have chosen a right-handed axis system such that C_3 and C_3^2 are rotations of $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$, respectively, around the z axis. The positive direction of the rotations is defined as the direction in which a right-handed screw will rotate when it advances in the positive direction of the z axis. The x and y axes are perpendicular to the z axis and chosen such that the group operation $\sigma^{(xz)}$ is a reflection in the xz plane. The operations $\sigma^{(2)}$ and $\sigma^{(3)}$ are then reflections in planes that contain the z axis and form angles of $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$, respectively, with the xz plane.

It is straightforward to verify the following relations

$$E = C_3 C_3 C_3 = \left(\sigma^{(xz)}\right)^2 \quad (5)$$

$$C_3^2 = C_3 C_3 \quad (6)$$

$$\sigma^{(2)} = C_3 C_3 \sigma^{(xz)} \quad (7)$$

$$\sigma^{(3)} = C_3 \sigma^{(xz)}. \quad (8)$$

In Equations (5)–(8) all operations in the group C_{3v} have been expressed as products of the two operations C_3 and $\sigma^{(xz)}$. These operations are called the *generating operations* for C_{3v} . It is clear that in order to symmetry classify an operator (or a function) in C_{3v} , it is sufficient to know how the operator (or function) transforms under the generating operations C_3 and $\sigma^{(xz)}$. With this knowledge, Equations (5)–(8) can be used to construct the transformation properties under all other operations. All point groups can be defined in terms of generating operations. Hegelund et al. [30] have shown that for a general group C_{nv} the generating operations can be chosen as C_n and $\sigma^{(xz)}$ by analogy with the choice for C_{3v} .

Two simple isomorphic cyclic groups, C_s and C_i , can now be introduced:

$$C_s = \{E, \sigma_h\} \quad (9)$$

$$C_i = \{E, i\} \quad (10)$$

where σ_h is a reflection in a horizontal plane (perpendicular to the n -fold axis) and i is the point group inversion. The irreps of these groups are given in Tables A-2 and A-3 of Ref. [1]. It can be shown [35] that the D_{nh} groups can be written as direct products of these simple groups:

$$D_{nh} = C_{nv} \otimes C_s \quad (n \text{ odd}) \quad (11)$$

$$D_{nh} = C_{nv} \otimes C_i \quad (n \text{ even}). \quad (12)$$

That is, an odd- n D_{nh} contains all elements $R \in C_{nv}$ together with all elements that can be written as $R\sigma_h$, and an even- n D_{nh} contains all elements $R \in C_{nv}$ together with all elements that can be written as Ri .

As explained in Section 12.4 of Ref. [1] all operations in a D_{nh} group can be obtained as products involving three generating operations which are typically denoted by R_+ , R'_+ , and R_- . The generating operations for the D_{nh} groups are summarized in Table 6. R_+ is chosen as C_n for all n , but for n odd, $(R'_+, R_-) = (\sigma_h, C_2^{(x)})$, whereas for n even, $(R'_+, R_-) = (i, C_2^{(x)})$, where $C_2^{(x)}$ is a rotation by π about the molecule-fixed x axis.

Table 6. Generating operations for the D_{nh} groups (n even and n odd).

Point Group	R_+	R'_+	R_-
D_{nh}, n odd	C_n	σ_h	$C_2^{(x)}$
D_{nh}, n even	C_n	i	$C_2^{(x)}$

Owing to the direct product structure of the D_{nh} groups (Equations (11) and (12)) it would in fact have been more logical to choose $\sigma^{(xz)}$ as a generating operation for D_{nh} instead of $C_2^{(x)}$. However, this does not seem to be the customary choice (see, for example, Hegelund et al. [30]) and we attempt here to following accepted practice as much as possible. With the relations

$$\sigma^{(xz)} = C_2^{(x)} \sigma_h \quad (n \text{ odd}), \text{ and} \quad (13)$$

$$\sigma^{(xz)} = C_2^{(x)} C_n^{n/2} i \quad (n \text{ even}). \quad (14)$$

It is straightforward to express the elements of D_{nh} in terms of the chosen generating operations. Here, $C_n^{n/2}$ is a rotation by π about the z axis.

When the transformation properties of an object under R_+ , R'_+ , and R_- are known, the transformation properties under all other operations in a D_{nh} point group can be unambiguously constructed.

3.2. Irreducible Representations

As described above, the structure of the D_{nh} point groups alternates for even and odd n -values. Consequently, so do the transformation matrices generated by the rotation-vibration basis functions (see Refs. [29,30] and Section 5.1.2 of Jensen and Hegelund [35]). The irreducible representations of D_{nh} point groups are easily constructed for arbitrary n as described in Section 5.8.2 of Ref. [1], as listed in Table 7. The irreps are expressed in terms of the characters under the generating operations R_+ , R'_+ , and R_- which are also given in Table 7 (The labelling of the irreducible representations by A , B , and E is recommended by the International Union of Pure and Applied Chemistry; see Section 2.3.3 of Ref. [36]. Why these three labels were chosen remains one of the mysteries in the weird and wonderful world of spectroscopic notation).

Comparison of Tables 1 and 7 shows that an even- n D_{nh} group has four 1D irreps called A_{1g} , A_{2g} , A_{1u} , and A_{2u} and $(n - 2)$ 2D irreps, of which half are called E_{rg} and the other half E_{ru} ($r = 1, 2, \dots, n/2 - 1$). All of these irreps correlate with irreps of $D_{\infty h}$ denoted by the same names in Table 1. In addition, the even- n D_{nh} group has another four 1D irreps called B_{1g} , B_{1u} , B_{2g} , B_{2u} associated with a sign change of the generating function under the C_n rotation (Table 7). These B -type irreps have no counterparts in $D_{\infty h}$ and so basis functions of these symmetries are useless, if not nonphysical, in the context of approximating $D_{\infty h}$ by D_{nh} . We noted above that the point group inversion operation i is contained in $D_{\infty h}$ and in even- n D_{nh} , but not in odd- n D_{nh} . Therefore the labelling of the irreps of odd- n D_{nh} differs from that used for $D_{\infty h}$ and in even- n D_{nh} . However, Table 8 gives the correspondence between the irreps of odd- n D_{nh} and those of even- n D_{nh} and $D_{\infty h}$, and so we have established the correlation between the D_{nh} and the $D_{\infty h}$ irreps for all n -values.

3.3. Transformation Matrices

In practical applications of representation theory, such as the symmetry adaptation and description of basis functions that are the subject of the present work, it is not sufficient to have the irreducible-representation characters of Table 7 only. We also need groups of matrices that constitute irreducible representations of the D_{nh} group with an arbitrary finite n -value. For the 1D irreps (of type A and B , in the notation of Tables 1 and 7) the 1×1 transformation matrix is simply equal to the character in Table 7. For the 2D irreps (of type E , in the notation of Table 1) we require 2×2 matrices whose traces are the characters in Table 7. Once a set of irreducible-representation matrices are known, symmetrized basis functions (with transformation properties defined by the irreducible-representation matrices) can in principle be determined by the projection-operator technique described in Section 6.3 of Ref. [1].

Table 7. Irreducible representations for the D_{nh} groups and their characters under the generating operations R_+ , R'_+ and R_- .

D_{nh} (n even)	E	R_+ ($=C_n$)	R'_+ ($=i$)	R_- ($=C_2^{(x)}$)
A_{1g}	1	1	1	1
A_{2g}	1	1	1	-1
B_{1g}	1	-1	1	1
B_{2g}	1	-1	1	-1
E_{rg}^a	2	$2 \cos \frac{2\pi r}{n}$	2	0
A_{1u}	1	1	-1	1
A_{2u}	1	1	-1	-1
B_{1u}	1	-1	-1	1
B_{2u}	1	-1	-1	-1
E_{ru}^a	2	$2 \cos \frac{2\pi r}{n}$	-2	0
D_{nh} (n odd)	E	R_+ ($=C_n$)	R'_+ ($=\sigma_h$)	R_- ($=C_2^{(x)}$)
A'_1	1	1	1	1
A'_2	1	1	1	-1
$E_r'^b$	2	$2 \cos \frac{2\pi r}{n}$	2	0
A''_1	1	1	-1	1
A''_2	1	1	-1	-1
$E_r''^b$	2	$2 \cos \frac{2\pi r}{n}$	-2	0

^a $r = 1, 2, \dots, \frac{n}{2} - 1$; ^b $r = 1, 2, \dots, \frac{n-1}{2}$.

