Article

The symmetry of linear molecules

Katy L. Chubb[1]*, Per Jensen[2], and Sergei N. Yurchenko[1]

[1] Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
[2] Physikalische und Theoretische Chemie, Fakultät für Mathematik und Naturwissenschaften, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany
* Correspondence: katy.chubb.14@ucl.ac.uk

Abstract: A numerical application of linear-molecule symmetry properties, described by the $\boldsymbol{D}_{\infty\text{h}}$ point group, is formulated in terms of lower-order symmetry groups $\boldsymbol{D}_{n\text{h}}$ with finite n. Character tables and irreducible representation transformation matrices are presented for $\boldsymbol{D}_{n\text{h}}$ groups with arbitrary n-values. These groups are subsequently used in the construction of symmetry-adapted ro-vibrational basis functions for solving the Schrödinger equations of linear molecules as part of the variational nuclear motion program TROVE. The TROVE symmetrisation procedure is based on a set of "reduced" vibrational eigenvalue problems with simplified Hamiltonians. The solutions of these eigenvalue problems have now been 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 $\boldsymbol{D}_{n\text{h}}$. $^{12}C_2H_2$ is used as an example of a linear molecule of $\boldsymbol{D}_{\infty\text{h}}$ point group symmetry to illustrate the symmetrisation procedure.

1. Introduction

The geometrical symmetry of a centrosymmetric linear molecule in its equilibrium geometry is described by the $\boldsymbol{D}_{\infty\text{h}}$ 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

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

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 spatial inversion operation [1], and $(p)^* = (p)\,E^*$. The irreps of $\boldsymbol{D}_{\infty\text{h}}(\text{M})$ are given in Table 2 (see also Table A-18 of Ref. [1]). We note already here that $\boldsymbol{D}_{\infty\text{h}}(\text{M})$ is isomorphic (and, for a triatomic linear molecule A–B–A like CO_2, identical) to the group customarily called $\boldsymbol{C}_{2\text{v}}(\text{M})$ (Table A-5 of Ref. [1]), the molecular symmetry group of, for example, the H_2O molecule, whose equilibrium structure is bent.[1] The molecular symmetry (MS) groups $\boldsymbol{D}_{\infty\text{h}}(\text{M})$ and $\boldsymbol{C}_{2\text{v}}(\text{M})$ 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–. . . –C–B–A, irrespective of

[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.

Table 1. Common character table for the point group $\boldsymbol{D}_{\infty\mathrm{h}}$ and the EMS group $\boldsymbol{D}_{\infty\mathrm{h}}$(EM).[a]

$\boldsymbol{D}_{\infty\mathrm{h}}$(EM):	E_0	E_ε	$\cdots$	$\infty E_\varepsilon{}^*$	$(12)_\pi{}^*$	$(12)^*_{\pi+\varepsilon}$	$\cdots$	$\infty(12)_\varepsilon$
	1	2	$\cdots$	∞	1	2	$\cdots$	∞
$\boldsymbol{D}_{\infty\mathrm{h}}$:	E	$2C_\infty{}^\varepsilon$	$\cdots$	$\infty\sigma_\mathrm{v}^{(\varepsilon/2)}$	i	$2S_\infty^{\pi+\varepsilon}$	$\cdots$	$\infty C_2^{(\varepsilon/2)}$
$\Sigma_\mathrm{g}{}^+$, $A_{1\mathrm{g}}$:	1	1	$\cdots$	1	1	1	$\cdots$	1
$\Sigma_\mathrm{u}{}^+$, $A_{2\mathrm{u}}$:	1	1	$\cdots$	1	-1	-1	$\cdots$	-1
$\Sigma_\mathrm{g}{}^-$, $A_{2\mathrm{g}}$:	1	1	$\cdots$	-1	1	1	$\cdots$	-1
$\Sigma_\mathrm{u}{}^-$, $A_{1\mathrm{u}}$:	1	1	$\cdots$	-1	-1	-1	$\cdots$	1
Π_g, $E_{1\mathrm{g}}$:	2	$2\cos\varepsilon$	$\cdots$	0	2	$2\cos\varepsilon$	$\cdots$	0
Π_u, $E_{1\mathrm{u}}$:	2	$2\cos\varepsilon$	$\cdots$	0	-2	$-2\cos\varepsilon$	$\cdots$	0
Δ_g, $E_{2\mathrm{g}}$:	2	$2\cos 2\varepsilon$	$\cdots$	0	2	$2\cos 2\varepsilon$	$\cdots$	0
Δ_u, $E_{2\mathrm{u}}$:	2	$2\cos 2\varepsilon$	$\cdots$	0	-2	$-2\cos 2\varepsilon$	$\cdots$	0
Φ_g, $E_{3\mathrm{g}}$:	2	$2\cos 3\varepsilon$	$\cdots$	0	2	$2\cos 3\varepsilon$	$\cdots$	0
Φ_u, $E_{3\mathrm{u}}$:	2	$2\cos 3\varepsilon$	$\cdots$	0	-2	$-2\cos 3\varepsilon$	$\cdots$	0
$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\vdots$	$\vdots$	$\cdots$	$\vdots$

[a]The elements of $\boldsymbol{D}_{\infty\mathrm{h}}$ are defined as follows: $C_\infty{}^\varepsilon$ is a rotation by ε about the molecular axis, $\sigma_\mathrm{v}^{(\varepsilon/2)}$ 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, ε=0$\cdots$2π. See the text for the definitions of the $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) operations.

these molecules having linear or bent equilibrium structures. Longuet-Higgins [2] (see also Ref. [1]) further showed that for a so-called rigid[2] non-linear molecule, 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 $\boldsymbol{C}_{2\mathrm{v}}$ point group which is indeed isomorphic to the MS group $\boldsymbol{C}_{2\mathrm{v}}$(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 $\boldsymbol{D}_{\infty\mathrm{h}}$ which obviously is not isomorphic to the MS group $\boldsymbol{D}_{\infty\mathrm{h}}(\mathrm{M}) = \boldsymbol{C}_{2\mathrm{v}}(\mathrm{M})$ of order four.

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 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 employ also 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

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2 In this context, a rigid molecule is defined as one whose vibration can be described as oscillations around a single potential energy minimum.

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Papoušek [4]. The latter authors introduced the so-called Extended Molecular Symmetry (EMS) Group which, for a centrosymmetric linear molecule, is isomorphic to the $\boldsymbol{D}_{\infty\mathrm{h}}$ point group. We discuss the EMS group in more detail below.

Table 2. Character table for the MS group $\boldsymbol{D}_{\infty\mathrm{h}}$(M).[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 $\boldsymbol{D}_{\infty\mathrm{h}}$(M). Γ_3 is customarily used for $\boldsymbol{C}_{2\mathrm{v}}$(M) and Γ_5 is for $\boldsymbol{C}_{2\mathrm{h}}$(M) (Table A-8 of Ref. [1]).

