

Article

# Artificial Symmetries for Calculating Vibrational Energies of Linear Molecules

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**Abstract:** Linear molecules usually represent a special case in rotational-vibrational calculations due to a singularity of the kinetic energy operator that arises from the rotation about the  $a$  (the principal axis of least moment of inertia, becoming the molecular axis at the linear equilibrium geometry) being undefined. Assuming the standard ro-vibrational basis functions, in the  $3N - 6$  approach, of the form  $|v_1, v_2, v_3^{\ell_3}; J, k, m\rangle$ , tackling the unique difficulties of linear molecules involves constraining the vibrational and rotational functions with  $k = \ell_3$ , which are the projections, in units of  $\hbar$ , of the corresponding angular momenta onto the molecular axis. These basis functions are assigned to irreducible representations (irreps) of the  $C_{2v}(M)$  molecular symmetry group. This, in turn, necessitates purpose-built codes that specifically deal with linear molecules. In the present work, we describe an alternative scheme and introduce an (artificial) group that ensures that the condition  $\ell_3 = k$  is automatically applied solely through symmetry group algebra. The advantage of such an approach is that the application of symmetry group algebra in ro-vibrational calculations is ubiquitous, and so this method can be used to enable ro-vibrational calculations of linear molecules in polyatomic codes with fairly minimal modifications. To this end, we construct a—formally infinite—artificial molecular symmetry group  $D_{\infty h}(AEM)$ , which consists of one-dimensional (non-degenerate) irreducible representations and use it to classify vibrational and rotational basis functions according to  $\ell$  and  $k$ . This extension to non-rigorous, artificial symmetry groups is based on cyclic groups of prime-order. Opposite to the usual scenario, where the form of symmetry adapted basis sets is dictated by the symmetry group the molecule belongs to, here the symmetry group  $D_{\infty h}(AEM)$  is built to satisfy properties for the convenience of the basis set construction and matrix elements calculations. We believe that the idea of purpose-built artificial symmetry groups can be useful in other applications.



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## 1. Introduction

To describe the rotation and vibration of a well-bent triatomic molecule, such as H<sub>2</sub>S, with a large, non-accessible barrier to linearity (of  $24,423 \pm 75 \text{ cm}^{-1}$  [1]), a molecular kinetic energy operator (KEO) in terms of the 3 vibrational (e.g., two stretching and one bending) and three rotational coordinates (usually Euler angles) [2] is constructed. The three vibrational modes correspond to the standard bent-molecule methodology that is based on the  $3N - 6$  vibrational modes. We traditionally start from selecting a zero-order Hamiltonian  $\hat{H}_{\text{bent}}^{(0)} = \hat{H}_{\text{vib,bent}}^{(0)} + \hat{H}_{\text{rot,bent}}^{(0)}$  appropriate for a simplified molecule with the rotation-vibration interaction neglected.  $\hat{H}_{\text{vib,bent}}^{(0)}$  is the Hamiltonian for the vibrational motion, obtained by entirely neglecting rotation in the complete Hamiltonian, while  $\hat{H}_{\text{rot,bent}}^{(0)}$  is the Hamiltonian for the molecule rotating rigidly in its equilibrium configuration. The eigenfunctions of  $\hat{H}_{\text{bent}}^{(0)}$  are products  $\psi_{\text{vib,bent}}^{(0)} \times \psi_{\text{rot,bent}}^{(0)}$  of an eigenfunction  $\psi_{\text{vib,bent}}^{(0)}$

of  $\hat{H}_{\text{vib,bent}}^{(0)}$  and an eigenfunction  $\psi_{\text{rot,bent}}^{(0)}$  of  $\hat{H}_{\text{rot,bent}}^{(0)}$ , and these products are used as basis functions for solving the Schrödinger problem for the complete rotating and vibrating molecule, which is done either by perturbation theory or in a variational approach.

For the description of a linear triatomic molecule, for example  $\text{CO}_2$  (and actually also  $\text{H}_2\text{O}$ ), whose potential energy surface would allow for the linear configuration to become feasible during (typical) vibration, we cannot proceed as described for  $\text{H}_2\text{S}$  above, as the corresponding KEO becomes singular at linear molecular geometries. The reason is that, in the linear equilibrium configuration, the molecule cannot rotate about its own axis (systematically called  $a$ , the axis of least moment of inertia [2]). The corresponding rotation is undefined and, thus, leads to a singularity in the KEO. Another way of expressing this is to say that, for a linear molecule, we cannot initially neglect the interaction between the bending motion and the rotation about the  $a$  axis, since this rotation only takes place when the molecule bends out of the linear equilibrium configuration, as discussed extensively in Ref. [3]. Therefore, in considering a simplified molecule with the rotation-vibration interaction neglected with the Hamiltonian  $\hat{H}_{\text{lin}}^{(0)} = \hat{H}_{\text{vib,lin}}^{(0)} + \hat{H}_{\text{rot,lin}}^{(0)}$ , we cannot practically include the rotation about the  $a$  axis in  $\hat{H}_{\text{rot,lin}}^{(0)}$ , and this operator now only describes the so-called end-over-end rotation about the  $b$  and  $c$  axes [2] in the equilibrium configuration. The  $b$  and  $c$  axes [2] are both perpendicular to the molecular axis  $a$ .

In the literature, there are two main approaches for resolving the singularity issue. The traditional textbook approach is to treat linear molecules as systems with  $3N - 5$  vibrational modes (four in the case of triatomics) with only two rotational degrees of freedom. This approach is usually associated with the normal coordinates as vibrational degrees of freedom. The kinetic energy operator is not singular in such a representation, which is the main point of the, so-called, “ $(3N - 5)$ ” methodology [4]. This method is very popular in quantum-chemistry calculations and it has also been used in ro-vibrational, variational calculations (for example, by Carter and Handy [5], Mátyus et al. [6], Bowman et al. [7], Schroeder and Sebald [8]). The main disadvantages of the  $3N - 5$  approach are (i) the normal coordinates are not very chemically intuitive when describing molecular potential energy surfaces (PES), so that, consequently, (ii) the convergence of the calculations that correspond to higher vibrational excitations is slow and, finally, (iii) this approach is not well defined for quasi-linear molecules (molecules with a bent equilibrium structure and a low, penetrable barrier to linearity), which is, when the linear configuration is accessible on the time scale of a typical experiment). A neat feature of the “ $(3N - 5)$ ” approach, which is relevant to this work, is that the corresponding vibrational basis functions, as well as the rotational (rigid-rotor) basis functions, transform according to the infinite symmetry groups  $C_{\infty v}$  or  $D_{\infty h}$ , which are not only an appropriate choice for linear molecules, but also give access to powerful symmetry group (or representation-theory) methods. As far as the ro-vibrational calculations are concerned, the more appropriate symmetry groups for description of the zero-order solutions of  $\hat{H}_{\text{vib,lin}}^{(0)}$  and  $\hat{H}_{\text{rot,lin}}^{(0)}$  (i.e., for the classification of the physically correct nuclear-rotation-vibrational states) are the finite groups  $C_{\infty v}(M)$  or  $D_{\infty h}(M)$ . Ref. [2] describes the extensions to the infinitely large extended molecular groups  $C_{\infty v}(\text{EM})$  and  $D_{\infty h}(\text{EM})$  [9] isomorphic to the point groups  $C_{\infty v}$  and  $D_{\infty h}$  [2], respectively, which we discuss further below. The symmetry group methods have proved to be important when solving the corresponding nuclear motion problems, see e.g., Chubb et al. [10].