Table 8. The correspondence between the g/u (gerade/ungerade) notation of the irreps of D_{nh} (even n) and the $'/'$ notation of the irreps of D_{nh} (odd n), based on K (the absolute value of the projection, in units of \hbar , onto the molecule-fixed z -axis of the rotational angular momentum).

K	Γ (even n)	Γ (odd n)	$D_{\infty h}$ (EM)
0	A_{1g}	A'_1	Σ_g^+
	A_{1u}	A_1	Σ_u^+
	A_{2g}	A'_2	Σ_g^-
	A_{2u}	A_2	Σ_u^-
>0 , even	E_{kg}	E'_k	$\Delta_g, \Gamma_g, I_g \dots$
	E_{ku}	E''_k	$\Delta_u, \Gamma_u, I_u \dots$
>0 , odd	E_{kg}	E''_k	$\Pi_g, \Phi_g, H_g \dots$
	E_{ku}	E'_k	$\Pi_u, \Phi_u, H_u \dots$

Representation matrices are not uniquely determined. Having determined one set of, say, 2×2 matrices \mathbf{M}_R that constitute an E -type irreducible representation of a D_{nh} group, for any 2×2 matrix \mathbf{V} with a non-vanishing determinant we can construct an equivalent representation consisting of the matrices $\mathbf{V}\mathbf{M}_R\mathbf{V}^{-1}$ as explained in Section 5.4.1 of Ref. [1]. We normally consider representation matrices effecting the transformation under the group operations of particular wavefunctions, coordinates or operators.

We consider here the transformation/representation matrices generated by the rotational basis functions $|J, k\rangle$. The relative phases of these functions are chosen in the customary manner as given in Section 11.2.3 of Ref. [1] so that the matrix elements of the “molecule-fixed” angular momentum ladder operators are real and positive. To determine all transformation matrices, it is sufficient initially to know the transformation properties of these functions under the generating operations R_+ , R'_+ , and R_- (see Table 7). When these are known, the transformation matrix for any group operation R is uniquely determined; one determines the product involving R_+ , R'_+ , and R_- that equals R and the desired transformation matrix for R is the analogous matrix product of the representation matrices of R_+ , R'_+ , and R_- , respectively.

The transformation properties of the $|J, k\rangle$ functions under the generating operations R_+ , R'_+ , and R_- are straightforwardly determined from the results of Hegelund et al. [30] which are reproduced in Section 12.4 of Ref. [1]. Table 9 gives the 1×1 matrices generated by $|J, 0\rangle$ and the 2×2 matrices \mathbf{M}_R generated by $(|J, K\rangle, |J, -K\rangle)$ under R_+ , R'_+ , and R_- for $K > 0$. It is advantageous also to generate the matrices $\mathbf{M}'_R = \mathbf{V}\mathbf{M}_R\mathbf{V}^{-1}$ generated by the so-called Wang functions $|J, 0, +\rangle = |J, 0\rangle$ for $K = 0$ and

$$\begin{pmatrix} |J, K, +\rangle \\ |J, K, -\rangle \end{pmatrix} = \mathbf{V} \begin{pmatrix} |J, K\rangle \\ |J, -K\rangle \end{pmatrix} \quad (15)$$

For $K > 0$, where

$$\mathbf{V} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & \frac{i}{\sqrt{2}} \end{pmatrix}. \quad (16)$$

The function $|J, 0, +\rangle$ obviously generates the same 1×1 matrices as $|J, 0\rangle$. These, along with the 2×2 matrices \mathbf{M}_R and \mathbf{M}'_R are included in Table 9.

Table 9. Transformation matrices for the D_{nh} groups generated by the rotational basis functions $|J, 0, +\rangle = |J, 0\rangle$ for $K = 0$ and $(|J, K\rangle, |J, -K\rangle)$ and $(|J, K, +\rangle, |J, K, -\rangle)$ for $K > 0$, with $\varepsilon = 2\pi/n$.

D_{nh} (n even)	E	$R_+ = C_n$	$R'_+ = i$	$R_- = C_2^{(x)}$
$ J, 0, +\rangle$	1	1	1	1
$\begin{pmatrix} J, K\rangle \\ J, -K\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{+iK\varepsilon} & 0 \\ 0 & e^{-iK\varepsilon} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\begin{pmatrix} J, K, +\rangle \\ J, K, -\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos K\varepsilon & -\sin K\varepsilon \\ \sin K\varepsilon & \cos K\varepsilon \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
D_{nh} (n odd)	E	$R_+ = C_n$	$R'_+ = \sigma_h$	$R_- = C_2^{(x)}$
$ J, 0, +\rangle$	1	1	1	$(-1)^J$
$\begin{pmatrix} J, K\rangle \\ J, -K\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{+iK\varepsilon} & 0 \\ 0 & e^{-iK\varepsilon} \end{pmatrix}$	$\begin{pmatrix} (-1)^K & 0 \\ 0 & (-1)^K \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^J \\ (-1)^J & 0 \end{pmatrix}$
$\begin{pmatrix} J, K, +\rangle \\ J, K, -\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos K\varepsilon & -\sin K\varepsilon \\ \sin K\varepsilon & \cos K\varepsilon \end{pmatrix}$	$\begin{pmatrix} (-1)^K & 0 \\ 0 & (-1)^K \end{pmatrix}$	$\begin{pmatrix} (-1)^J & 0 \\ 0 & -(-1)^J \end{pmatrix}$

We are now in a situation to generate the 2×2 transformation matrices for 2D irreps of the D_{nh} group, spanned by $(|J, K, +\rangle, |J, K, -\rangle)$ for $K > 0$. Towards this end, we use the fact that any element $R \in D_{nh}$ can be expressed as a product of the generating operations R_+ , R'_+ , and R_- , and that the transformation matrix \mathbf{M}'_R generated by R can be expressed as the analogous matrix product

of the representation matrices \mathbf{M}'_{R_+} , $\mathbf{M}'_{R'_+}$, and \mathbf{M}'_{R_-} in Table 9. In forming the matrix products, one can make use of the fact that all $\mathbf{M}'_R = \mathbf{V} \mathbf{M}_R \mathbf{V}^{-1}$, where the \mathbf{M}_R matrices are generated by $(|J, K\rangle, |J, -K\rangle)$ (Table 9) for $K > 0$ and the matrix \mathbf{V} is defined in Equation (15). For example, all D_{nh} groups contain the operations C_n^r , where $r = 1, 2, \dots, n - 1$. The operation $C_n^r = R_+^r$ thus generates the transformation matrix

$$\begin{aligned} \mathbf{M}'_{C_n^r} &= \left(\mathbf{M}'_{C_n}\right)^r = \mathbf{V} \left(\mathbf{M}_{C_n}\right)^r \mathbf{V}^{-1} \\ &= \mathbf{V} \begin{pmatrix} e^{+irK\varepsilon} & 0 \\ 0 & e^{-irK\varepsilon} \end{pmatrix} \mathbf{V}^{-1} = \begin{pmatrix} \cos(rK\varepsilon) & -\sin(rK\varepsilon) \\ \sin(rK\varepsilon) & \cos(rK\varepsilon) \end{pmatrix}, \end{aligned} \quad (17)$$