The aim of the present work is to implement the application of $\boldsymbol{D}_{\infty\mathrm{h}}$ symmetry in the nuclear motion program TROVE [5,6], a numerical variational method to solve for the ro-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]. We work towards extending the symmetrization produre of TROVE to enable symmetry classification, in particular of vibrational basis functions, in the $\boldsymbol{D}_{\infty\mathrm{h}}$ 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. [22]). In practice, it turns out that the infinitely many elements in $\boldsymbol{D}_{\infty\mathrm{h}}$ represent a problem in the numerical calculations of TROVE; we circumvent this by employing, instead of $\boldsymbol{D}_{\infty\mathrm{h}}$, one of its subgroups $\boldsymbol{D}_{n\mathrm{h}}$ with a finite value of n which is input to TROVE. We discuss below how to choose an adequate n-value.

In the TROVE 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. [1,18,22–24]). 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 TROVE 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 $K_{\mathrm{max}} = L_{\mathrm{max}} = J_{\mathrm{max}}$. 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 $\boldsymbol{D}_{n\mathrm{h}}$ suitable for symmetry classification in the TROVE calculation has an n-value determined by $K_{\mathrm{max}} = L_{\mathrm{max}}$.

The TROVE symmetrisation 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 commute with the operations in the symmetry group of the molecule in question [25], 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 $\boldsymbol{D}_{n\mathrm{h}}$. The matrices are chosen to describe the transformation of vibrational basis

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Peer-reviewed version available at Symmetry 2018, 10, 137; doi:10.3390/sym10050137

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 $\boldsymbol{D}_{\infty\text{h}}$ have been reported in the literature although the corresponding character tables have been published many times (see, for example [26]). Hegelund *et al.* [27] have described the transformation properties of the customary rigid-rotor/harmonic-oscillator basis functions (see, for example, Refs. [1,22,28]) for $\boldsymbol{D}_{n\text{h}}$ point groups with arbitrary $n \geqslant 3$ (see also Section 12.4 of Ref. [1]). The basis functions span the irreducible representations of $\boldsymbol{D}_{n\text{h}}$ 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 $\boldsymbol{D}_{\infty\text{h}}$. As an illustration, we present how this symmetry information is implemented in TROVE as part of the automatic symmetry adaptation technique [25].

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 corrsponding irreducible-representation transformation matrices and character tables. The symmetrisation 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 $\boldsymbol{D}_{\infty\text{h}}$(M), $\boldsymbol{D}_{\infty\text{h}}$(EM), and $\boldsymbol{D}_{\infty\text{h}}$

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 [25]. We employ basis functions that are products of rotational and vibrational factor functions:

$$\Phi_{J,k,v,l} = \Phi^{\text{rot}}_{J,k}\Phi^{\text{vib}}_{v,\ell}, \tag{2}$$

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 $k = \ell$ [1,22]. A common choice for the rotational basis functions are the rigid-symmetric-rotor functions [1,22] $\Phi^{\text{rot}}_{J,k} = |J,k,m\rangle$, where we omit the rotational quantum number m (the projection of the rotational angular momentum on the space-fixed z-axis) from $\phi^{\text{rot}}_{J,k}$ 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 Eq. (2), and Φ_{ns} is a nuclear-spin wavefunction. Nuclear spin statistics requires Φ_{int} to change sign under the operation (p) in Eq. (1) if (p) involves an odd number of odd permutations of fermions [1], and to be invariant under (p) in all other cases. If $(p)\,\Phi_{\text{int}} = +\Phi_{\text{int}}(-\Phi_{\text{int}})$, Φ_{int} has Σ_{g}^+ or Σ_{u}^-(Σ_{u}^+ or Σ_{g}^-) symmetry in in the group $\boldsymbol{D}_{\infty\text{h}}$(M) of Eq. (1) (Table 2), depending on whether the parity p is $+1(-1)$. The parity is the character under E^*: $E^*\,\Phi_{\text{int}} = p\,\Phi_{\text{int}}$.

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 $\boldsymbol{D}_{\infty\text{h}}$. 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 $\boldsymbol{D}_{\infty\text{h}}$(M) (Table 2).

We note that only the operation $(p) \in \boldsymbol{D}_{\infty\text{h}}$(M) [Eq. (1)] is relevant for the discussion of Fermi-Dirac and Bose-Einstein statistics in connection with the complete internal wavefunction Φ_{int}. $E^* \in \boldsymbol{D}_{\infty\text{h}}$(M) is also a "true" symmetry operation, but the operations in the point group $\boldsymbol{D}_{\infty\text{h}}$ do not occur naturally

 doi:10.20944/preprints201804.0142.v1

Peer-reviewed version available at Symmetry 2018, 10, 137; doi:10.3390/sym10050137

in this context. However, as mentioned above it is advantageous also to make use of the $\boldsymbol{D}_{\infty\mathrm{h}}$ symmetry, and for this purpose Bunker and Papoušek [4] defined the EMS group $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) which is isomorphic to $\boldsymbol{D}_{\infty\mathrm{h}}$. The operations in $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) can be written as (see also Section 17.4.2 of Ref. [1])

$$E(=E_0), E_\varepsilon, (p)_\varepsilon, E^*_\varepsilon, (p)^*_\varepsilon \tag{3}$$

where the angle ε satisfies $0 \leqslant \varepsilon < 2\pi$ and is chosen independently for the operations in Eq. (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 $\boldsymbol{D}_{\infty\mathrm{h}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) are listed in Table 1. Four of them are one-dimensional (1D): $\Sigma_\mathrm{g}{}^+$, $\Sigma_\mathrm{g}{}^-$, $\Sigma_\mathrm{u}{}^+$, and $\Sigma_\mathrm{u}{}^-$ and an infinite number are two-dimensional (2D): $\Pi_{\mathrm{g/u}}$, $\Delta_{\mathrm{g/u}}$, $\Phi_{\mathrm{g/u}}$, $\Gamma_{\mathrm{g/u}}$, $H_{\mathrm{g/u}}$, $I_{\mathrm{g/u}}$, ... As indicated in the table, an equivalent notation is $A_{1\mathrm{g}}$, $A_{2\mathrm{g}}$, $A_{2\mathrm{u}}$, $A_{1\mathrm{u}}$ for 1D irreps and $E_{n\mathrm{g}}$ and $E_{n\mathrm{u}}$, where $n = 1, 2, \ldots, \infty$ for 2D irreps, see Table 1. The rotational basis functions $\Phi^{\mathrm{rot}}_{J,k} = |J,k\rangle$ span the irreducible representations of $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) as given in Table 3.

Table 3. The irreducible representation Γ of $\boldsymbol{D}_{\infty\mathrm{h}}$(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	(J even)	$\Sigma_\mathrm{g}{}^+$
	(J odd)	$\Sigma_\mathrm{g}{}^-$
±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 $\boldsymbol{D}_{\infty\mathrm{h}}$(EM). This group is defined such that the effect of the operations on the vibronic coordinates are identical to those of the point group $\boldsymbol{D}_{\infty\mathrm{h}}$. It follows from the discussion given above, however, that only the operations in the MS group $\boldsymbol{D}_{\infty\mathrm{h}}$(M) [corresponding to $\varepsilon = 0$ for the operations in $\boldsymbol{D}_{\infty\mathrm{h}}$(EM)] are relevant for determining the requirements of Fermi-Dirac and Bose-Einstein statistics. $\boldsymbol{D}_{\infty\mathrm{h}}$(EM) operations with $\varepsilon > 0$ are artificial (in the sense that the complete rovibrational Hamiltonian does not commute with them [1]) and therefore the basis function $\Phi_{J,k,v,l}$ from Eq. (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 artifical 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 $\Sigma_\mathrm{g}{}^+$, $\Sigma_\mathrm{g}{}^-$, $\Sigma_\mathrm{u}{}^+$, and $\Sigma_\mathrm{u}{}^-$ of the EMS group $\boldsymbol{D}_{\infty\mathrm{h}}$(EM). In Footnote 1, 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. [29], the four irreps $\Sigma_\mathrm{g}{}^+$, $\Sigma_\mathrm{g}{}^-$, $\Sigma_\mathrm{u}{}^+$, and $\Sigma_\mathrm{u}{}^-$ 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.