The disadvantages of the linear  $3N - 5$  approach motivated the development of an alternative treatment for all chain molecules (linear, quasi-linear, and bent) 50 years ago [11] (also see Refs. [12–15]), based on  $3N - 6$  vibrational coordinates and three rotational (Euler) angles, which is more typical for bent systems. The KEO is singular at the linear configuration (as well as the zero-order Hamiltonians) and, therefore, requires specially designed basis functions to resolve this singularity. The  $3N - 6$  vibrational coordinates have the advantage of being chemically intuitive when describing the molecular PES.

The main trick to resolve the singularity in the KEO is to construct the corresponding bending basis functions to have the correct asymptotic behaviour when the molecule approaches the linear configuration; see, for example, the discussion by Jensen [13]. This is

achieved by including the rotation about the  $a$  axis in  $\hat{H}_{\text{vib,lin}}^{(0)}$  for a linear molecule. The corresponding ro-vibrational basis set becomes dependent on the projections of the vibrational and rotational angular momenta (in units of  $\hbar$ ) onto the molecular axis  $a$  ( $k$  and  $\ell$ , respectively), subject to the constraint  $k = \ell$  [4,16–18]. Among the popular choices of the bending basis functions with correct behaviour are the associated Legendre polynomials [12,19]  $L_v^\ell$ , with  $v$  and  $\ell$  as the corresponding vibrational (bending) quantum numbers.

The vibrational basis functions are effectively wavefunctions of a bent molecule and, therefore, they do not reflect the symmetry properties of a linear molecule,  $C_{\infty v}$  or  $D_{\infty h}$ . Indeed, for a centrosymmetric molecule, such as  $\text{CO}_2$  they transform as  $D_{\infty h}(\text{M})$  (isomorphic to  $C_{2v}$ ) and only span four irreducible representations (irreps),  $\Sigma_g^+$ ,  $\Sigma_g^-$ ,  $\Sigma_u^+$ , and  $\Sigma_u^-$ . For a non-centrosymmetric linear molecule, such as  $\text{HCN}$ , they transform as  $C_{\infty v}(\text{M})$  (isomorphic to  $C_s$ ) and they span two irreducible representations,  $\Sigma^+$  and  $\Sigma^-$ . The vibrational basis set is orthogonal in  $\ell$  due to the constraint  $k = \ell$ .

This should be compared to the infinitely versatile symmetries that were obtained when the same molecule is treated as linear via  $D_{\infty h}$  (EM) or  $C_{\infty v}$  (EM) [9] with their much more detailed options for classification of the rotational and vibrational wavefunctions. In these groups, the vibrational and rotational basis functions span irreducible representations of  $C_{\infty v}$  or  $D_{\infty h}$  and transform as  $\Sigma, \Pi, \Delta, \Phi, \dots$  for  $\ell = 0, 1, 2, 3, \dots$  and  $k = 0, 1, 2, 3$ , respectively. Moreover, their intrinsic properties offer efficient tools of associated irreducible representations of molecular symmetry groups when constructing the Hamiltonian matrix elements or building symmetry adapted ro-vibrational basis functions, which are not available for the bent molecule approaches.

These rich properties of the infinite symmetry groups have motivated us to extend the molecular symmetry  $D_{\infty h}(\text{M})$  to an infinite group with the group structure that is similar to  $D_{\infty h}$  (or, analogously, extend  $C_{\infty v}(\text{M})$  to an infinite group with a group structure that is similar to  $C_{\infty v}$  for a non-centro-symmetric linear molecule). The corresponding irreducible representations  $\Pi, \Delta, \Phi, \dots$  ( $\ell > 0$ , or  $k > 0$ , respectively) are doubly degenerate and, therefore, are not directly suitable for this purpose. Therefore, the aim of these extensions is to obtain a more flexible classification of the rotational and vibrational wavefunctions than that provided by  $D_{\infty h}(\text{M})$  and  $C_{\infty v}(\text{M})$ , allowing for non-degenerate irreps, as required for bent molecules. The corresponding extended symmetries do not necessarily have to have any physical meaning or to be connected with energy conservation, as in the case of traditional "true" molecular symmetry groups. Instead, a group is constructed in such a way, so that the irreps have properties that are formalised from the outset, rather than the behaviour of the irreps being a result of the symmetry of the molecule itself. Thus, any "artificial" group, constructed in this way, which satisfies the standard group theorems and fulfills the purpose of being directly associated with the  $\ell = k$  classification will do. The approach described here, then, is, in effect, a reversal of the standard procedure where the properties of the basis set are based on the symmetry group of the molecule. Here, we design the symmetry group to fulfill the required structure of the ro-vibrational basis functions and the matrix elements of the Hamiltonian.

To this end, in the present work we introduce a formally infinite molecular symmetry (MS) group by extending  $D_{\infty h}(\text{M})$  [ $C_{\infty v}(\text{M})$ ] with some artificial irreps with the four [two] 'physical' irreps  $\Sigma_g^+$ ,  $\Sigma_g^-$ ,  $\Sigma_u^+$  and  $\Sigma_u^-$  [ $\Sigma^+$  and  $\Sigma^-$ ] retained. The group is referred to as  $D_{\infty h}(\text{AEM})$  [ $C_{\infty v}(\text{AEM})$ ], where AEM stands for 'artificial extended molecular' (group). We will also introduce a finite analogy  $D_{nh}(\text{AEM})$  [ $C_{nv}(\text{AEM})$ ], where  $n$  depends on the value of  $\ell_{\text{max}}$ , and use it to classify the vibrational and rotational basis functions of the bent ( $3N - 6$  approach) similar to the classification used for linear,  $D_{\infty h}$  [ $C_{\infty v}$ ] (EM)-based  $3N - 5$  systems.

The new symmetry group  $D_{nh}(\text{AEM})$  [ $C_{nv}(\text{AEM})$ ] has been implemented in the variational program TROVE (Theoretical ROVibrational Energies) [20,21], with the aim to facilitate the computation of vibrational energies and wavefunctions for linear molecules. TROVE is a general, efficient computer program for simulating, by variational methods, hot rotation-vibration spectra of small- to medium-sized polyatomic molecules of arbitrary

structure. It has been applied to a large number of polyatomic species [21–41] with various symmetry types [2], such as  $C_{2v}$ ,  $C_{2h}$ ,  $C_{3v}(M)$ ,  $D_{nh}(M)$ ,  $T_d(M)$ ,  $G_{36}$  etc. TROVE is one of the main tools of the ExoMol project [42,43]. Updates of TROVE have been recently reported in Refs. [19,43,44], with the most recent extension [19] being the implementation in TROVE of the  $3N - 6$  methodology with a singularity resolution based on the inclusion of interaction between the bending motions and the rotation about the  $a$  axis. Additionally, the adaptation of linear-molecule symmetry that was described in Ref. [10] was implemented. The theory and programming work reported in Ref. [19] and in the present work have already been employed for generating hot molecular line lists for  $SiO_2$  [45] and  $CO_2$  [46] as well as to produce a quadrupole spectrum of  $H_2O$  [47]. TROVE uses an automatic approach for constructing a symmetry-adapted basis set to be used in setting up a matrix representation of the molecular rotation-vibration Hamiltonian [48], in the present case for  $D_{nh}(AEM)$  [ $C_{nv}(AEM)$ ].