With $C_n^r = R_+^r \in C_{nv}$, $r = 1, 2, 3, \dots, n - 1$. In general, C_{nv} further contains n reflections in planes that contain the C_n axis, customarily chosen as the z axis of the molecule-fixed axis system. As discussed for C_{3v} in connection with Equations (5)–(8), we can start with one such reflection, $\sigma^{(xz)}$ say, and then obtain the other $n - 1$ reflections as $C_n^r \sigma^{(xz)}$, $r = 1, 2, 3, \dots, n - 1$. However, $\sigma^{(xz)}$ is not chosen as a generating operation for D_{nh} (see Table 7), but we can use Equations (13) and (14) to express the n reflections as

$$\sigma^{(r)} = C_n^r C_2^{(x)} \sigma_h \quad (n \text{ odd}), \text{ and} \quad (18)$$

$$\sigma^{(r)} = C_n^r C_2^{(x)} C_n^{n/2} i \quad (n \text{ even}) \quad (19)$$

where $r = 0, 1, 2, 3, \dots, n - 1$. Again, $C_n^{n/2}$ is a rotation by π about the z axis. For n odd, all n reflections are of the same type and the reflection planes all contain one vertex of the regular n -gon whose geometrical symmetry we consider. For n even, we obtain two different reflection types: $n/2$ reflections obtained for even $r = 0, 2, 4, n - 2$, and $n/2$ reflections obtained for odd $r = 1, 3, 5, n - 1$. The even- r type reflection are of the σ_v type, with the reflection plane containing two vertices of the regular n -gon, while the reflection planes of the odd- r type, said to be of σ_d type, bisect the angle between neighbouring pairs of σ_v reflection planes and contain no vertices of the n -gon (the use of the label subscripts v (for vertical) and d (for diagonal) is recommended by the International Union of Pure and Applied Chemistry; see Section 2.1.2 of Ref. [36]. Why v and d were chosen vanishes in the historical fog occupying a large part of the world of spectroscopic notation). We have now constructed all elements of C_{nv} , and we straightforwardly augment this group by $2n$ elements; Ri for n even and $R\sigma_h$ for n odd, with $R \in C_{nv}$ (Equations (11) and (12)). The $n - 1$ operations $C_n^r i (C_n^r \sigma_h)$, $r = 1, 2, 3, \dots, n - 1$ are improper rotations $S_n^{(r)}$ for n even(odd). We see from Equations (18)–(19) that the remaining operations of type $\sigma^{(r)} i$ (n even) and $\sigma^{(r)} \sigma_h$ (n odd) can be written as

$$C_2^{(r)} = \sigma^{(r)} \sigma_h = C_n^r C_2^{(x)} \quad (n \text{ odd}), \text{ and} \quad (20)$$

$$C_2^{(r)} = \sigma^{(r)} i = C_n^r C_2^{(x)} C_n^{n/2} \quad (n \text{ even}). \quad (21)$$

These operations are rotations by π about axes perpendicular to the C_n axis which are contained in the plane of the regular n -gon. For n odd, each of these C_2 axes passes through one vertex of the n -gon and all of the C_2 rotations are equivalent. For n even, there are two types of C_2 rotations, depending on whether the $\sigma^{(r)}$ operation in Equation (21) is of type σ_v or σ_d . If it is σ_v then the rotation by π is of type C_2' and the corresponding rotation axis passes through two vertices of the n -gon. If, on the other hand, it is of type σ_d then the rotation axis of the corresponding C_2'' rotation is contained in a σ_d reflection plane and bisects the angle between two neighbouring C_2' axes.

We have now explained how for an arbitrary n -value, each operation in D_{nh} can be expressed as a product of the generating operations given in Table 7. To generate a corresponding set of representation/transformation matrices, we must derive the analogous matrix products of the representation matrices in Table 9. The resulting representation matrices are given in Table 10 for n even and in Table 11 for n odd.

Table 10. Irreducible-representation transformation matrices of the D_{nh} group for n even, generated by the rotational basis functions ($|J, K, +\rangle, |J, K, -\rangle$) for $K > 0$. $\varepsilon = \frac{2\pi}{n}$, r is an integer used to identify the group operations, and $\kappa = |K + nt|$; the integer t is determined such that $1 \leq \kappa \leq n/2 - 1$.

	ε_r	r	$E_{\kappa g}$	$E_{\kappa u}$
E			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
C_n^r	$rK\varepsilon$	$1 \dots n - 1$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$
C_2'	$2rK\varepsilon$	$0 \dots \frac{n}{2} - 1$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
C_2''	$(2r + 1)K\varepsilon$	$0 \dots \frac{n}{2} - 1$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
i			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
σ_h			$(-1)^K \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$-(-1)^K \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
σ_v	$2rK\varepsilon$	$0 \dots \frac{n}{2} - 1$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$-(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
σ_d	$(2r + 1)K\varepsilon$	$0 \dots \frac{n}{2} - 1$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$-(-1)^K \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
$S_n^{(r)}$	$rK\varepsilon$	$1, 2, 3, \dots, n/2 - 1, n/2 + 1, \dots, n - 1^a$	$(-1)^K \begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$	$-(-1)^K \begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$

^a We omit $r = 0$ and $r = n/2$ from this list because $S_n^{(0)} = \sigma_h$ and $S_n^{(n/2)} = i$.

Table 11. Irreducible-representation transformation matrices of the D_{nh} group for n odd, generated by the rotational basis functions ($|J, K, +\rangle, |J, K, -\rangle$) for $K > 0$.^a $\varepsilon = \frac{2\pi}{n}$, r is an integer used to identify the group operations, and $\kappa = |K + nt|$; the integer t is determined such that $1 \leq \kappa \leq (n - 1)/2$.

	ε_r	r	E'_κ	E''_κ
E			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
C_n^r	$rK\varepsilon$	$1 \dots n - 1$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$
C_2'	$rK\varepsilon$	$0 \dots n - 1$	$(-1)^J \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$(-1)^J \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
σ_h			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
σ_v	$rK\varepsilon$	$0 \dots n - 1$	$(-1)^J \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$	$(-1)^J \begin{pmatrix} \cos \varepsilon_r & \sin \varepsilon_r \\ \sin \varepsilon_r & -\cos \varepsilon_r \end{pmatrix}$
$S_n^{(r)}$	$rK\varepsilon$	$1 \dots n - 1$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos \varepsilon_r & -\sin \varepsilon_r \\ \sin \varepsilon_r & \cos \varepsilon_r \end{pmatrix}$

^a $E'_\kappa(E''_\kappa)$ functions have even(odd) K (Table 12). The present table has been simplified accordingly.

It is seen in Table 12 that the rotational basis functions $|J, 0\rangle$ and ($|J, K, +\rangle, |J, K, -\rangle$) generate g -type (even) symmetries of D_{nh} only for n even. This is because, as explained in Section 4.5 of Ref. [1], the point group inversion i and its MS-group counterpart \hat{O}_i do not change the Euler angles, i.e., the rotational coordinates. Consequently, the rotational functions are invariant to these operations. We have added to Table 10 transformation matrices also for u -type (odd) irreps. These matrices can be thought of as generated by functions ($|J, K, \pm\rangle |v_u = 1\rangle$), where $|v_u = 1\rangle$ is the vibrational wavefunction for the fundamental level of a (probably hypothetical) vibrational mode ν_u of A_{1u} symmetry.

Table 12. Irreducible representations of the D_{nh} groups generated by the rotational basis functions $|J, 0\rangle$ for $K = 0$ and $(|J, K, +\rangle, |J, K, -\rangle)$ for $K > 0$. The integer t is determined such that $0 \leq \kappa \leq n/2$ for n even and $0 \leq \kappa \leq (n-1)/2$ for n odd, with $\kappa = |K + nt|$.