The rotational and vibrational factor wavefunctions $\Phi^{\mathrm{rot}}_{J,k}$ and $\Phi^{\mathrm{vib}}_{v,\ell}$, respectively, in Eq. (2) are symmetry classified in $\boldsymbol{D}_{\infty\mathrm{h}}$(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 $\Phi^{\mathrm{rot}}_{J,k}$ and $\Phi^{\mathrm{vib}}_{v,\ell}$; these restrictions limit the physically useful combinations to those with $k = \ell$. For example, the vibrational state ν_5 [with vibrational basis functions $\Phi^{\mathrm{vib}}_{v_5=1,\ell=\pm1}$ of Π_u symmetry in $\boldsymbol{D}_{\infty\mathrm{h}}$(EM)] of acetylene C_2H_2 can be combined with the $\Phi^{\mathrm{rot}}_{J,k}$ rotational

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Table 4. Symmetry labels for the ro-vibrational states of a linear molecule such as $^{12}C_2H_2$. The e/f labels are defined in Ref. [30] and *ortho*/*para* define the nuclear-spin state [29,31].

				e/f	*ortho*/*para*
J odd:	$\Sigma_g{}^+$	A_{1g}	$+s$	f	*para*
	$\Sigma_u{}^-$	A_{1u}	$-s$	e	*para*
	$\Sigma_g{}^-$	A_{2g}	$-a$	e	*ortho*
	$\Sigma_u{}^+$	A_{2u}	$+a$	f	*ortho*
J even:	$\Sigma_g{}^+$	A_{1g}	$+s$	e	*para*
	$\Sigma_u{}^-$	A_{1u}	$-s$	f	*para*
	$\Sigma_g{}^-$	A_{2g}	$-a$	f	*ortho*
	$\Sigma_u{}^+$	A_{2u}	$+a$	e	*ortho*

wavefunctions having $(J,k) = (1,\pm1)$ (and Π_g symmetry) to produce three ro-vibrational combinations with symmetries $\Sigma_u{}^+$, $\Sigma_u{}^-$ and Π_u in $\boldsymbol{D}_{\infty h}$(EM). However only the $\Sigma_u{}^+$ and $\Sigma_u{}^-$ states can be used in practice and the Π_u state must be discarded.

2.2. *The point groups $\boldsymbol{D}_{nh}$ and their correlation with $\boldsymbol{D}_{\infty h}$*

In numerical, variational calculations such as those carried out with TROVE, the symmetrisation and symmetry classification of rotational and vibrational basis functions facilitate the actual calculations, since the matrix representation of the rovibrational 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 $^{12}C_2H_2$ the spin-statistical weight factors are 1 for $\Sigma_g{}^+$ and $\Sigma_u{}^-$ (*para*) rovibrational states and 3 for $\Sigma_g{}^-$ and $\Sigma_u{}^+$ (*ortho*) states]. There are no allowed electric dipole transitions between *ortho* and *para* states [17,29].

$\boldsymbol{D}_{\infty h}$ 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, $\boldsymbol{D}_{nh}$ 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 $\boldsymbol{D}_{\infty h}$ as the limiting case of a progression of $\boldsymbol{D}_{nh}$ groups: $\boldsymbol{D}_{\infty h} = \lim_{n\to\infty} \boldsymbol{D}_{nh}$. As mentioned above, we aim at implementing $\boldsymbol{D}_{\infty h}$ symmetry for the rovibrational basis functions employed in TROVE calculations. However, owing to the infinitely many operations, and the corresponding infinitely many irreps, of $\boldsymbol{D}_{\infty h}$, 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 $\boldsymbol{D}_{\infty h}$ by $\boldsymbol{D}_{nh}$ with a suitably large n-value. In order to do this, we must discuss the correlation between $\boldsymbol{D}_{nh}$ and $\boldsymbol{D}_{\infty h}$.

In Table 5 we list the symmetry operations in $\boldsymbol{D}_{nh}$. 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[3] i is present in $\boldsymbol{D}_{nh}$,

[3] As explained in connection with Eq. (4-7) of Ref. [1], the point group inversion operation i is *different* from the spatial inversion operation E^*. One should be careful to distinguish between the two.

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Table 5. Symmetry operations of the $\boldsymbol{D}_{n\text{h}}$ 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 $r(\frac{2\pi}{n})$ $(r = 1 \ldots n-2)$ 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 $r = 1 \ldots n-1$. 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:	$4n$	

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whereas for n odd it is not. Since $i \in \boldsymbol{D}_{\infty\mathrm{h}}$, in some sense an even-$n$ $\boldsymbol{D}_{n\mathrm{h}}$ is more similar to $\boldsymbol{D}_{\infty\mathrm{h}}$ than an odd-n $\boldsymbol{D}_{n\mathrm{h}}$.

It will be shown (see Sections 4 and 5) that the optimum value for n for the $\boldsymbol{D}_{n\mathrm{h}}$ group used in a TROVE calculation to approximate $\boldsymbol{D}_{\infty\mathrm{h}}$ depends on the maximum value L_{max} of the vibrational angular momentum number ℓ required for a given calculation. We have $L_{\mathrm{max}} = K_{\mathrm{max}}$, 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 $\boldsymbol{D}_{n\mathrm{h}}$ for arbitrary n is outlined in Section 3 below.

3. General formulation of the character tables and the irreducible representation transformation matrices of the $\boldsymbol{D}_{n\mathrm{h}}$ groups.

3.1. General structure.

Let us consider for a moment the point group $\boldsymbol{C}_{3\mathrm{v}}$. It contains the six operations

$$\boldsymbol{C}_{3\mathrm{v}} = \left\{E, C_3, C_3^2, \sigma^{(xz)}, \sigma^{(2)}, \sigma^{(3)}\right\}. \tag{4}$$

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

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

$$C_3^2 = C_3\, C_3 \tag{6}$$

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

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

In Eqs. (5)–(8) *all* operations in the group $\boldsymbol{C}_{3\mathrm{v}}$ have been expressed as products of the two operations C_3 and $\sigma^{(xz)}$. These operations are called the *generating operations* for $\boldsymbol{C}_{3\mathrm{v}}$. It is clear that in order to symmetry classify an operator (or a function) in $\boldsymbol{C}_{3\mathrm{v}}$, it is sufficient to know how the operator (or function) transforms under the generating operations C_3 and $\sigma^{(xz)}$. With this knowledge, Eqs. (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.* [27] have showed that for a general group $\boldsymbol{C}_{n\mathrm{v}}$ the generating operations can be chosen as C_n and $\sigma^{(xz)}$ by analogy with the choice for $\boldsymbol{C}_{3\mathrm{v}}$.