### 1.1. Symmetry Properties of the Linear Molecule ( $3N - 5$ ) Basis Functions: $D_{\infty h}(EM)$

In order to compute the vibrational energies for a linear molecule, we solve the Schrödinger equation for the Hamiltonian  $\hat{H}_{\text{vib,lin}}^{(0)}$ , which involves the bending and stretching motions and, as explained in Introduction, the rotational motion about the  $a$  axis. In general, an  $N$ -atomic chain molecule has  $N - 1$  stretching vibrations, one for each bond, and  $N - 2$  bending vibrations, one at each “inner” nucleus; there is no bending motion at the two “terminal” nuclei. It is well known (see, for example, Ref. [2]) that, if we transform  $\hat{H}_{\text{vib,lin}}^{(0)}$  to depend on normal coordinates  $Q_i$  for non-degenerate vibrations and  $(Q_{ja}, Q_{jb})$  for doubly degenerate vibrations, and we express the Born–Oppenheimer potential energy function in  $\hat{H}_{\text{vib,lin}}^{(0)}$  in the harmonic approximation, i.e., as a second-order polynomial in the normal coordinates  $Q$ , the eigenfunctions of  $\hat{H}_{\text{vib,lin}}^{(0)}$  are products of harmonic oscillator functions

$$|v_1, v_2, \dots, v_{N-1}; v_N^{\ell_N}, v_{N+1}^{\ell_{N+1}}, v_{N+2}^{\ell_{N+2}}, \dots, v_{2N-3}^{\ell_{2N-3}}\rangle = \prod_{i=1}^{N-1} \Phi_{v_i}(Q_i) \prod_{j=N}^{2N-3} \Phi_{v_j, \ell_j}(Q_{ja}, Q_{jb}). \quad (1)$$

Each of the  $N - 1$  stretching vibrations is described by a one-dimensional harmonic oscillator eigenfunction  $\Phi_{v_i}(Q_i)$  ( $i = 1, 2, 3, \dots, N - 1$ ), and each of the  $N - 2$  bending vibrations is described by a two-dimensional harmonic oscillator eigenfunction  $\Phi_{v_j, \ell_j}(Q_{ja}, Q_{jb})$  ( $j = N, N + 1, \dots, 2N - 3$ ). Here,  $\ell_j$  is the corresponding vibrational angular momentum quantum number and  $Q_a$  and  $Q_b$  are the degenerate vibrational modes that are often represented by polar coordinates  $Q_3$  and  $\chi$  via  $(Q_{3a}, Q_{3b}) = (Q_3 \cos \chi, Q_3 \sin \chi)$  (see Chapter 11.3 of Ref. [2]). These two-dimensional (2D) bending functions  $\Phi_{v_j, \ell_j}(Q_{ja}, Q_{jb})$  transform according to the irreps of the MS group  $D_{\infty h}(EM)$  [9] (see Table 1), with  $\ell_j$  identifying the corresponding irrep  $\Sigma, \Pi, \Delta, \dots$ , for  $\ell_j = 0, 1, 2, \dots$ , respectively, and  $\ell_j$  spanning  $v_j, v_j - 2, v_j - 4, \dots, -v_j$ . When combined with the rotational, rigid-rotor, basis function  $|J, k, m\rangle$ , the constraint  $k = \ell = \sum_j \ell_j$  is used, where  $\ell$  is the total vibrational angular momentum (in units of  $\hbar$ ) of the product-type vibrational basis. Here,  $J$  is the total angular momentum,  $k\hbar$  is the projection of the angular momentum on the molecular  $z (= a)$  axis and  $m\hbar$  is the projection on the laboratory-fixed  $Z$  axis. The rotational basis functions  $|J, k, m\rangle$  transform according to the operations of  $D_{\infty h}(EM)$ , with the similar mapping between the irreps and the rotational quantum number  $k$ , as found for  $\ell$ :  $\Sigma$  ( $k = 0$ ),  $\Pi$  ( $k = 1$ ),  $\Delta$  ( $k = 2$ ), etc. The correlation between the  $D_{\infty h}(EM)$  [9] irreps and the quantum numbers  $\ell, k$  is very useful, as it enables the use of powerful group symmetry tools for classifying and even constructing the ro-vibrational (bending) basis functions, with the vibrational basis function in Equation (1) now given by:

$$|v_1, v_2, v_3^{\ell_3}\rangle = \Phi_{v_1}(Q_1) \Phi_{v_2}(Q_2) \Phi_{v_3, \ell_3}(Q_{3a}, Q_{3b}). \quad (2)$$

The two bending modes  $\nu_{3a}$  and  $\nu_{3b}$  have identical harmonic vibrational wavenumbers,  $\omega_{3a} = \omega_{3b}$ . As discussed above, both the vibrational  $|v_1, v_2, v_3^{\ell_3}\rangle$  and rotational  $|J, k, m\rangle$  basis functions of the linear molecule  $\text{CO}_2$  are described by the irreps of  $D_{\infty h}$  (EM), and they are fully defined by the corresponding values of  $\ell \equiv \ell_3$  and  $k$  shown in Table 1. The  $\ell$ -dependent vibrational basis functions span the  $g$ -type and  $u$ -type representations, while the  $k$ -dependent rotational functions can only be of  $g$  (i.e., do not change upon the  $\sigma_h$  transformation). These functions are linked via the condition  $\ell = k$ . The ro-vibrational eigenfunctions of a linear  $\text{XY}_2$  type molecule can only transform as one of the four irreps of  $D_{\infty h}(\text{M})$  that are listed in Table 2 (in fact, due to the zero-nuclear spins of C and O, the ro-vibrational wavefunctions of  $\text{CO}_2$  can only span two representations,  $\Sigma_g^+$  and  $\Sigma_u^-$ ). Therefore, physically meaningful combinations of  $|v_1, v_2, v_3^{\ell_3}\rangle$  and rotational  $|J, k, m\rangle$  from their direct products can only span these four irreps. These properties can be efficiently explored by the efficient symmetry group algebra via projection and symmetry reduction techniques, as was shown, e.g., in Chubb et al. [10].

**Table 1.** The irreducible representation  $\Gamma$  of  $D_{\infty h}$  (EM) spanned by the rotational  $|J, k, m\rangle$  or vibrational  $|v_3, \ell_3\rangle$  wavefunction of a linear molecule in the absence of external electric and magnetic fields. The irrep depends on  $k$  or  $\ell$ .

$k/\ell$	$\Gamma_{\text{vib}}$	$\Gamma_{\text{rot}}$	
0	$\Sigma_g^+$	$\Sigma_g^+$	( $J$ even)
0		$\Sigma_g^-$	( $J$ odd)
$\pm 1$	$\Pi_u$	$\Pi_g$	
$\pm 2$	$\Delta_g$	$\Delta_g$	
$\pm 3$	$\Phi_u$	$\Phi_g$	
$\vdots$		$\vdots$	

**Table 2.** Character table for the molecular symmetry (MS) group  $D_{\infty h}(\text{M})^a$ . The last four columns show the group operations, with two labels for each operation.