K	κ		D_{nh} (n even)	$D_{\infty h}$ (EM)
=0	0		A_{1g}	Σ_g^+
>0	0		$A_{1g} \oplus A_{2g}$	$\Sigma_g^+ \oplus \Sigma_g^+$
>0	$n/2$		$B_{1g} \oplus B_{2g}$	$\Sigma_g^+ \oplus \Sigma_g^+$
>0	$\kappa = 1, 2, \dots, n/2 - 1$		$E_{\kappa g}$	$\Pi_g, \Delta_g, \Phi_g, \Gamma_g, \dots$
K	κ		D_{nh} (n odd)	$D_{\infty h}$ (EM)
=0	0	J even	A_1'	Σ_g^+
		J odd	A_2'	Σ_g^-
>0, odd	0		$A_1'' \oplus A_2''$	$\Sigma_u^+ \oplus \Sigma_u^-$
>0, even	0		$A_1' \oplus A_2'$	$\Sigma_g^+ \oplus \Sigma_g^-$
>0, odd	$1, 2, \dots, (n-1)/2$		E_{κ}''	$\Pi_g, \Phi_g, H_g, \dots$
>0, even	$1, 2, \dots, (n-1)/2$		E_{κ}'	$\Delta_u, \Gamma_u, I_u, \dots$

If one uses Tables 10 and 11 to determine a set of representation/transformation matrices for a given 2D irrep, it is important to realize that the matrices given are generated by the $(|J, K, +\rangle, |J, K, -\rangle)$ rotational basis functions or, in the case of $E_{\kappa u}$ for n even, by the ro-vibrational functions $|J, K, \pm\rangle |v_u = 1\rangle$ defined above. One must choose J and K values so that they are commensurable with the irrep considered. The most important restriction here is that for n odd, $E_{\kappa}'(E_{\kappa}'')$ symmetry requires even(odd) K (see Table 12). For a given K value, one can make the always-physical choice of $J = K$.

4. Symmetrization Using the TROVE Approach

In this section we use the variational nuclear-motion program TROVE as an example of a practical implementation of the symmetrization of ro-vibrational basis states using D_{nh} representations. TROVE uses a general numerical symmetrization approach to build a symmetry-adapted ro-vibrational basis set [22]. The procedure will be outlined here and extended to include classification based on the vibrational angular momentum quantum number, ℓ , as necessary for dealing with linear molecules of $D_{\infty h}$ point group symmetry, using $^{12}\text{C}_2\text{H}_2$ as an example. This classification is general and can be implemented into other similarly constructed variational routines.

The use of a symmetry-adapted basis set can considerably reduce the size of the Hamiltonian matrix to be diagonalized. This is due to the useful property that the matrix elements between basis functions of different symmetry are zero by definition:

$$\langle \Psi_{\mu}^{J, \Gamma_s, \alpha} | H^{rv} | \Psi_{\mu'}^{J, \Gamma_t, \alpha'} \rangle = H_{\mu, \mu'} \delta_{s,t} \delta_{\alpha, \alpha'}, \quad (22)$$

where Γ_s and Γ_t give the irreducible representations (irreps) of D_{nh} that the basis functions, $\Psi_{\mu}^{J, \Gamma_s, \alpha}$ and $\Psi_{\mu'}^{J, \Gamma_t, \alpha'}$, transform according to, and α and α' represent their degenerate components (if present). The block diagonal structure of a Hamiltonian matrix in the D_{nh} irreducible representation is given in Figure 1; the symmetry blocks of non-vanishing matrix elements can be diagonalized separately.

TROVE utilises the concept of a sum-of-product basis set, where the primitive basis functions are

$$\Phi_{k,v,l}^J(\theta, \phi, \chi, \xi_1, \xi_2, \dots, \xi_N) = |J, k, m\rangle \phi_{v_1}(\xi_1) \phi_{v_2}(\xi_2) \dots \phi_{v_N}(\xi_N), \quad (23)$$

With 1D vibrational basis functions $\phi_{v_i}(\xi_i)$ (where ξ_i is a generalised vibrational coordinate) and rigid-rotor (spherical harmonics) rotational basis functions $|J, k, m\rangle$. The 1D vibrational basis functions are either obtained by solving the corresponding reduced 1D Schrödinger equations or are taken as the harmonic or Morse oscillators.

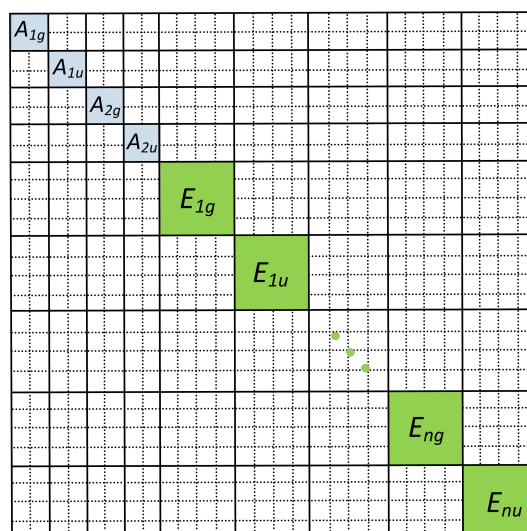


Figure 1. The block diagonal structure of a Hamiltonian matrix in the D_{nh} irreducible representation. The empty (white) cells indicate blocks of vanishing matrix elements. It should be noted that, although B -symmetries will be present for even values of n , they are not physical and do not appear as a block of matrix elements to be diagonalized.

4.1. Symmetrization of the Basis Set for $^{12}\text{C}_2\text{H}_2$ Using the $(3N - 5)$ Coordinate TROVE Implementation

As an illustration of the practical application of the finite D_{nh} group being used in place of $D_{\infty h}$, we show an example of the construction of the vibrational basis set in case of the linear molecule $^{12}\text{C}_2\text{H}_2$. We use the recent implementation of the $(3N - 5)$ coordinates approach in TROVE (see Ref. [18]) and select a set of seven vibrational coordinates used for $^{12}\text{C}_2\text{H}_2$: ΔR , Δr_1 , Δr_2 , Δx_1 , Δy_1 , Δx_2 , Δy_2 , as illustrated in Figure 2. The transformation matrices defining their symmetry properties are listed in Table 13 (with even n used in this example). These relate to the symmetry operations of Table 5, and the general irrep transformation matrices for D_{nh} of even n given in Table 10.

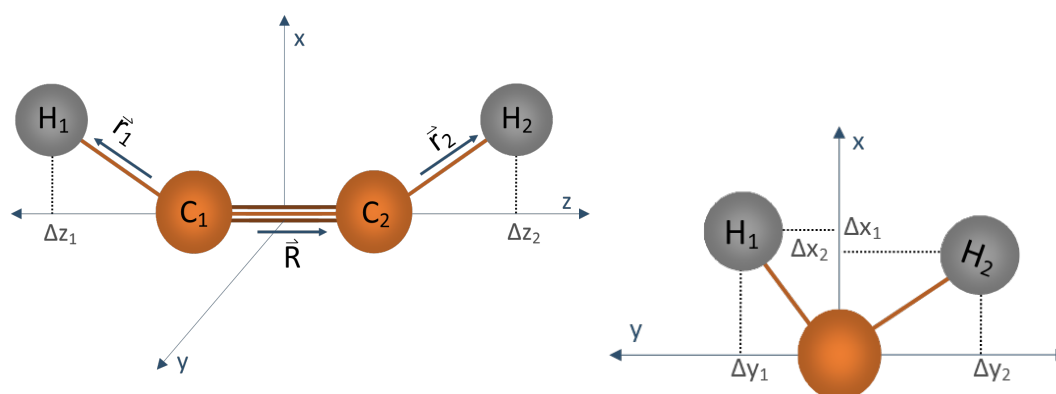


Figure 2. HCCH as described using the $(3N - 5)$ coordinates employed in TROVE. \vec{R} is the vector (of length R) pointing from the first to the second carbon atom, C_1 to C_2 , while \vec{r}_i are the two CH_i bond vectors (of lengths r_i). The Δx_1 , Δx_2 , Δy_1 and Δy_2 notation of this diagram is to reflect the Cartesian projections of the CH_i bond vectors.