Two simple isomorphic groups, $\boldsymbol{C}_{\mathrm{s}}$ and $\boldsymbol{C}_{\mathrm{i}}$, can now be introduced:

$$\boldsymbol{C}_{\mathrm{s}} = \{E, \sigma_{\mathrm{h}}\} \tag{9}$$

$$\boldsymbol{C}_{\mathrm{i}} = \{E, i\} \tag{10}$$

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where $\sigma_{\rm h}$ 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 [32] that the $\boldsymbol{D}_{n\rm h}$ groups can be written as direct products of these simple groups:

$$\boldsymbol{D}_{n\rm h} = \boldsymbol{C}_{n\rm v} \otimes \boldsymbol{C}_{\rm s} \quad (n \text{ odd}) \tag{11}$$

$$\boldsymbol{D}_{n\rm h} = \boldsymbol{C}_{n\rm v} \otimes \boldsymbol{C}_{\rm i} \quad (n \text{ even}). \tag{12}$$

That is, an odd-n $\boldsymbol{D}_{n\rm h}$ contains all elements $R \in \boldsymbol{C}_{n\rm v}$ together with all elements that can be written as $R\,\sigma_{\rm h}$, and an even–n $\boldsymbol{D}_{n\rm h}$ contains all elements $R \in \boldsymbol{C}_{n\rm v}$ together with all elements that can be written as $R\,i$.

As explained in Section 12.4 of Ref. [1] all operations in a $\boldsymbol{D}_{n\rm h}$ group can be obtained as products involving three generating operations which are denoted by R_+, R'_+, and R_-. The generating operations for the $\boldsymbol{D}_{n\rm h}$ groups are summarised in Table 6.

Table 6. Generating operations for the $\boldsymbol{D}_{n\rm h}$ groups (n even and n odd).[a]

Point group	R_+	R'_+	R_-
$\boldsymbol{D}_{n\rm h}$, n odd	C_n	$\sigma_{\rm h}$	$C_2^{(x)}$
$\boldsymbol{D}_{n\rm h}$, n even	C_n	i	$C_2^{(x)}$

[a] R_+ is chosen as C_n for all n, but for n odd, $(R'_+, R_-) = (\sigma_{\rm h}, C_2^{(x)})$, 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.

Owing to the direct product structure of the $\boldsymbol{D}_{n\rm h}$ groups [Eq. (11)–(12)] it would in fact have been more logical to choose $\sigma^{(xz)}$ as a generating operation for $\boldsymbol{D}_{n\rm h}$ instead of $C_2^{(x)}$. However, this does not seem to be the customary choice (see, for example, Hegelund *et al.* [27]) and we attempt here to follow accepted practice as much as possible. With the relations

$$\sigma^{(xz)} = C_2^{(x)}\,\sigma_{\rm h} \quad (n \text{ odd}), \text{ and} \tag{13}$$

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

it is straightforward to express the elements of $\boldsymbol{D}_{n\rm h}$ in terms of the chosen generating operations.

When the transformation properties of an object under R_+, R'_+, and R_- are known, the transformation properties under all other operations in a $\boldsymbol{D}_{n\rm h}$ point group can be unambigously constructed.

3.2. *Irreducible representations.*

As described above, the structure of the $\boldsymbol{D}_{n\rm h}$ point groups alternates for even and odd n-values. Consequently, so do the transformation matrices generated by the rotation-vibration basis functions (see Refs. [26,27] and Section 5.1.2 of Jensen and Hegelund [32]). The irreducible representations of $\boldsymbol{D}_{n\rm h}$ 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.

Comparison of Tables 1 and 7 shows that an even-n $\boldsymbol{D}_{n\rm h}$ group has four 1D irreps called $A_{1\rm g}$, $A_{2\rm g}$, $A_{1\rm u}$, and $A_{2\rm u}$ and $n-2$ 2D irreps, of which half are called $E_{r\rm g}$ and the other half $E_{r\rm u}$ (r = 1,2, . . . , $n/2-1$). All of these irreps correlate with irreps of $\boldsymbol{D}_{\infty\rm h}$ denoted by the same names in Table 1. In addition, the even-n $\boldsymbol{D}_{n\rm h}$ group has another four 1D irreps called $B_{1\rm g}$, $B_{1\rm u}$, $B_{2\rm g}$, $B_{2\rm u}$ associated with a sign change of the generating function under the C_n rotation (Table 7). These B-type irreps have no

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Table 7. Irreducible representations for the $\boldsymbol{D}_{n\mathrm{h}}$ groups and their characters under the generating operations R_+, R'_+ and R_-.

$\boldsymbol{D}_{n\mathrm{h}}$ (n even)	E	R_+ ($= C_n$)	R'_+ ($= i$)	R_- ($= C_2^{(x)}$)
$A_{1\mathrm{g}}$	1	1	1	1
$A_{2\mathrm{g}}$	1	1	1	−1
$B_{1\mathrm{g}}$	1	−1	1	1
$B_{2\mathrm{g}}$	1	−1	1	−1
$E_{r\mathrm{g}}$ [a]	2	$2\cos\frac{2\pi r}{n}$	2	0
$A_{1\mathrm{u}}$	1	1	−1	1
$A_{2\mathrm{u}}$	1	1	−1	−1
$B_{1\mathrm{u}}$	1	−1	−1	1
$B_{2\mathrm{u}}$	1	−1	−1	−1
$E_{r\mathrm{u}}$ [a]	2	$2\cos\frac{2\pi r}{n}$	−2	0
$\boldsymbol{D}_{n\mathrm{h}}$ (n odd)	E	R_+ ($= C_n$)	R'_+ ($= \sigma_\mathrm{h}$)	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] $r = 1, 2, \ldots, \frac{n}{2} - 1$. [b] $r = 1, 2, \ldots, \frac{n-1}{2}$.

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counterparts in $\boldsymbol{D}_{\infty\mathrm{h}}$ and so basis functions of these symmetries are useless, if not unphysical, in the context of approximating $\boldsymbol{D}_{\infty\mathrm{h}}$ by $\boldsymbol{D}_{n\mathrm{h}}$. We noted above that the point group inversion operation i is contained in $\boldsymbol{D}_{\infty\mathrm{h}}$ and in even-n $\boldsymbol{D}_{n\mathrm{h}}$, but not in odd-$n$ $\boldsymbol{D}_{n\mathrm{h}}$. Therefore the labelling of the irreps of odd-n $\boldsymbol{D}_{n\mathrm{h}}$ differs from that used for $\boldsymbol{D}_{\infty\mathrm{h}}$ and in even-n $\boldsymbol{D}_{n\mathrm{h}}$. However, Table 8 gives the correspondence between the irreps of odd-n $\boldsymbol{D}_{n\mathrm{h}}$ and those of even-n $\boldsymbol{D}_{n\mathrm{h}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$, and so we have established the correlation between the $\boldsymbol{D}_{n\mathrm{h}}$ and the $\boldsymbol{D}_{\infty\mathrm{h}}$ irreps for all n-values.