$\Gamma$	$E$	$(p)$	$(p)^*$	$E^*$
	$E$	$C_2(z)$	$\sigma(xz)$	$\sigma_h(xy)$
$\Sigma_g^+$	1	1	1	1
$\Sigma_g^-$	1	-1	1	-1
$\Sigma_u^-$	1	1	-1	-1
$\Sigma_u^+$	1	-1	-1	1

<sup>a</sup>  $g$  and  $u$  stand for the German gerade (even) and ungerade (odd), related to the permutation-inversion operation  $(p)^*$ .

### 1.2. Symmetry Properties of the Bent $3N - 6$ Basis Functions

In the  $3N - 6$  (bent molecule) framework applied to a linear molecule, the initial treatment is based on the ‘zero-order’ Hamiltonian

$$\hat{H}_{\text{lin}}^{(0)} = \hat{H}_{\text{vib,lin}}^{(0)} + \hat{H}_{\text{rot,lin}}^{(0)}$$

where, now,  $\hat{H}_{\text{rot,lin}}^{(0)}$  describes the end-over-end rotation only while the rotation about the  $a$  axis is included in  $\hat{H}_{\text{vib,lin}}^{(0)}$ , since  $a$ -axis rotation only takes place when the molecule bends out of the linear equilibrium configuration. For a linear centrosymmetric triatomic molecule, a vibrational basis function is given by

$$|v_1, v_2, v_3^{\ell}\rangle = \varphi_{v_1}(r_1) \varphi_{v_2}(r_2) \varphi_{v_3, \ell}(\rho), \quad (3)$$

where  $\rho$  measures the bending displacement from the linear equilibrium configuration and the stretching vibrations are described by the bond lengths  $r_1$  and  $r_2$ . The bending function  $\varphi_{v_3,\ell}(\rho)$  shown in Equation (3) plays the central role in the  $3N - 6$  formalism via two main properties: (i) it is constructed to possess the correct dependence at  $\rho \rightarrow 0$  to resolve the singularity of the KEO [13,19]:

$$\varphi_{v_3,\ell}(\rho) \sim \sqrt{\rho^{2\ell+1}}$$

and (ii) it is linked to the rotational basis functions  $|J, k, m\rangle$  via  $\ell = k$  as a general property of the basis sets of linear polyatomic molecules with the *Sayvetz condition*  $k = \ell = \sum_{j=N}^{2N-3} \ell_j$  [16] (also see Ref. [10]).

The harmonic-oscillator basis functions  $\Phi_{v_3,\ell_3}(Q_{3a}, Q_{3b})$  in Equation (2), used in the  $3N - 5$  approach, are orthogonal because they are eigenfunctions for the vibrational angular momentum operator  $\hat{L}_a$  with different eigenvalues  $\ell_3 \hbar$ . In the calculations described here for triatomic molecules, the bending basis functions  $\varphi_{v_3,\ell_3}(\rho)$  in Equation (3) (which only depend on  $Q_3$  and not on  $\chi$ ) are typically generated by Numerov–Cooley numerical integration [49–51], for example, Section 6 of Jensen [13]) with the value of  $k = \ell_3$  entering as a parameter. Two such functions with different values of  $v_3$ , but the same values of  $\ell_3$  are orthogonal, the orthogonality resulting from integration over  $\rho$ . In order to generate basis functions for the  $3N - 6$  calculation, we multiply the vibrational basis functions of Equation (3) by the  $\chi$ -dependent functions  $|J, k = \ell_3, m\rangle$  and the resulting complete basis functions

$$|v_1, v_2, v_3^{\ell_3}; J, k = \ell_3, m\rangle = \varphi_{v_1}(r_1) \varphi_{v_2}(r_2) \varphi_{v_3,\ell_3}(\rho) |J, k = \ell_3, m\rangle \quad (4)$$

are generally orthogonal, the orthogonality being manifested by the integration over  $\chi$  for functions with different values of  $\ell_3$  and over  $\rho$  for functions with the same value of  $\ell_3$ , but different values of  $v_3$ . On a practical level, it is discussed for a triatomic molecule in Section 6 of Jensen [13] that

$$|J, k, m\rangle = \frac{1}{\sqrt{2\pi}} \exp(ik\chi) S_{Jkm}(\theta, \phi) \quad (5)$$

and it is recognised that the factor  $\exp(ik\chi)$  is also contained in  $\Phi_{v_3,\ell_3}(Q_{3a}, Q_{3b})$ , where it is written as  $\exp(i\ell_3\chi)$ . This identity is taken into account when forming a harmonic-oscillator/rigid-rotor basis set for diagonalizing  $\hat{H}_{\text{vib,lin}}^{(0)}$ ; the harmonic-oscillator functions in Equation (2) are not multiplied by the complete  $|J, k, m\rangle$ , but only by the  $(\theta, \phi)$ -dependent functions  $S_{Jkm}(\theta, \phi)$  from Equation (5).

The purely vibrational part of the linear-molecule Hamiltonian,  $\hat{H}_{\text{vib,lin}}^{(0)}$ , commutes with  $\hat{L}_a$  and, so,  $\ell_3$  (in general  $\ell$ ) is a good quantum number for its eigenfunctions; they can be labelled by  $\ell_3$  ( $\ell$ ). The part of the kinetic energy operator that describes end-over-end rotation about the  $b$  and  $c$  axes, however, mixes basis functions with different  $\ell$ -values; it gives rise to non-vanishing off-diagonal matrix elements with  $|\Delta\ell| \leq 2$ . It is interesting to note that, in the case of the  $3N - 5$  linear molecule approach (Section 1.1), the orthogonality between basis functions with different  $\ell$  values is automatically satisfied due to different symmetries (irreps) that correspond to different values of  $\ell$ . The symmetry properties of the wavefunctions of linear molecules under the  $3N - 6$  (bent) approach are much less informative than those under the  $3N - 5$  approach. In the case of a centrosymmetric triatomic, the  $3N - 6$  approach employs  $D_{\text{oh}}(\text{M})$  with four irreps (see Table 2) in contrast to the irreps of the infinite group  $D_{\text{oh}}(\text{EM})$ . Moreover, the bending wavefunctions  $\varphi_{v_3,k}(\rho)$  can only be of  $\Sigma_g^+$  symmetry of  $D_{\text{oh}}(\text{M})$ . Yet, the property of orthogonality between basis functions with different  $\ell$ -values is very similar to the orthogonality that arises from different irreps being generated by the wavefunctions in Equation (2) in the  $3N - 5$  treatment.