For the stretching primitive basis functions, $\phi_{v_1}(\xi_1)$, $\phi_{v_2}(\xi_2)$ and $\phi_{v_3}(\xi_3)$, we use eigenfunctions of the corresponding 1D reduced stretching Hamiltonian operators $\hat{H}_i^{(1D)}$ obtained by freezing all other degrees of freedom at their equilibrium values in the $J = 0$ Hamiltonian. We use the Numerov-Cooley approach [5,37,38] to solve these eigenvalue problems. For the bending basis

functions $\phi_{v_4}(\xi_4), \dots, \phi_{v_7}(\xi_7)$, 1D harmonic oscillators are used. Here $\xi = \{ \Delta R^{\text{lin}}, \Delta r_1^{\text{lin}}, \Delta r_2^{\text{lin}}, \Delta x_1, \Delta y_1, \Delta x_2, \Delta y_2 \}$, where $R^{\text{lin}}, \Delta r_1^{\text{lin}}$, and Δr_2^{lin} are linearized (rectilinear) versions of $\Delta R, \Delta r_1, \Delta r_2$, respectively, as described in Ref. [18].

Table 13. Transformation properties based on those of Table 10 for the D_{nh} group (relating to the symmetry operations of Table 5), where n is even, for transforming the set of 7 vibrational coordinates ($\Delta R, \Delta r_1, \Delta r_2, \Delta x_1, \Delta y_1, \Delta x_2, \Delta y_2$) used in the calculations of Ref. [18] for linear molecule $^{12}\text{C}_2\text{H}_2$, as illustrated in Figure 2. The two-component vectors $\vec{\rho}_1 = (\Delta x_1, \Delta y_1)^T$ and $\vec{\rho}_2 = (\Delta x_2, \Delta y_2)^T$ transform as E_{1u} , with the transformation matrices $\mathbf{M}_R^{E_{1u}}$ from Table 10. m is an integer for the bounds given for each operation, used to form ε_m , where $\varepsilon = \frac{2\pi}{n}$ in all cases.

Irrep	ε_m	m	Transformation
E			ΔR Δr_1 Δr_2 $\vec{\rho}_1$ $\vec{\rho}_2$
C_n^m	$m\varepsilon$	$1 \dots n - 1$	ΔR Δr_1 Δr_2 $\mathbf{M}_{C_n^m}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_1$ $\mathbf{M}_{C_n^m}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_2$
C_2' C_2''	$2m\varepsilon$ $\varepsilon(2m + 1)$	$0 \dots \frac{n}{2} - 1$ $0 \dots \frac{n}{2} - 1$	ΔR Δr_2 Δr_1 $\mathbf{M}_{C_2''}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_2$ $\mathbf{M}_{C_2'}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_1$
i			ΔR Δr_2 Δr_1 $-\vec{\rho}_2$ $-\vec{\rho}_1$
σ_h			ΔR Δr_2 Δr_1 $\vec{\rho}_2$ $\vec{\rho}_1$
σ_d σ_v	$\varepsilon(2m + 1)$ $2m\varepsilon$	$0 \dots \frac{n}{2} - 1$ $0 \dots \frac{n}{2} - 1$	ΔR Δr_1 Δr_2 $\mathbf{M}_{\sigma_{d/v}}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_1$ $\mathbf{M}_{\sigma_{d/v}}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_2$
S_n^m	$m\varepsilon$	$1 \dots n - 2$	ΔR Δr_2 Δr_1 $\mathbf{M}_{S_n^m}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_2$ $\mathbf{M}_{S_n^m}^{E_{1u}}(\varepsilon_m) \cdot \vec{\rho}_1$

According to the TROVE symmetrization technique [22], the symmetry adapted vibrational basis functions are formed from linear combinations of the products of the 1D vibrational basis functions

$\phi_{v_i}(\xi_i)$ as follows, with $^{12}\text{C}_2\text{H}_2$ used as an example. For $^{12}\text{C}_2\text{H}_2$, the vibrational part of the basis set of Equation (23) is divided into three sub-sets:

$$\phi_{v_1}^{(1D)}(\xi_1) = \phi_{v_1}(\xi_1), \quad (24)$$

$$\phi_{v_2v_3}^{(2D)}(\xi_2, \xi_3) = \phi_{v_2}(\xi_2)\phi_{v_3}(\xi_3), \quad (25)$$

$$\phi_{v_4v_5v_6v_7}^{(4D)}(\xi_4, \xi_5, \xi_6, \xi_7) = \phi_{v_4}(\xi_4)\phi_{v_5}(\xi_5)\phi_{v_6}(\xi_6)\phi_{v_7}(\xi_7). \quad (26)$$

These sub-sets are then used as basis sets for the corresponding reduced Hamiltonian operators: stretching $\hat{H}^{(1D)}$ and $\hat{H}^{(2D)}$, and bending $\hat{H}^{(4D)}$. The reduced Hamiltonians $\hat{H}^{(ND)}$ ($N = 1, 2, 4$) are constructed by averaging the total vibrational Hamiltonian operator $\hat{H}^{(J=0)}$ over the other ground vibrational basis functions. For example, $\hat{H}^{(4D)}$ is given by:

$$\hat{H}^{(4D)} = \langle 0 | \langle 0, 0 | \hat{H}^{(J=0)} | 0, 0 \rangle | 0 \rangle, \quad (27)$$

where $|0\rangle = \phi_0^{(1D)}(\xi_1)$ and $|0, 0\rangle = \phi_{0,0}^{(2D)}(\xi_2, \xi_3)$.

According to the idea of the so-called complete set of commuting operators (CSCO) [22] which the TROVE symmetrization approach is based on, the eigenfunctions of the reduced operator $\hat{H}^{(ND)}$ must transform according to one of the irreps of the symmetry group of the system, since $\hat{H}^{(ND)}$ commutes with the symmetry operators of this group. Thus the symmetrization of the basis set is generated automatically by solving the appropriate eigenvalue problem, provided that the corresponding irreps have been determined. To this end, the symmetry operators of the appropriate group can be applied to the eigenfunctions and their transformation properties on a set of sampled geometries (usually 40–60 in the case of TROVE) analysed. Some states of the same energy (either with accidental or actual degeneracy) may appear as random mixtures of each other, and have to be processed simultaneously and even further reduced to irreps, if necessary (see Section 5 for an example).

Applying this procedure to stretching functions gives rise to *A*-type symmetries: e.g., for D_{nh} (even n), the eigenfunctions of $\hat{H}^{(1D)}$ span the A_{1g} irrep, while the eigenfunctions of $\hat{H}^{(2D)}$ span the A_{1g} and A_{2u} irreps.

The 4D bending basis set, based on the 1D harmonic oscillators of Equation (26), has the disadvantage of being extremely degenerate: combinations of $\phi_{v_4v_5v_6v_7}^{(4D)}$ give rise to large clusters of the same energies. According to the TROVE symmetrization approach these combinations must be processed together, which makes this process extremely slow. In order to facilitate this step we first transform the 4D bending sets (Equation (26)) to become eigenfunctions of the vibrational angular momentum operator,

$$\hat{L}_z = \sum_{\lambda, \lambda'} \xi_\lambda \zeta_{\lambda, \lambda'}^z \hat{p}_{\lambda'} \quad (28)$$

where p_λ is a vibrational momentum operator and $\zeta_{\lambda, \lambda'}^z$ are Coriolis coefficients [39] as described in Ref. [18].