Table 8. The correspondence between the g/u (gerade/ungerade) notation of the irreps of $\boldsymbol{D}_{n\mathrm{h}}$ (even n) and the $'/''$ notation of the irreps of $\boldsymbol{D}_{n\mathrm{h}}$ (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)	$\boldsymbol{D}_{\infty\mathrm{h}}$(EM)
0	$A_{1\mathrm{g}}$	A_1'	$\Sigma_\mathrm{g}{}^+$
	$A_{1\mathrm{u}}$	A_1''	$\Sigma_\mathrm{u}{}^+$
	$A_{2\mathrm{g}}$	A_2'	$\Sigma_\mathrm{g}{}^-$
	$A_{2\mathrm{u}}$	A_2''	$\Sigma_\mathrm{u}{}^-$
>0, even	$E_{k\mathrm{g}}$	E_k'	$\Delta_\mathrm{g}, \Gamma_\mathrm{g}, I_\mathrm{g} \cdots$
	$E_{k\mathrm{u}}$	E_k''	$\Delta_\mathrm{u}, \Gamma_\mathrm{u}, I_\mathrm{u} \cdots$
>0, odd	$E_{k\mathrm{g}}$	E_k''	$\Pi_\mathrm{g}, \Phi_\mathrm{g}, H_\mathrm{g} \cdots$
	$E_{k\mathrm{u}}$	E_k'	$\Pi_\mathrm{u}, \Phi_\mathrm{u}, H_\mathrm{u} \cdots$

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 need also groups of matrices that constitute irreducible representations of the $\boldsymbol{D}_{n\mathrm{h}}$ group with an arbitrary finite n-value. For the 1D irreps (of type A and B) the 1×1 transformation matrix is simply equal to the character in Table 7. For the 2D irreps (of type E) 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].

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 $\boldsymbol{D}_{n\mathrm{h}}$ 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.

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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.* [27] 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

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

for $K>0$, where

$$\mathbf{V} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{\mathrm{i}}{\sqrt{2}} & \frac{\mathrm{i}}{\sqrt{2}} \end{pmatrix}. \tag{16}$$

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 $\boldsymbol{D}_{n\mathrm{h}}$ 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 $\varepsilon = 2\pi/n$.

$\boldsymbol{D}_{n\mathrm{h}}$ (n even)	E	$R_+ = C_n$	$R'_+ = i$	$R_- = C_2^{(x)}$
$\|J,0,+\rangle$	1	1	1	1
$\begin{pmatrix} \|J,K\rangle \\ \|J,-K\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \mathrm{e}^{+\mathrm{i}K\varepsilon} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}K\varepsilon} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\begin{pmatrix} \|J,K,+\rangle \\ \|J,K,-\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos K\varepsilon & -\sin K\varepsilon \\ \sin K\varepsilon & \cos K\varepsilon \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\boldsymbol{D}_{n\mathrm{h}}$ (n odd)	E	$R_+ = C_n$	$R'_+ = \sigma_\mathrm{h}$	$R_- = C_2^{(x)}$
$\|J,0,+\rangle$	1	1	1	$(-1)^J$
$\begin{pmatrix} \|J,K\rangle \\ \|J,-K\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \mathrm{e}^{+\mathrm{i}K\varepsilon} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}K\varepsilon} \end{pmatrix}$	$\begin{pmatrix} (-1)^K & 0 \\ 0 & (-1)^K \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^J \\ (-1)^J & 0 \end{pmatrix}$
$\begin{pmatrix} \|J,K,+\rangle \\ \|J,K,-\rangle \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \cos K\varepsilon & -\sin K\varepsilon \\ \sin K\varepsilon & \cos K\varepsilon \end{pmatrix}$	$\begin{pmatrix} (-1)^K & 0 \\ 0 & (-1)^K \end{pmatrix}$	$\begin{pmatrix} (-1)^J & 0 \\ 0 & -(-1)^J \end{pmatrix}$

We are now in a situation to generate the 2×2 transformation matrices for 2D irreps of the $\boldsymbol{D}_{n\mathrm{h}}$ group, spanned by $(|J,K,+\rangle, |J,K,-\rangle)$ for $K>0$. Towards this end, we use that any element $R \in \boldsymbol{D}_{n\mathrm{h}}$ 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 Eq. (15). For example, all $\boldsymbol{D}_{n\mathrm{h}}$ groups contain the operations C_n^r, where $r = 1, 2, \ldots, n-1$. The operation $C_n^r = R_+^r$ thus generates the transformation matrix

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

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with $C_n^r = R_+^r \in \boldsymbol{C}_{n\mathrm{v}}$, $r = 1, 2, 3, \ldots, n-1$. In general, $\boldsymbol{C}_{n\mathrm{v}}$ 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 $\boldsymbol{C}_{3\mathrm{v}}$ in connection with Eqs. (5)–(8), we can start with one such reflection, $\sigma^{(xz)}$ say, and then obtain the other $n-1$ reflections as $C_n^r\,\sigma^{(xz)}$, $r = 1, 2, 3, \ldots, n-1$. However, $\sigma^{(xz)}$ is not chosen as a generating operation for $\boldsymbol{D}_{n\mathrm{h}}$ (see Table 7), but we can use Eqs. (13) and (14) to express the n reflections as

$$\sigma^{(r)} = C_n^r\, C_2^{(x)}\, \sigma_\mathrm{h} \;\; (n \;\text{odd}), \;\; \text{and} \tag{18}$$

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

$r = 0, 1, 2, 3, \ldots, n-1$. Here, $C_n^{n/2}$ 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 reflection bisect the angle between neighbouring pairs of σ_v reflection planes and contain no vertices of the n-gon. We have now constructed all elements of $\boldsymbol{C}_{n\mathrm{v}}$, and we straightforwardly augment this group by $2n$ elements; $R\,i$ for n even and $R\,\sigma_\mathrm{h}$ for n odd, with $R \in \boldsymbol{C}_{n\mathrm{v}}$ (Eqs. (11) and (12)). The $n-1$ operations $C_n^r\, i (C_n^r\, \sigma_\mathrm{h})$, $r = 1, 2, 3, \ldots, n-1$ are improper rotations $S_n^{(r)}$ for n even(odd). We see from Eqs. (18)–(19) that the remaining operations of type $\sigma^{(r)}\, i$ (n even) and $\sigma^{(r)}\, \sigma_\mathrm{h}$ (n odd) can be written as

$$C_2^{(r)} = \sigma^{(r)}\, \sigma_\mathrm{h} = C_n^r\, C_2^{(x)} \;\; (n \;\text{odd}), \;\; \text{and} \tag{20}$$

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

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 Eq. (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 $\boldsymbol{D}_{n\mathrm{h}}$ 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.

It is seen in Table 12 that the rotational basis functions $|J, 0\rangle$ and $(|J, K, +\rangle, |J, K, -\rangle)$ generate g-type (gerade) symmetries of $\boldsymbol{D}_{n\mathrm{h}}$ 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 irreps. These matrices can be thought of as generated by functions $(|J, K, \pm\rangle\, |v_\mathrm{u} = 1\rangle$, where $|v_\mathrm{u} = 1\rangle$ is the vibrational wavefunction for the fundamental level of a (probably hypothetical) vibrational mode ν_u of $A_{1\mathrm{u}}$ symmetry.