In the present work, we investigate whether the  $D_{\infty h}(M)$  symmetry description of the basis functions in Equation (3), naturally arising for the  $3N - 6$  case, can be extended in such a manner that it becomes similar to the much more detailed description, in terms of  $D_{\infty h}(EM)$ , obtained for the  $3N - 5$  case. In particular, we would like a description in which basis functions with different  $\ell$ -values span different irreps so that we can take advantage of the specific properties of the linear-molecule basis set functions. For example, the vibrational Hamiltonian matrix, constructed in an extended-symmetry-adapted basis set, will automatically be block diagonal in  $\ell$  and thus its construction and diagonalization can be optimally cost-effective. There exists no “true” molecular symmetry group, based on permutation-inversion symmetry, with  $\ell$ -dependent irreps. Thus, our theory does not automatically yield such irreps. However, in the following, we show that it is possible to introduce an “artificial” symmetry group that is based on the property of cyclic groups of prime-order that produces the desired  $\ell$ -dependent irreps. By analogy to the extended group  $D_{\infty h}(EM)$ , the new artificially extended group will be referenced as  $D_{\infty h}(AEM)$ , where AEM stands for ‘artificial extended molecular’.

### 1.3. “Artificial” Molecular Group Symmetry $D_{\infty h}(AEM)$ for Centrosymmetric Triatomic Molecules

We define the finite artificial extended MS group  $D_{nh}(AEM)$ , as follows

$$D_{nh}(AEM) = \mathbf{Z}_2 \underbrace{\otimes \dots \otimes}_{n-1} \mathbf{Z}_2 \quad (6)$$

where  $\mathbf{Z}_2$  is the cyclic group of order 2 and, therefore, it consists of the set  $\{0, 1\}$  with addition modulo 2. The integer  $n$  depends on the value of  $\ell_{\max}$ . Taking the limit  $n \rightarrow \infty$  defines the infinite  $D_{\infty h}(AEM)$  group. Note that this is a countable infinity, as opposed to the group  $D_{\infty h}(EM)$ . The vibrational  $|v_1, v_2, v_3^\ell\rangle$  and rotational  $|J, k, m\rangle$  basis set functions of differing  $\ell$  (or  $k$ ) values are assigned to different irreps of this group.

The group  $D_{nh}(AEM)$  must fulfil certain conditions necessary for our purposes. First, all irreps should be one-dimensional and, for simplicity, real. The former condition is so that each irrep of  $D_{nh}(AEM)$  is correlated with one irrep of  $D_{\infty h}(M)$ . The irreps of  $D_{nh}(AEM)$  will be labelled as  $\Gamma_3 = C_{2v}$  irreps with an extra superscript (see Table 2), e.g.,  $A_1^4$ . The bending function  $\psi_{v_3, \ell}(\rho)$  or rotational function  $|J, k, m\rangle$ , if they transform as irrep  $\Gamma$  in  $C_{2v}$ , would be assigned to  $\Gamma^\ell$  or  $\Gamma^k$ , respectively. For example, a vibrational function with  $\ell = 4$  and transforming as  $A_1$  in  $C_{2v}$  would be assigned the symmetry  $A_1^4$  in the  $D_{nh}(AEM)$ .

From  $D_{\infty h}(AEM)$  and  $D_{nh}(AEM)$ , we select four elements and match each with a  $C_{2v}$  element. Subsequently, the characters of those elements for each 0-superscripted irrep should be the same as the corresponding  $C_{2v}$  irrep. When combining a bending function that transforms as  $\Gamma_1^\ell$  with a rotational function which transforms as  $\Gamma_2^k$ , their product should transform as  $\Gamma_1^\ell \times \Gamma_2^k = (\Gamma_1 \times \Gamma_2)^m$  for some  $m \neq 0$  if  $\ell \neq k$ . If  $\ell = k$ , then they should transform as  $\Gamma_1^\ell \times \Gamma_2^\ell = (\Gamma_1 \times \Gamma_2)^0$ . For example,  $A_2^4 \times B_1^4$  should be  $B_2^0$ .

We illustrate these rules with the group  $D_{4h}(AEM)$  in Table 3 for the characters and Table 4 for the multiplication table of the irreps.

These properties are intended to allow us to assign each vibrational basis function to an irrep, which depends on  $\ell$ , as discussed above. It will also combine  $k$  and  $\ell$  basis set functions correctly, so that the condition of  $k = \ell$  can be imposed by giving an irrep with superscript  $\neq 0$  a statistical weight factor of 0.

In variational calculations utilising finite basis sets, it is practical to use the finite analogy  $D_{nh}(AEM)$  of the infinite group  $D_{\infty h}$ , see Chubb et al. [10]. Accordingly, the practical procedure introduced and developed here involves  $D_{nh}(AEM)$ , rather than  $D_{\infty h}(AEM)$ . Here  $n$  is some integer value defined to cover the highest excitations of  $k = \ell$  in the bending  $\varphi_{v_3, \ell}(\rho)$  and rotational  $|J, k, m\rangle$  functions.

**Table 3.** Character table for the  $D_{4h}$ (AEM) group. The operations of the group that are 0-superscripted correspond to the  $C_{2v}$  group. Note that the characters of the 0-superscripted irreps for these operations are the same as those of the corresponding irreps for the  $C_{2v}$  group.

$D_{4h}$ (AEM)	$E^0$	$C_2^0$	$\sigma^0$	$\sigma_v^0$	$E^1$	$C_2^1$	$\sigma^1$	$\sigma_v^1$	$E^2$	$C_2^2$	$\sigma^2$	$\sigma_v^2$	$E^3$	$C_2^3$	$\sigma^3$	$\sigma_v^3$
$A_1^0$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$B_1^0$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
$A_2^0$	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
$B_2^0$	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
$A_1^1$	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
$B_1^1$	1	-1	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1
$A_2^1$	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	-1	1
$B_2^1$	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1
$A_1^2$	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
$B_1^2$	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
$A_2^2$	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
$B_2^2$	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1	-1	1	1	-1
$A_1^3$	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
$B_1^3$	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1
$A_2^3$	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1
$B_2^3$	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1

**Table 4.** Multiplication table for the irreps of the  $D_{4h}$ (AEM) group. The vertical and horizontal lines demarcate the blocks of different superscript values. Note that the diagonal blocks are all 0-superscripted, while off diagonal ones are non-0-superscripted.