TROVE is equipped to compute matrix elements of quadratic forms, therefore we use \hat{L}_z^2 instead of \hat{L}_z . Using the $\phi_{v_4v_5v_6v_7}^{(4D)}$ basis functions we find eigenfunctions of \hat{L}_z^2 by diagonalizing the matrix formed by combinations of the 4D bending basis set of Equation (26):

$$\langle \phi_{v_4v_5v_6v_7}^{(4D)} | \hat{L}_z^2 | \phi_{v'_4v'_5v'_6v'_7}^{(4D)} \rangle. \quad (29)$$

The eigenfunctions of \hat{L}_z^2 are consequently characterized by their vibrational angular momentum quantum number $\ell = |\ell| = \sqrt{\ell^2}$ and can thus be divided into independent sub-sets with different symmetry properties: the $L = 0$ sub-set must be a mixture of *A*-type functions, while the $L > 0$ sub-sets consist of the E_L -type irreps (E_{Lg} and E_{Lu}). These mixtures are then further reduced to irreps using the

TROVE symmetrization scheme outlined above, in which the reduced 4D-eigenvalue problem, using the eigenfunctions of \hat{L}_z^2 as the basis set, is solved for a 4D isotropic harmonic oscillator Hamiltonian:

$$\hat{H}^{4D} = \frac{1}{2} (\hat{p}_4^2 + \hat{p}_5^2 + \hat{p}_6^2 + \hat{p}_7^2) + \frac{1}{2} \lambda (\zeta_4^2 + \zeta_5^2 + \zeta_6^2 + \zeta_7^2), \quad (30)$$

where λ is a related to the harmonic vibrational wavenumber and \hat{p}_i are the vibrational momenta, conjugate to ζ_i . Thus we obtain eigenfunctions which can be divided into sub-sets of the same energies and values of ℓ . These sub-sets must transform independently, thereby significantly decreasing the time spent on the symmetry sampling step by breaking the symmetry space into small sets and making numerical calculations more computationally viable. Although the \hat{L}_z^2 -diagonalisation step is not strictly necessary for the general symmetrization procedure that follows it, this increase in efficiency is a big advantage.

As mentioned above, in addition to the ℓ -quantum number being advantageous in building the vibrational basis sets, it is also required for coupling the basis set functions according to the linear molecule angular momentum rule $k = \ell$ (see, for example, Refs. [18,27,28]). The maximum value for $L_{\max} = K_{\max}$ is specified as an input into the TROVE numerical routine.

As a result of applying the procedure described above, a symmetry-adapted vibrational basis set $\Phi_{v,L}^{\Gamma_{\text{vib}},\alpha}$ is generated. Here Γ_{vib} is the irrep of the basis function according to D_{nh} , and α indicates a degenerate component in the case of 2D irreps.

The symmetry-adapted rotational basis set in TROVE is represented by:

$$|J, K, \tau\rangle^{\Gamma_{\text{rot}}} = \frac{i^\sigma}{\sqrt{2}} \left[|J, K\rangle + (-1)^{J+K+\tau} |J, -K\rangle \right], \quad (31)$$

where $K = 0$ is a special case, given by:

$$|J, 0, \tau\rangle^{\Gamma_{\text{rot}}} = |J, 0\rangle. \quad (32)$$

Here $|J, k\rangle$ is a rigid rotor wavefunction, $\tau (= 0, 1)$ is a parameter used to define the parity of a state, where $\sigma = (K \bmod 3)$ for $\tau = 1$ and $\sigma = 0$ for $\tau = 0$ (see [22,40,41]). The irreps Γ_s of these functions are listed in Table 14, where τ defines their degenerate component. The symmetry properties of $|J, K, \tau\rangle^{\Gamma_{\text{rot}}}$ can be derived from those of $|J, k\rangle$ using the method described in Section 3.3.

Table 14. Symmetries of the symmetrized rotational basis set used by TROVE, Eqs. (31,32) for different combinations of J , K and τ (where $\tau (= 0, 1)$ and $K = |k|$); each 2D representation E_{Kg} state has an a and b component, represented by the different values of τ . See Table 8 for an explanation of the differing notation of Γ_{rot} for even and odd values of n .

K	τ	Γ_{rot}	
		Even n	Odd n
0	0	A_{1g}	A'_1
	1	A_{2g}	A'_2
>0, odd	0	E_{kgb}	E''_{kb}
	1	E_{kga}	E''_{ka}
>0, even	0	E_{kga}	E'_{ka}
	1	E_{kgb}	E'_{kb}

The symmetrized rotational and vibrational basis functions are then combined to form a full ro-vibrational symmetry-adapted basis set:

$$\Psi_{v,K}^{J,\Gamma_s} = \sum_{\alpha,\tau} T_{\alpha,\tau}^{(\Gamma_{\text{vib}},\Gamma_{\text{rot}})\rightarrow\Gamma_s} \Phi_{v,K}^{\Gamma_{\text{vib}},\alpha} |J, K, \tau\rangle^{\Gamma_{\text{rot}}}, \quad (33)$$

where $T_{\alpha,\tau}^{(\Gamma_{\text{vib}},\Gamma_{\text{rot}})\rightarrow\Gamma_s}$ are symmetrization coefficients with α indicating a degenerate component in the case of 2D irreps, Γ_s is a 1D irrep in $D_{\infty h}$ (see Section 3) and the $K = L$ condition for linear molecules in the $(3N - 5)$ -approach [18] was applied. Note that the symmetrized basis functions use K and L instead of k and ℓ in Equation (23).

5. Numerical Example

Some test calculations were carried out using TROVE [5] for $^{12}\text{C}_2\text{H}_2$ using a small basis set. These calculations utilise the symmetrization procedure of Section 4.

5.1. Symmetrization

Here we give an example of building a symmetry adapted basis set for the 4D bending function of Equation (26) using the TROVE symmetrization approach. In this example, the size of the primitive basis sets was controlled by the polyad number

$$P = 2v_1 + v_2 + v_3 + v_4 + v_5 + v_6 + v_7 \leq P_{\text{max}}, \quad (34)$$

With $P_{\text{max}}=2$. Here, the quantum numbers v_k for $k=1 \dots 7$ correspond to the vibrational primitive functions $\phi_{v_k}(\xi_k)$.

Using the 4D reduced Hamiltonian in Equation (27) with this small basis set we obtain the following contracted eigenfunctions (with only the first seven given here):

$$\begin{aligned} \Psi_1^{L=0} &= -0.9793|0000\rangle - 0.0095(|2000\rangle + |0200\rangle + |0020\rangle + |0002\rangle) + 0.1425(|1010\rangle + |0101\rangle), \\ \Psi_2^{L=1} &= \frac{1}{\sqrt{2}}(|1000\rangle - |0010\rangle), \\ \Psi_3^{L=1} &= \frac{1}{\sqrt{2}}(|0100\rangle - |0010\rangle), \\ \Psi_4^{L=1} &= \frac{1}{\sqrt{2}}(|1000\rangle + |0100\rangle), \\ \Psi_5^{L=1} &= \frac{1}{\sqrt{2}}(|0100\rangle + |0010\rangle), \\ \Psi_6^{L=2} &= -0.3505(|2000\rangle - |0200\rangle + |0020\rangle - |0002\rangle) + 0.4957(|1010\rangle - |0101\rangle) + \\ &\quad + 0.0651(|1100\rangle - |1001\rangle - |0110\rangle + |0011\rangle), \\ \Psi_7^{L=2} &= 0.0460(|2000\rangle - |0200\rangle + |0020\rangle - |0002\rangle) - 0.0651(|1010\rangle - |0101\rangle) + \\ &\quad + 0.4957(|1100\rangle - |1001\rangle - |0110\rangle + |0011\rangle), \end{aligned}$$

One can see that after this step some of the eigenfunctions ($\Psi_1, \Psi_2, \Psi_3, \Psi_4$ and Ψ_5) are already in the form of an irreducible representation, while Ψ_6 and Ψ_7 need to be further reduced.