If one uses Tables 10 and Table 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 $E_{\kappa\mathrm{u}}$ for n even, by the ro-vibrational functions $|J, K, \pm\rangle\, |v_\mathrm{u} = 1\rangle$ 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 $J = K$.

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Table 10. Irreducible-representation transformation matrices of the $\boldsymbol{D}_{n\mathrm{h}}$ 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 $1 \leqslant \kappa \leqslant n/2-1$.

	ε_r	r	$E_{\kappa\mathrm{g}}$	$E_{\kappa\mathrm{u}}$
E			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
C_n^r	$rK\varepsilon$	$1\ldots n-1$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$
C_2'	$2rK\varepsilon$	$0\ldots\frac{n}{2}-1$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
C_2''	$(2r+1)K\varepsilon$	$0\ldots\frac{n}{2}-1$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
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	$2rK\varepsilon$	$0\ldots\frac{n}{2}-1$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$-(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
σ_d	$(2r+1)K\varepsilon$	$0\ldots\frac{n}{2}-1$	$(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$-(-1)^K\begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
$S_n^{(r)}$	$rK\varepsilon$	$1,\ 2,\ 3,\ \ldots,\ n/2-1,\ n/2+1,\ldots,n-1$[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 $S_n^{(0)} = \sigma_\mathrm{h}$ and $S_n^{(n/2)} = i$.

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Table 11. Irreducible-representation transformation matrices of the $\boldsymbol{D}_{n\mathrm{h}}$ 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 $1 \leqslant \kappa \leqslant (n-1)/2$.

	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	$rK\varepsilon$	$1 \ldots n-1$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$
C'_2	$rK\varepsilon$	$0 \ldots n-1$	$(-1)^J \begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$(-1)^J \begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
σ_h			$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
σ_v	$rK\varepsilon$	$0 \ldots n-1$	$(-1)^J \begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$	$(-1)^J \begin{pmatrix} \cos\varepsilon_r & \sin\varepsilon_r \\ \sin\varepsilon_r & -\cos\varepsilon_r \end{pmatrix}$
$S_n^{(r)}$	$rK\varepsilon$	$1 \ldots n-1$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$	$\begin{pmatrix} \cos\varepsilon_r & -\sin\varepsilon_r \\ \sin\varepsilon_r & \cos\varepsilon_r \end{pmatrix}$

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

Table 12. Irreducible representations of the $\boldsymbol{D}_{n\mathrm{h}}$ 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 $0 \leqslant \kappa \leqslant n/2$ for n even and $0 \leqslant \kappa \leqslant (n-1)/2$ for n odd, with $\kappa = |K+nt|$.

K	κ		$\boldsymbol{D}_{n\mathrm{h}}$ (n even)	$\boldsymbol{D}_{\infty\mathrm{h}}$(EM)
$=0$	0		$A_{1\mathrm{g}}$	$\Sigma_\mathrm{g}{}^+$
>0	0		$A_{1\mathrm{g}} \oplus A_{2\mathrm{g}}$	$\Sigma_\mathrm{g}{}^+ \oplus \Sigma_\mathrm{g}{}^+$
>0	$n/2$		$B_{1\mathrm{g}} \oplus B_{2\mathrm{g}}$	$\Sigma_\mathrm{g}{}^+ \oplus \Sigma_\mathrm{g}{}^+$
>0	$\kappa = 1, 2, \ldots, n/2-1$		$E_{\kappa\mathrm{g}}$	$\Pi_\mathrm{g}, \Delta_\mathrm{g}, \Phi_\mathrm{g}, \Gamma_\mathrm{g}, \ldots$
K	κ		$\boldsymbol{D}_{n\mathrm{h}}$ (n odd)	$\boldsymbol{D}_{\infty\mathrm{h}}$(EM)
$=0$	0	J even	A'_1	$\Sigma_\mathrm{g}{}^+$
		J odd	A'_2	$\Sigma_\mathrm{g}{}^-$
>0, odd	0		$A''_1 \oplus A''_2$	$\Sigma_\mathrm{u}{}^+ \oplus \Sigma_\mathrm{u}{}^-$
>0, even	0		$A'_1 \oplus A'_2$	$\Sigma_\mathrm{g}{}^+ \oplus \Sigma_\mathrm{g}{}^-$
>0, odd	$1, 2, \ldots, (n-1)/2$		E''_κ	$\Pi_\mathrm{g}, \Phi_\mathrm{g}, H_\mathrm{g} \cdots$
>0, even	$1, 2, \ldots, (n-1)/2$		E'_κ	$\Delta_\mathrm{u}, \Gamma_\mathrm{u}, I_\mathrm{u} \cdots$

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4. Symmetrisation using the TROVE approach

TROVE uses a general numerical symmetrisation approach to build a symmetry adapted ro-vibrational basis set, as outlined recently in [25]. This will be summarised here and extended to include classification based on the vibrational angular momentum quantum number, ℓ, as necessary for dealing with linear molecules of $\boldsymbol{D}_{\infty \mathrm{h}}$ point group symmetry, using $^{12}C_2H_2$ as an example.

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

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

where Γ_s and Γ_t give the irreducible representations (irreps) of $\boldsymbol{D}_{n\mathrm{h}}$ 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 $\boldsymbol{D}_{n\mathrm{h}}$ irreducible representation is given in Figure 1; the symmetry blocks of non-vanishing matrix elements can be diagonalised separately.

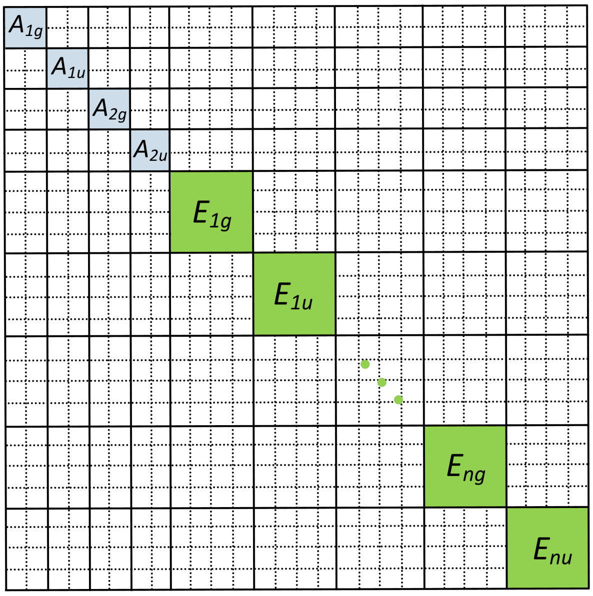

Figure 1. The block diagonal structure of a Hamiltonian matrix in the $\boldsymbol{D}_{n\mathrm{h}}$ irreducible representation. The empty (white) cells indicate blocks of vanishing matrix elements. It should be noted that, although B-symmetries will be present for even values of n, they are not physical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

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

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

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.