$\otimes$	$A_1^0$	$B_1^0$	$A_2^0$	$B_2^0$	$A_1^1$	$B_1^1$	$A_2^1$	$B_2^1$	$A_1^2$	$B_1^2$	$A_2^2$	$B_2^2$	$A_1^3$	$B_1^3$	$A_2^3$	$B_2^3$
$A_1^0$	$A_1^0$	$B_1^0$	$A_2^0$	$B_2^0$	$A_1^1$	$B_1^1$	$A_2^1$	$B_2^1$	$A_1^2$	$B_1^2$	$A_2^2$	$B_2^2$	$A_1^3$	$B_1^3$	$A_2^3$	$B_2^3$
$B_1^0$	$B_1^0$	$A_1^0$	$B_2^0$	$A_2^0$	$B_1^1$	$A_1^1$	$B_2^1$	$A_2^1$	$B_1^2$	$A_1^2$	$B_2^2$	$A_2^2$	$B_1^3$	$A_1^3$	$B_2^3$	$A_2^3$
$A_2^0$	$A_2^0$	$B_2^0$	$A_1^0$	$B_1^0$	$A_2^1$	$B_2^1$	$A_1^1$	$B_1^1$	$A_2^2$	$B_2^2$	$A_1^2$	$B_1^2$	$A_2^3$	$B_2^3$	$A_1^3$	$B_1^3$
$B_2^0$	$B_2^0$	$A_2^0$	$B_1^0$	$A_1^0$	$B_2^1$	$A_2^1$	$B_1^1$	$A_1^1$	$B_2^2$	$A_2^2$	$B_1^2$	$A_1^2$	$B_2^3$	$A_2^3$	$B_1^3$	$A_1^3$
$A_1^1$	$A_1^1$	$B_1^1$	$A_2^1$	$B_2^1$	$A_1^0$	$B_1^0$	$A_2^0$	$B_2^0$	$A_1^3$	$B_1^3$	$A_2^3$	$B_2^3$	$A_1^2$	$B_1^2$	$A_2^2$	$B_2^2$
$B_1^1$	$B_1^1$	$A_1^1$	$B_2^1$	$A_2^1$	$B_1^0$	$A_1^0$	$B_2^0$	$A_2^0$	$B_1^3$	$A_1^3$	$B_2^3$	$A_2^3$	$B_1^2$	$A_1^2$	$B_2^2$	$A_2^2$
$A_2^1$	$A_2^1$	$B_2^1$	$A_1^1$	$B_1^1$	$A_2^0$	$B_2^0$	$A_1^0$	$B_1^0$	$A_2^3$	$B_2^3$	$A_1^3$	$B_1^3$	$A_2^2$	$B_2^2$	$A_1^2$	$B_1^2$
$B_2^1$	$B_2^1$	$A_2^1$	$B_1^1$	$A_1^1$	$B_2^0$	$A_2^0$	$B_1^0$	$A_1^0$	$B_2^3$	$A_2^3$	$B_1^3$	$A_1^3$	$B_2^2$	$A_2^2$	$B_1^2$	$A_1^2$
$A_1^2$	$A_1^2$	$B_1^2$	$A_2^2$	$B_2^2$	$A_1^3$	$B_1^3$	$A_2^3$	$B_2^3$	$A_1^0$	$B_1^0$	$A_2^0$	$B_2^0$	$A_1^1$	$B_1^1$	$A_2^1$	$B_2^1$
$B_1^2$	$B_1^2$	$A_1^2$	$B_2^2$	$A_2^2$	$B_1^3$	$A_1^3$	$B_2^3$	$A_2^3$	$B_1^0$	$A_1^0$	$B_2^0$	$A_2^0$	$B_1^1$	$A_1^1$	$B_2^1$	$A_2^1$
$A_2^2$	$A_2^2$	$B_2^2$	$A_1^2$	$B_1^2$	$A_2^3$	$B_2^3$	$A_1^3$	$B_1^3$	$A_2^0$	$B_2^0$	$A_1^0$	$B_1^0$	$A_2^1$	$B_2^1$	$A_1^1$	$B_1^1$
$B_2^2$	$B_2^2$	$A_2^2$	$B_1^2$	$A_1^2$	$B_2^3$	$A_2^3$	$B_1^3$	$A_1^3$	$B_2^0$	$A_2^0$	$B_1^0$	$A_1^0$	$B_2^1$	$A_2^1$	$B_1^1$	$A_1^1$
$A_1^3$	$A_1^3$	$B_1^3$	$A_2^3$	$B_2^3$	$A_2^0$	$B_2^0$	$A_2^0$	$B_2^0$	$A_1^1$	$B_1^1$	$A_2^1$	$B_2^1$	$A_1^0$	$B_1^0$	$A_2^0$	$B_2^0$
$B_1^3$	$B_1^3$	$A_1^3$	$B_2^3$	$A_2^3$	$B_2^1$	$A_2^1$	$B_2^1$	$A_2^1$	$B_1^1$	$A_1^1$	$B_2^1$	$A_2^1$	$B_1^0$	$A_1^0$	$B_2^0$	$A_2^0$
$A_2^3$	$A_2^3$	$B_2^3$	$A_1^3$	$B_1^3$	$A_2^2$	$B_2^2$	$A_1^2$	$B_2^2$	$A_2^1$	$B_2^1$	$A_1^1$	$B_2^1$	$A_2^0$	$B_2^0$	$A_1^0$	$B_1^0$
$B_2^3$	$B_2^3$	$A_2^3$	$B_1^3$	$A_1^3$	$B_2^2$	$A_2^2$	$B_2^2$	$A_2^2$	$B_2^1$	$A_2^1$	$B_2^1$	$A_2^1$	$B_2^0$	$A_2^0$	$B_1^0$	$A_1^0$

To show that  $D_{nh}$ (AEM) has the required properties, and it is effectively the only group that does, first note that, since the irreps are one-dimensional, the group is abelian, and, thus, by the fundamental theorem of finite abelian groups [52], can be expressed as a direct product of cyclic groups of prime order, i.e.,

$$\mathbf{Z}_{m_1} \otimes \dots \otimes \mathbf{Z}_{m_n} \tag{7}$$



where  $m_i$  is prime and the  $Z_{m_i}$  consists of the set  $\{0, 1, \dots, m_i - 1\}$  with addition modulo  $m_i$  for  $i \in \{0, \dots, n\}$ . However, the cyclic group  $Z_m$  has a representation where element  $i$  is associated with  $e^{2\pi i/m}$ , which is only real for all  $i$  if  $m = 2$ , thus our group can only be of the form

$$D_{nh}(\text{AEM}) = Z_2 \underbrace{\otimes \dots \otimes}_{n-1} Z_2 \tag{8}$$

for some  $n$ . For a given  $\ell_{\max}$  (or the same  $k_{\max}$ ), we must have at least  $4(\ell_{\max} + 1)$  representations (four for each  $\ell$  including  $\ell = 0$ ).  $D_{nh}(\text{AEM})$  has  $2^n$  representations, hence

$$n = \lceil \log_2 4(\ell_{\max} + 1) \rceil \tag{9}$$

where  $\lceil \cdot \rceil$  rounds up to the nearest integer. In order to show that the irrep product properties hold, first consider  $Z_2$ . It has character table shown in Table 5.

**Table 5.** Character table for the  $Z_2$  group.

$Z_2$	<b>0</b>	<b>1</b>
A	1	1
B	1	-1

In the following, we omit labelling the elements and the irreps, and simply write the character table as a matrix. Then  $Z_2$  is written

$$\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}. \tag{10}$$

The character table of a direct product of two groups can then be found by taking an outer product of a matrix. This is defined by

$$\begin{pmatrix} a_{11} & \dots & a_{1n} \\ \vdots & & \vdots \\ a_{m1} & \dots & a_{mn} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & \dots & b_{1s} \\ \vdots & & \vdots \\ b_{r1} & \dots & b_{rs} \end{pmatrix} = \tag{11}$$

$$\begin{pmatrix} a_{11}b_{11} & \dots & a_{1n}b_{11} & \dots & a_{11}b_{1s} & \dots & a_{1n}b_{1s} \\ \vdots & & \vdots & & \vdots & & \vdots \\ a_{m1}b_{11} & \dots & a_{mn}b_{11} & \dots & a_{m1}b_{1s} & \dots & a_{mn}b_{1s} \\ \vdots & & \vdots & & \vdots & & \vdots \\ a_{11}b_{r1} & \dots & a_{1n}b_{r1} & \dots & a_{11}b_{rs} & \dots & a_{1n}b_{rs} \\ \vdots & & \vdots & & \vdots & & \vdots \\ a_{m1}b_{r1} & \dots & a_{mn}b_{r1} & \dots & a_{m1}b_{rs} & \dots & a_{mn}b_{rs} \end{pmatrix}. \tag{12}$$