In order to define the L -values, the matrix elements of \hat{L}_z are computed as in Equations (28) and (29). In this example, the sets with degenerate eigenvalues and identical L values are: $\{\Psi_1^{L=0}\}$ ($\tilde{E}_1 = 0 \text{ cm}^{-1}$), $\{\Psi_2^{L=1}, \Psi_3^{L=1}\}$ ($\tilde{E}_2 = 636.11 \text{ cm}^{-1}$), $\{\Psi_4^{L=1}, \Psi_5^{L=1}\}$ ($\tilde{E}_3 = 763.12 \text{ cm}^{-1}$), $\{\Psi_6^{L=2}, \Psi_7^{L=2}\}$ ($\tilde{E}_4 = 1215.84 \text{ cm}^{-1}$). The pair of eigenfunctions $\Psi_2^{L=1}$ and $\Psi_3^{L=1}$, for example, both have $L = 1$ and are also degenerate ($\pm 10^{-12}$) with the eigenvalue 636.11 cm^{-1} . All degenerate states are combined into the same set and are assumed to share the symmetry transformation properties, now with the additional constraint that those states in the same set must also possess the same value

of L . For our example, this gives the following symmetries and L -values: $\{\Psi_1^{L=0}\}^{A_{1g}}$, $\{\Psi_2^{L=1}, \Psi_3^{L=1}\}^{E_{1g}}$, $\{\Psi_4^{L=1}, \Psi_5^{L=1}\}^{E_{1u}}$, $\{\Psi_6^{L=2}, \Psi_7^{L=2}\}^{E_{2g}}$.

The irreducible form of the wavefunctions Ψ_6, Ψ_7 is now given by:

$$\Psi_6^{L=2} = \frac{\sqrt{2}}{4}(|2000\rangle - |0200\rangle + |0020\rangle - |0002\rangle) - \frac{1}{2}(|1010\rangle - |0101\rangle), \quad (35)$$

$$\Psi_7^{L=2} = \frac{1}{2}(|1100\rangle - |1001\rangle - |0110\rangle + |0011\rangle). \quad (36)$$

5.2. Even vs. Odd $D_{\infty n}$ Symmetries

For the example calculations using even vs. odd D_{nh} that are outlined below the primitive and contracted basis sets were controlled by the polyad number as given by Equation (34), with $P_{\max} = 8$ for the primitive basis set and reduced to 6 after contraction (see Refs. [5,18] for more details).

In place of using the infinite group $D_{\infty h}$, we use a finite group D_{nh} , with a value of n large enough to cover all required excitations of the vibrational angular momentum $L = |\ell|$ up to up L_{\max} and of the rotational quantum number K up to K_{\max} (with the constraint $L_{\max} = K_{\max}$) such that $n = 2L_{\max} + 1$ or $n = 2L_{\max} + 2$ (depending on whether n is odd or even, respectively). For example, in order to be able to cover the rotational excitation up to $K = 10$ (E_{10g} and E_{10u}), it is necessary to use at least the D_{21h} symmetry.

Even though odd and even values of n lead to different symmetry operations (see Table 5), both lead to the same resulting eigenvalues energies in the TROVE calculations, with example energies and assignments given in Table 15, on the condition that $n \geq 2L_{\max} + 1$ (odd n) or $n \geq 2L_{\max} + 2$ (even n). For a maximum value of the z -projection of the vibrational angular momentum, $L_{\max} = K_{\max} = 4$, different values of n were used for D_{nh} in the symmetrization approach described in Section 4.

Table 15. An example of some rotational, vibrational and ro-vibrational assignments (see Section 4 for the meaning of the rotational assignments and e.g., [32] for the vibrational assignments) with associated symmetries (Γ_r , Γ_v and Γ_{r-v} , respectively) from ro-vibrational calculations using TROVE of $^{12}\text{C}_2\text{H}_2$ using different (even/odd) values of n for D_{nh} . In each case $L_{\max} = 4$. The energies are identical for symmetries of higher n than those shown here, but converge towards the experimental values as the polyad number (Equation 34) is increased; a low value is used here for demonstration purposes. The symmetry assignment will remain unchanged for more accurate calculations; these will be published elsewhere.

Exp. Energy (cm^{-1}) [32]	Energy (cm^{-1}) This Work	J	K	τ	$\nu_1\nu_2\nu_3\nu_4^l\nu_5^l$	D_{12h}			D_{13h}		
						Γ_{r-v}	Γ_r	Γ_v	Γ_{r-v}	Γ_r	Γ_v
2.353286	2.356491	1	0	1	0000 ⁰ 0 ⁰	A_{2g}	A_{2g}	A_{1g}	A_2'	A_2'	A_1'
614.044355	625.810547	1	1	1	0001 ¹ 0 ⁰	A_{2g}	E_{1g}	E_{1g}	A_2'	E_1''	E_1''
1232.749162	1283.603736	1	0	1	0002 ⁰ 0 ⁰	A_{2g}	A_{2g}	A_{1g}	A_2'	A_2'	A_1'
7.059822	7.069433	2	0	0	0000 ⁰ 0 ⁰	A_{1g}	A_{1g}	A_{1g}	A_1'	A_1'	A_1''
618.745653	630.518518	2	1	1	0001 ¹ 0 ⁰	A_{1g}	E_{1g}	E_{1g}	A_1'	E_1''	E_1''
1235.874392	1276.518756	2	2	0	0002 ² 0 ⁰	A_{1g}	E_{2g}	E_{2g}	A_1'	E_2'	E_2'

If a lower value than $n = 2L_{\max} + 1$ (for odd n) or $n = 2L_{\max} + 2$ (for even n) is used, then the symmetrization procedure will lead to the wrong classification of states, resulting in, for example, the wrong nuclear statistics in intensity calculations. It should be noted that for practical numerical calculations we are limited by the maximum number of vibrational bending quanta which can be included in calculations, giving a limit on L_{\max} . We therefore refer to this as the deciding factor in what n for D_{nh} to use. However, it is also dependent on K_{\max} , the maximum value required for the z -projection of rotational angular momentum quantum number J , which would ideally be limited

by J_{\max} (working under the assumption that $K = L$ for the $(3N - 5)$ -approach to dealing with linear molecules; see [18] and, for example, [27,28]).

6. Conclusions

We have presented an outline of the method used to treat linear molecules of the $D_{\infty h}$ point group using finite D_{nh} symmetry (with arbitrary user-defined n) in numerical calculations, and given the implementation in nuclear motion routine TROVE as an example application. We have shown how a symmetrization scheme such as that used in TROVE can be extended by including the vibrational angular momentum operator \hat{L}_z into the set of commuting operators, allowing the classification of basis sets based on vibrational angular momentum quantum number, L . Character tables and irreducible representation transformation matrices for D_{nh} of general integer odd or even n have been presented, along with some numerical examples for $^{12}\text{C}_2\text{H}_2$.

The work on $^{12}\text{C}_2\text{H}_2$ presented in Ref. [18] utilises this symmetrization procedure for linear molecules, as does work extending the room temperature line list of Ref. [18] to higher temperatures, which is currently in progress.

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References

1. Bunker, P.R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Research Press: Ottawa, ON, Canada, 1998.
2. Longuet-Higgins, H. The symmetry groups of non-rigid molecules. *Mol. Phys.* **1963**, *6*, 445–460.
3. Hougen, J.T. Classification of Rotational Energy Levels. II. *J. Chem. Phys.* **1963**, *39*, 358–365.
4. Bunker, P.; Papoušek, D. The symmetry groups of linear molecules. *J. Mol. Spectrosc.* **1969**, *32*, 419–429.
5. Yurchenko, S.N.; Thiel, W.; Jensen, P. Theoretical ROVibrational Energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules. *J. Mol. Spectrosc.* **2007**, *245*, 126–140.
6. Yachmenev, A.; Yurchenko, S.N. Automatic differentiation method for numerical construction of the rotational-vibrational Hamiltonian as a power series in the curvilinear internal coordinates using the Eckart frame. *J. Chem. Phys.* **2015**, *143*, 014105.
7. Yurchenko, S.N.; Tennyson, J. ExoMol line lists IV: The rotation-vibration spectrum of methane up to 1500 K. *Mon. Not. R. Astron. Soc.* **2014**, *440*, 1649–1661.
8. Yurchenko, S.N.; Barber, R.J.; Yachmenev, A.; Thiel, W.; Jensen, P.; Tennyson, J. A variationally computed $T = 300$ K line list for NH_3 . *J. Phys. Chem. A* **2009**, *113*, 11845–11855.
9. Sousa-Silva, C.; Hesketh, N.; Yurchenko, S.N.; Hill, C.; Tennyson, J. High Temperature partition functions and thermodynamic data for ammonia and phosphine. *J. Quant. Spectrosc. Radiat. Transf.* **2014**, *142*, 66–74.
10. Sousa-Silva, C.; Al-Refaie, A.F.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists-VII. The rotation-vibration spectrum of phosphine up to 1500 K. *Mon. Not. R. Astron. Soc.* **2015**, *446*, 2337–2347.
11. Underwood, D.S.; Yurchenko, S.N.; Tennyson, J.; Jensen, P. Rotational spectrum of SO_3 and a theoretical evidence for the formation of rotational, energy level clusters in its vibrational ground state. *J. Chem. Phys.* **2014**, *140*, 244316.
12. Underwood, D.S.; Tennyson, J.; Yurchenko, S.N.; Clausen, S.; Fateev, A. ExoMol line lists XVII: A line list for hot SO_3 . *Mon. Not. R. Astron. Soc.* **2016**, *462*, 4300–4313.
13. Al-Refaie, A.F.; Yurchenko, S.N.; Yachmenev, A.; Tennyson, J. ExoMol line lists-VIII: A variationally computed line list for hot formaldehyde. *Mon. Not. R. Astron. Soc.* **2015**, *448*, 1704–1714.

14. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Tennyson, J.; Thiel, W. Accurate *ab initio* vibrational energies of methyl chloride. *J. Chem. Phys.* **2015**, *142*, 244306.
15. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Thiel, W.; Tennyson, J. ExoMol molecular line lists XXII. The rotation-vibration spectrum of silane up to 1200 K. *Mon. Not. R. Astron. Soc.* **2017**, *471*, 5025–5032.
16. Al-Refaie, A.F.; Ovsyannikov, R.I.; Polyansky, O.L.; Yurchenko, S.N.; Tennyson, J. A variationally calculated room temperature line-list for H₂O₂. *J. Mol. Spectrosc.* **2015**, *318*, 84–90.
17. Al-Refaie, A.F.; Polyansky, O.L.; I., R.; Ovsyannikov.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists XV: A hot line-list for hydrogen peroxide. *Mon. Not. R. Astron. Soc.* **2016**, *461*, 1012–1022.
18. Chubb, K.L.; Yachmenev, A.; Tennyson, J.; Yurchenko, S.N. TROVE: Treating linear molecule HCCH. *J. Chem. Phys.* **2018**, submitted.
19. Mant, B.P.; Yachmenev, A.; Tennyson, J.; Yurchenko, S.N. ExoMol molecular line lists-XXVII: Spectra of C₂H₄. *Mon. Not. R. Astron. Soc.* 2018, submitted for publication.
20. Tennyson, J.; Yurchenko, S.N. ExoMol: Molecular line lists for exoplanet and other atmospheres. *Mon. Not. R. Astron. Soc.* **2012**, *425*, 21–33.
21. Tennyson, J.; Yurchenko, S.N.; Al-Refaie, A.F.; Barton, E.J.; Chubb, K.L.; Coles, P.A.; Diamantopoulou, S.; Gorman, M.N.; Hill, C.; Lam, A.Z.; et al. The ExoMol database: molecular line lists for exoplanet and other hot atmospheres. *J. Mol. Spectrosc.* **2016**, *327*, 73–94.
22. Yurchenko, S.N.; Yachmenev, A.; Ovsyannikov, R.I. Symmetry-Adapted Ro-vibrational Basis Functions for Variational Nuclear Motion Calculations: TROVE Approach. *J. Chem. Theory Comput.* **2017**, *13*, 4368–4381.
23. Laane, J.; Ocola, E.J. Applications of Symmetry and Group Theory for the Investigation of Molecular Vibrations. *Acta Appl. Math.* **2012**, *118*, 3–24.
24. Fritzsche, S. Application of point-group symmetries in chemistry and physics: A computer-algebraic approach. *Int. J. Quantum Chem.* **2005**, *106*, 98–129.
25. Häser, M. Molecular point-group symmetry in electronic structure calculations. *J. Chem. Phys.* **1991**, *95*, 8259–8265.
26. Papoušek, D.; Aliev, M.R. *Molecular Vibrational-Rotational Spectra: Theory and Applications of High Resolution Infrared*; Studies in Physical and Theoretical Chemistry; Elsevier: Amsterdam, The Netherlands, 1982.
27. Watson, J.K.G. Vibration-rotation hamiltonian of linear molecules. *Mol. Phys.* **1970**, *19*, 465–487.
28. Włodarczyk, G. Linear Polyatomic Molecules: Introduction. In *Linear Polyatomic Molecules*; Springer: Berlin/Heidelberg, Germany, 2012; pp. 6–24.
29. Chen, C. Symmetry Adapted Analysis of Linear Molecules. *J. Chin. Chem. Soc.* **1973**, *20*, 191–202.
30. Hegelund, F.; Rasmussen, F.; Brodersen, S. The selection rules and the transition moment for rotation–vibrational transitions in axial molecules. *J. Raman Spectrosc.* **1973**, *1*, 433–453.
31. Hirano, T.; Nagashima, U.; Jensen, P. Bending wavefunctions for linear molecules. *J. Mol. Spectrosc.* **2018**, *343*, 54–61.
32. Chubb, K.L.; Joseph, M.; Franklin, J.; Choudhury, N.; Furtenbacher, T.; Császár, A.G.; Gaspard, G.; Oguoko, P.; Kelly, A.; Yurchenko, S.N.; et al. MARVEL analysis of the measured high-resolution spectra of C₂H₂. *J. Quant. Spectrosc. Radiat. Transf.* **2018**, *204*, 42–55.
33. Brown, J.M.; Hougen, J.T.; Huber, K.P.; Johns, J.W.C.; Kopp, I.; Lefebvre-Brion, H.; Merer, A.J.; Ramsay, D.A.; Rostas, J.; Zare, R.N. The labeling of parity doublet levels in linear molecules. *J. Mol. Spectrosc.* **1975**, *55*, 500–503.
34. Herman, M.; Lievin, J. Acetylene—From intensity alternation in spectra to ortho and para molecule. *J. Chem. Educ.* **1982**, *59*, 17.
35. Jensen, P.; Hegelund, F. *Lecture Notes: Molecular Rotation-Vibration Theory*; ResearchGate: Gatersleben, Germany, 2014; pp. 1–97; <https://dx.doi.org/10.13140/RG.2.2.15191.57764>.
36. Schutte, C.J.H.; Bertie, J.E.; Bunker, P.R.; Hougen, J.T.; Mills, I.M.; Watson, J.K.G.; Winnewisser, B.P. Notations and conventions in molecular spectroscopy: Part 2. Symmetry notation. *Pure Appl. Chem.* **1997**, *69*, 1641–1650.
37. Noumerov, B.V. A method of extrapolation of perturbations. *Mon. Not. R. Astron. Soc.* **1924**, *84*, 592–602.
38. Cooley, J.W. An Improved eigenvalue corrector formula for solving the Schrödinger equation for central fields. *Math. Comp.* **1961**, *15*, 363–374.
39. Sørensen, G.O. A New Approach to the Hamiltonian of Nonrigid Molecules. In *Large Amplitude Motion in Molecules II*; Topics in Current Chemistry; M. J. S. Dewar et al., Eds.; Springer: Berlin/Heidelberg, Germany, 1979; Volume 82, pp. 97–175.

40. Bunker, P.R.; Jensen, P. Spherical top molecules and the molecular symmetry group. *Mol. Phys.* **1999**, *97*, 255–264.
41. Yurchenko, S.N.; Carvajal, M.; Jensen, P.; Lin, H.; Zheng, J.J.; Thiel, W. Rotation-vibration motion of pyramidal XY_3 molecules described in the Eckart frame: Theory and application to NH_3 . *Mol. Phys.* **2005**, *103*, 359–378.



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