4.1. *Symmetrisation of the basis set for* $^{12}C_2H_2$ *using the* $(3N-5)$ *coordinate* TROVE *implementation*

As an illustration of the practical application of the finite $\boldsymbol{D}_{n\mathrm{h}}$ group being used in place of $\boldsymbol{D}_{\infty \mathrm{h}}$, we show an example of the construction of the vibrational basis set in case of the linear molecule

$^{12}C_2H_2$. 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 $^{12}C_2H_2$: 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 $\boldsymbol{D}_{n\mathrm{h}}$ of even n given in Table 10.

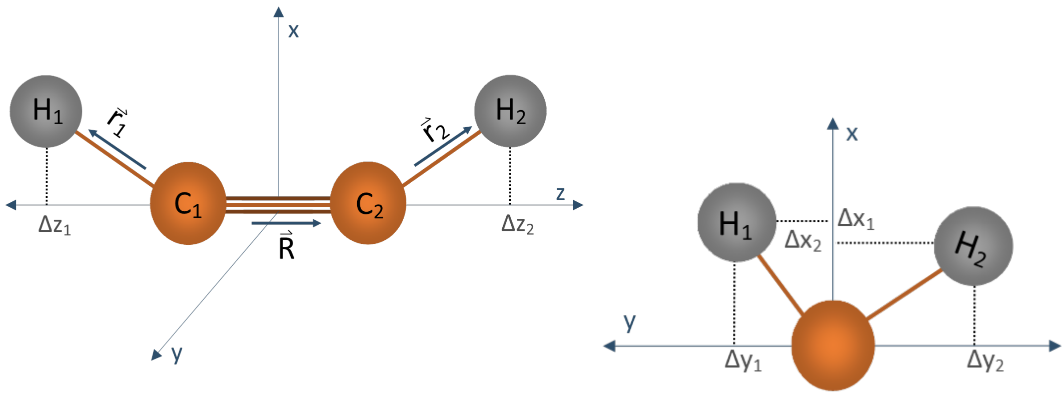

Figure 2. HCCH as described using the $(3N-5)$ coordinates employed in TROVE. $\vec{R}$ is the vector (of length R) pointing from the first to the second carbon atom, C_1 to C_2, while $\vec{r}_i$ are the two CH_i bond vectors (of lengths r_i). The Δx_1, Δx_2, Δy_1 and Δy_2 notation of this diagram is 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 [5,33,34] to solve these eigenvalue problems. For the bending basis functions $\phi_{v_4}(\xi_4),\ldots,\phi_{v_7}(\xi_7)$, 1D harmonic oscillators are used.

According to the the TROVE symmetrisation technique [25], 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 $^{12}C_2H_2$ used as an example. For $^{12}C_2H_2$, the vibrational part of the basis set of Eq. (23) is divided into three sub-sets:

$$\phi^{(1D)}_{v_1}(\xi_1) = \phi_{v_1}(\xi_1), \tag{24}$$

$$\phi^{(2D)}_{v_2 v_3}(\xi_2,\xi_3) = \phi_{v_2}(\xi_2)\phi_{v_3}(\xi_3), \tag{25}$$

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

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:

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

where $|0\rangle = \phi^{(1D)}_0(\xi_1)$ and $|0,0\rangle = \phi^{(2D)}_{0,0}(\xi_2,\xi_3)$.

According to the idea of the so-called complete set of commuting operators (CSCO) [25] which the TROVE symmetrisation 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 symmetrisation of the basis set is generated automatically by solving the appropriate eigenvalue problem, provided that the corresponding irreps

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Table 13. Transformation properties based on those of Table 10 for the $\boldsymbol{D}_{nh}$ group (relating to the symmetry operations of Table 5), where n is even, for transforming the set of 7 vibrational coordinates (ξ) used in the calculations of Ref. [18] for linear molecule $^{12}C_2H_2$. ξ = {ΔR, Δr_1, Δr_2, Δx_1, Δy_1, Δx_2, Δy_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 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	$m\varepsilon$	$1 \ldots n-1$	ΔR Δr_1 Δr_2 $\mathbf{M}^{E_{1u}}_{C_n^r}(\varepsilon_m) \cdot \vec{\rho}_1$ $\mathbf{M}^{E_{1u}}_{C_n^r}(\varepsilon_m) \cdot \vec{\rho}_2$
C_2' C_2''	$2m\varepsilon$ $\varepsilon(2m+1)$	$0 \ldots \frac{n}{2}-1$ $0 \ldots \frac{n}{2}-1$	ΔR Δr_2 Δr_1 $\mathbf{M}^{E_{1u}}_{C_2^{\prime/\prime\prime}}(\varepsilon_m) \cdot \vec{\rho}_2$ $\mathbf{M}^{E_{1u}}_{C_2^{\prime/\prime\prime}}(\varepsilon_m) \cdot \vec{\rho}_1$
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	$\varepsilon(2m+1)$ $2m\varepsilon$	$0 \ldots \frac{n}{2}-1$ $0 \ldots \frac{n}{2}-1$	ΔR Δr_1 Δr_2 $\mathbf{M}^{E_{1u}}_{\sigma_{d/v}}(\varepsilon_m) \cdot \vec{\rho}_1$ $\mathbf{M}^{E_{1u}}_{\sigma_{d/v}}(\varepsilon_m) \cdot \vec{\rho}_2$
S_n^m	$m\varepsilon$	$1 \ldots n-2$	ΔR Δr_2 Δr_1 $\mathbf{M}^{E_{1u}}_{S_n^r}(\varepsilon_m) \cdot \vec{\rho}_2$ $\mathbf{M}^{E_{1u}}_{S_n^r}(\varepsilon_m) \cdot \vec{\rho}_1$

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have been determined. To this end, TROVE applies the symmetry operators of the appropriate group to the eigenfunctions and analyses their transformation properties on a set of sampled geometries (usually 40-60). 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 $\boldsymbol{D}_{n\mathrm{h}}$ (even n), the eigenfunctions of $\hat{H}^{(1D)}$ span the $A_{1\mathrm{g}}$ irrep, while the eigenfunctions of $\hat{H}^{(2D)}$ span the $A_{1\mathrm{g}}$ and $A_{2\mathrm{u}}$ irreps.