Now,  $C_{2v} = Z_2 \otimes Z_2$ . Hence,  $D_{2h}(\text{AEM})$  works for  $k_{\max} = 0$ , where we label the 0-superscripted irreps of  $D_{2h}(\text{AEM})$  in the same order as Table 3. We call the  $D_{2h}(\text{AEM})$  character table matrix  $G$ , i.e.,

$$G = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \tag{13}$$

and say that this has the property that  $G \times G = G$  in that for any irreps of  $\Gamma_1$  and  $\Gamma_2$  of  $D_{2h}(\text{AEM})$ , the result of  $\Gamma_1 \times \Gamma_2$  is another irrep in  $D_{2h}(\text{AEM})$ . If we now consider the case  $\ell_{\max} = 4$ , we have the character matrix

$$\begin{pmatrix} G & G & G & G \\ G & -G & G & -G \\ G & G & -G & -G \\ G & -G & -G & G \end{pmatrix}. \quad (14)$$

This is a more succinct way to write Table 3. The first row containing four irreps is 0-superscripted, labelled as in Table 3. The next four are 1-superscripted, in the same order as the corresponding 0-superscripted irreps, and so on. With this construction, for any two irreps of  $\Gamma_1$  and  $\Gamma_2$  of  $D_{4h}$ (AEM), if they have the same superscript,  $\Gamma_1 \times \Gamma_2$  will cancel the  $-$ s of the  $G$ s and the result will be an irrep of the 0-superscripted block. Moreover, this will be the same irrep one would obtain had one used the  $C_{2v}$  group. If the irreps do not have the same superscript, then we will have  $-G \times G = -G$  type multiplication whose result will be an irrep not in the 0-superscripted block. We can see that this easily generalises to any  $\ell_{\max}$ . This concludes the definition of  $D_{nh}$ (AEM). Table 6 describes how the characters for  $D_{nh}$ (AEM) are defined for an arbitrary  $n$ , although, in practice, one would use the outer product formulation to build the character table.

**Table 6.** The character table for the  $D_{nh}$ (AEM) group for some  $n$ . The character corresponding to the  $i$ th row and  $j$ th column is given by  $f(i, j) = f(j, i)$ . Here,  $k$  is given by  $k = 2^{n-2} - 1$ . Starting the row and column number from zero, the output of the function  $f$  is as follows: first,  $i$  and  $j$  are converted into binary numbers and their bitwise sum is calculated. If the number of 1s in the result is odd, character is  $-1$ ; if it is even, the character is 1. For example, 7 and 4 would be  $111 \& 100 = 100$ , so the number of 1s is 1 (odd) and, thus, the character is  $-1$ .

$D_{nh}$ (AEM)	$E^0$	$C_2^0$	$\sigma^0$	$\sigma_v^0$	...	$\sigma_v^k$
$A_1^0$	1	1	1	1		$f(4k + 3, 0)$
$B_1^0$	1	-1	1	-1		$f(4k + 3, 1)$
$A_2^0$	1	1	-1	-1		$f(4k + 3, 2)$
$B_2^0$	1	-1	-1	1		$f(4k + 3, 3)$
$\vdots$						
$B_2^k$						$f(4k + 3, 4k + 3)$

The introduced structure is similar to that of Extended molecular symmetry groups  $G$ (EM), which are used in the ro-vibrational problems of non-rigid molecules, such as hydrogen peroxide ( $H_2O_2$ ) [34] and ethane ( $C_2H_6$ ) [53].

In these cases, the group structure is

$$G(\text{EM}) = G(\text{M}) \otimes \{E, E'\} \cong G(\text{M}) \otimes Z_2 \quad (15)$$

while  $D_{nh}$ (AEM) is given by

$$Z_2 \otimes \underbrace{\dots \otimes}_{n-1} Z_2 = C_{2v} \otimes Z_2 \otimes \underbrace{\dots \otimes}_{n-3} Z_2 \quad (16)$$

which clarifies how this sort of construction would work for any arbitrary group  $G$ :

$$G \otimes Z_2 \otimes \dots \otimes Z_2. \quad (17)$$

The basis functions for these types of molecules also contain artificial, unphysical irreps. For example, the rotational or vibrational wavefunctions of  $G_{36}$ (EM), the MS group of ethane  $C_2H_6$ , can transform as odd or even under  $E'$ , labelled as  $s$  and  $d$ , respectively. Likewise, the full rotation-vibrational wavefunction can only be of  $s$  type and the artificial  $d$  types must be eliminated [53].

The artificial symmetry group that has been introduced here has been implemented in the existing structure of the TROVE program, as illustrated below.

## 2. Example of $D_{nh}$ (AEM) in Ro-Vibrational Calculations of CO<sub>2</sub> Energies with TROVE

Let us consider a ro-vibrational basis set of a centrosymmetric linear triatomic (CO<sub>2</sub>) in a symmetry adapted form (compare to Equation (3)) and a bisecting embedding [19]:

$$\Phi^\Gamma = \left\{ [\phi_{i_1}(r_1, r_2)]^{\Gamma_1} [\phi_{i_2, \ell}(\rho)]^{\Gamma_2} |J, K, m, \Gamma_{\text{rot}}\rangle \right\}^{\Gamma_{\text{tot}}},$$

where  $\Gamma$ s are the irreps,  $K = |k|$ ,  $i$ s are function labels,  $r_1$  and  $r_2$  are the equivalent stretches, and  $\rho = 180^\circ - \alpha$  with  $\alpha$  as an inter-bond angle.

Assuming a small rotational problem with  $J_{\text{max}} = 4$ , we need  $k_{\text{max}} = 4$ , and, hence,  $n = \lceil \log_2 20 \rceil = 5$  (Equation (9)). There are  $2^5 = 32$  irreps in the group  $D_{5h}$  (AEM), but our basis functions can be only one of (for  $k_{\text{max}} = 4$ )  $4(4 + 1) = 20$  irreps, and the remainder is not utilised. However, they are still necessary when combining basis functions, as was illustrated in Table 4.

The procedure works as follows: initially, the reduced Hamiltonian matrix (see Appendix A for details) for the bending motion is manually made block diagonal in  $\ell$  and the whole matrix is diagonalized. In principle, TROVE could treat these blocks separately and diagonalize each individually. However, in practice, the dimension is small enough that diagonalizing the entire matrix is computationally acceptable.

In order to obtain symmetrized (in  $D_{5h}$  (AEM)) eigenfunctions for both the bending and stretching Hamiltonians, the standard TROVE symmetrisation procedure is applied, as described in [48]. The resulting irreps are the 0-superscripted ones of  $D_{5h}$  (AEM) and they correspond to the  $C_{2v}$  (M) ones. To correctly symmetrise this way, the operation  $O^m$ , using the notation of Table 3, has the same behaviour on the coordinates as operation  $O^0$ .