The 4D bending basis set, based on the 1D harmonic oscillators of Eq. (26), has the disadvantage of being extremely degenerate: combinations of $\phi^{(4D)}_{v_4 v_5 v_6 v_7}$ give rise to large clusters of the same energies. According to the TROVE symmetrisation 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 (Eq. (26)) to become eigenfunctions of the vibrational angular momentum operator,

$$\hat{L}_z = \sum_{\lambda,\lambda'} \xi^{\mathrm{lin}}_{\lambda} \zeta^{z}_{\lambda,\lambda'} \hat{p}_{\lambda'} \tag{28}$$

where p_λ is a vibrational momentum operator, $\zeta^{z}_{\lambda,\lambda'}$ are Coriolis coefficients [35], and $\xi^{\mathrm{lin}}_{\lambda}$ are linearised internal coordinates, both 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 $\phi^{(4D)}_{v_4 v_5 v_6 v_7}$ basis functions we find eigenfunctions of $\hat{L}_z^2$ by diagonalising the matrix formed by combinations of the 4D bending basis set of Eq. (26):

$$\langle \phi^{(4D)}_{v_4 v_5 v_6 v_7} | \hat{L}_z^2 | \phi^{(4D)}_{v'_4 v'_5 v'_6 v'_7} \rangle. \tag{29}$$

The eigenfunctions of $\hat{L}_z^2$ are consequently characterized by their vibrational angular momentum ℓ $= |\ell| = \sqrt{\ell^2}$ 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 symmetrisation 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:

$$\hat{H}^{4D} = \frac{1}{2}\left(\hat{p}_4^2 + \hat{p}_5^2 + \hat{p}_6^2 + \hat{p}_7^2\right) + \frac{1}{2}\lambda\left(q_4^2 + q_5^2 + q_6^2 + q_7^2\right), \tag{30}$$

where λ is a related to the harmonic vibrational wavenumber and $\hat{p}_i$ are the vibrational momenta, conjugate to q_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 TROVE symmetrisation 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], [23], [24]). The maximum value for $L_{\mathrm{max}} = K_{\mathrm{max}}$ 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 $\Phi^{\Gamma_{\mathrm{vib}},\alpha}_{v,L}$ is generated. Here Γ_{vib} is the irrep of the basis function according to $\boldsymbol{D}_{n\mathrm{h}}$, and α indicates a degenerate component in the case of 2D irreps.

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

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

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

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

Here $|J,k\rangle$ is a rigid rotor wavefunction, with Z-projection of the rotational quantum number m omitted here. τ $(=0,1)$ is a parameter used to define the parity of a state, where $\sigma = (K \mod 3)$ for $\tau = 1$ and $\sigma = 0$ for $\tau = 0$ (see [25,36,37]). The irreps Γ_s of these functions are listed in Table 14, where τ defines their degenerate component. The symmetry properties of $|J,K,\tau\rangle^{\Gamma_{\rm rot}}$ can be derived from those of $|J,k\rangle$ using the method described in Section 3.3.

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

$$\Psi^{J,\Gamma_s}_{v,K} = \sum_{\alpha,\tau} T^{(\Gamma_{\rm vib},\Gamma_{\rm rot})\to\Gamma_s}_{\alpha,\tau}\Phi^{\Gamma_{\rm vib},\alpha}_{v,K}|J,K,\tau\rangle^{\Gamma_{\rm rot}}, \quad (33)$$

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

Table 14. Symmetries of the symmetrised rotational basis set used by TROVE, Eqs. (31,32) for different combinations of J, K and τ (where τ $(=0,1)$ 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.

		Γ_{rot}	
K	τ	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}

5. Numerical example

Some test calculations were carried out using TROVE [5] for $^{12}C_2H_2$ using a small basis set. These calculations utilise the symmetrisation procedure of Section 4.

5.1. Symmetrisation

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

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

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

Using the 4D reduced Hamiltonian in Eq. (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 Eqs. (28) and (29). In this example, the sets with degenerate eigenvalues and identical L values are: $\{\Psi_1^{L=0}\}$ ($\tilde{E}_1 = 0$ cm^{-1}), $\{\Psi_2^{L=1}, \Psi_3^{L=1}\}$ ($\tilde{E}_2 = 636.11$ cm^{-1}), $\{\Psi_4^{L=1}, \Psi_5^{L=1}\}$ ($\tilde{E}_3 = 763.12$ cm^{-1}), $\{\Psi_6^{L=2}, \Psi_7^{L=2}\}$ ($\tilde{E}_4 = 1215.84$ 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 with the eigenvalue 636.11 cm^{-1} ($\pm 10^{-12}$). 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:

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

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

5.2. Even vs. odd $\mathbf{D}_{\infty n}$ symmetries

For the example calculations using even vs odd $\mathbf{D}_{n\mathrm{h}}$ that are outlined below the primitive and contracted basis sets were controlled by the polyad number as given by Eq. (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 $\mathbf{D}_{\infty\mathrm{h}}$, we use a finite group $\mathbf{D}_{n\mathrm{h}}$, 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 $\mathbf{D}_{21\mathrm{h}}$ 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

 doi:10.20944/preprints201804.0142.v1

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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 $\boldsymbol{D}_{n\mathrm{h}}$ in the symmetrisation 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. [29] for the vibrational assignments) with associated symmetries (Γ_r, Γ_v and Γ_{r-v}, respectively) from ro-vibrational calculations using TROVE of $^{12}C_2H_2$ using different (even/odd) values of n for $\boldsymbol{D}_{n\mathrm{h}}$. In each case $L_{\max} = 4$. The energies are identical for symmetries of higher n than those shown here.

Energy (cm^{-1})	J	K	τ	$\nu_1\nu_2\nu_3\nu_4^{l_4}\nu_5^{l_5}$	$\boldsymbol{D}_{12\mathrm{h}}$ Γ_{r-v}	Γ_r	Γ_v	$\boldsymbol{D}_{13\mathrm{h}}$ Γ_{r-v}	Γ_r	Γ_v
2.356491	1	0	1	0000^00^0	A_{2g}	A_{2g}	A_{1g}	A_2'	A_2'	A_1'
625.810547	1	1	1	0001^10^0	A_{2g}	E_{1g}	E_{1g}	A_2'	E_1''	E_1''
1283.603736	1	0	1	0002^00^0	A_{2g}	A_{2g}	A_{1g}	A_2'	A_2'	A_1'
7.069433	2	0	0	0000^00^0	A_{1g}	A_{1g}	A_{1g}	A_1'	A_1'	A_1'
630.518518	2	1	1	0001^10^0	A_{1g}	E_{1g}	E_{1g}	A_1'	E_1''	E_1''
1276.518756	2	2	0	0002^20^0	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 symmetrisation procedure will lead to the wrong classification of states, resulting in, for example, the wrong nuclear statistics in intensity calculations. It should be noted, for practical numerical calculations we are limited by the maximum number of vibrational bending quanta that can be included in calculations, which gives a limit on $L_{\max}$. We therefore refer to this as the deciding factor in what n for $\boldsymbol{D}_{n\mathrm{h}}$ 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, [23], [24]).

6. Conclusion

We have presented an outline of the method used to treat linear molecules of the $\boldsymbol{D}_{\infty\mathrm{h}}$ point group using finite $\boldsymbol{D}_{n\mathrm{h}}$ symmetry (with arbitrary user-defined n) as implemented in nuclear motion routine TROVE. The TROVE symmetrisation scheme was 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 $\boldsymbol{D}_{n\mathrm{h}}$ of general integer odd or even n have been presented, along with some numerical examples for $^{12}C_2H_2$.

The work on $^{12}C_2H_2$ presented in Ref. [18] utilises this symmetrisation procedure for linear molecules, as will work currently in progress extending the room temperature line list of Ref. [18] to higher temperatures.

Acknowledgements

This work was supported by the ERC under Advanced Investigator Project 267219 and by STFC Projects No. ST/M001334/1 and ST/J002925. We acknowledge the use of the UCL Legion High Performance Computing Facility (Legion@UCL), and associated support services, in the completion of this work. We also acknowledge use of the DiRAC@Darwin HPC cluster, which is the UK HPC facility for particle physics, astrophysics and cosmology and is supported by STFC and BIS.

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