Once 0-superscripted irreps are obtained, the rotational and bending wavefunctions are reassigned to the appropriate  $k$ - or  $\ell$ -superscripted irrep.

In our example,  $P_{\text{max}} = 2$ . The same polyad value is used for the symmetrized basis set.

Table 7 lists a few vibrational energies with their symmetry assignment in  $D_{5h}$  (AEM). The irreps that are generated by the bending basis functions can only be  $A_1$ , and they are assigned to  $A_1^\ell$  for a given  $\ell$ . In this case,  $\ell \leq 4$ . The stretching functions are all assigned as a 0-superscripted irrep. This ensures that, when they are combined with the bending function, the "base" irrep obtained (i.e., the letter and subscript of the irrep label) would have been the same if we had used the  $C_{2v}$  group. The only 0-superscripted irrep is the one where  $\ell = k$ , as expected, and only this would be retained from this set.

Table 8 shows the  $A_1^0$  and  $A_2^0$  states for the  $J = 2$  case. Here, we see that  $k$  ranges from 0 to 2, and the rotational irreps are superscripted accordingly. The combined stretching and bending irreps are the same as their corresponding rotational irrep and, thus, the full functions are of type  $A_1^0$  or  $A_2^0$ . It should be noted that our assignment in Tables 7 and 8 of  $K, v_1, v_2, \ell$ , and  $v_3$  is based on the largest basis set contribution approach and, therefore, can deviate from the experimental assignment of these states as formed from the corresponding analysis using effective Hamiltonian solutions.

**Table 7.** The  $J = 0$  vibrational states, including the symmetry  $\Gamma$  in  $D_{\infty h}$ (AEM) of the full state.  $v_1$ ,  $v_2$ ,  $\ell$  and  $v_3$  are the linear molecule quantum numbers of  $\text{CO}_2$ .

$\Gamma$	$E$ ( $\text{cm}^{-1}$ )	$v_1$	$v_2$	$\ell$	$v_3$
$A_1^0$	0.00	0	0	0	0
$A_1^1$	667.75	0	1	1	0
$A_1^0$	1285.40	0	2	0	0
$A_1^2$	1336.67	0	2	2	0
$A_1^0$	1388.21	1	0	0	0
$A_1^1$	1932.82	0	3	1	0
$A_1^3$	2006.73	0	3	3	0
$A_1^1$	2077.23	1	1	1	0
$B_2^0$	2349.17	0	0	0	1
$A_1^0$	2548.34	1	2	0	0
$A_1^2$	2586.55	0	4	2	0
$A_1^0$	2671.14	2	0	0	0
$A_1^4$	2677.94	0	4	4	0
$A_1^2$	2762.27	1	2	2	0
$A_1^0$	2797.16	1	2	0	0
$B_2^1$	3004.45	0	1	1	1
$A_1^1$	3181.79	1	3	1	0

**Table 8.** The  $J = 2$  ro-vibrational states including the symmetry of the full state and the symmetry of the rotational, stretching, and bending parts. The assignment of  $v_1$ ,  $v_2$ ,  $\ell$ ,  $v_3$  and  $K$  is approximate and based on the largest contribution to the eigenfunction. Only states with non-zero nuclear statistical weights are shown.

$\Gamma_{\text{tot}}$	$E$ ( $\text{cm}^{-1}$ )	$\Gamma^{\text{rot}}$	$K$	$\Gamma^{\text{stretch}}$	$\Gamma^{\text{bend}}$	$v_1$	$v_2$	$\ell$	$v_3$
$A_1^0$	2.34	$A_1^0$	0	$A_1^0$	$A_1^0$	0	0	0	0
$A_2^0$	669.71	$A_2^0$	1	$A_1^0$	$A_1^1$	0	1	1	0
$A_1^0$	1287.75	$A_1^0$	0	$A_1^0$	$A_1^0$	0	2	0	0
$A_1^0$	1337.46	$A_1^2$	2	$A_1^0$	$A_1^2$	0	2	2	0
$A_1^0$	1390.55	$A_1^0$	0	$A_1^0$	$A_1^0$	1	0	0	0
$A_2^0$	1934.78	$A_2^1$	1	$A_1^0$	$A_1^1$	0	3	1	0
$A_2^0$	2079.19	$A_2^1$	1	$A_1^0$	$A_1^1$	1	1	1	0
$A_1^0$	2550.69	$A_1^0$	0	$A_1^0$	$A_1^0$	1	2	0	0
$A_1^0$	2587.33	$A_1^2$	2	$A_1^0$	$A_1^2$	0	4	2	0
$A_1^0$	2673.48	$A_1^0$	0	$A_1^0$	$A_1^0$	2	0	0	0
$A_1^0$	2763.06	$A_1^2$	2	$A_1^0$	$A_1^2$	1	2	2	0
$A_1^0$	2799.50	$A_1^0$	0	$A_1^0$	$A_1^0$	1	2	0	0
$A_1^0$	3006.39	$B_2^1$	1	$B_2^0$	$A_1^1$	0	1	1	1
$A_2^0$	3183.76	$A_2^1$	1	$A_1^0$	$A_1^1$	1	3	1	0

### 3. Conclusions

The artificial symmetry group  $D_{\infty h}$ (AEM) introduced here was designed to take advantage of the detailed symmetry information that is available in the linear-molecule  $3N - 5$  treatment, even when the bent-molecule  $3N - 6$  approach is used. The construction of  $D_{\infty h}$ (AEM) is based on the cyclic group of order 2.  $D_{\infty h}$ (AEM) is shown to have all the properties required: basis functions with different  $\ell$  or  $k$  functions (vibrational or rotational, respectively) generate different irreducible representations of  $D_{\infty h}$ (AEM). This is a natural property for the linear molecule  $3N - 5$  treatment and we can now also employ it for quasi-linear or bent molecules treated in the  $3N - 6$  approach, but using non-degenerate irreps that are required for bent systems.

In this work, we showed that it is possible to build a symmetry group to satisfy a set of criteria required to simplify the basis set and Hamiltonian matrix elements for variational calculations. This is opposite to the usual practice, where the symmetry group, to a large extent, is dictated by the physics of the molecule itself, which, in turn, defines the computational approach. Our main criterion here is to associate the projections  $\ell$  and  $k$  with one-dimensional (1D) irreducible representations with the goal of applying a general symmetry-adapted variational approach to the ro-vibrational calculations of a linear triatomic molecule. Thus, the very specific  $k = \ell$  constraints and associated  $k$ -structured block-diagonal Hamiltonian matrix, which are typical for the  $3N - 6$  linear molecule calculations, have been formulated in terms of irreducible representation algebra, as implemented in TROVE.

The authors of this paper originally tried an alternative approach that would make use of the Extended Molecular Symmetry (EMS) Groups  $C_{\text{ov}}(\text{EMS})$  and  $D_{\text{oh}}(\text{EMS})$  of Chapter 17 of Ref. [2]. As discussed above, these groups are obtained by, among other changes, extending the MS groups  $C_s(\text{M})$  and  $C_{2v}(\text{M})$  [2] by artificial operations, such as  $C_{\infty}^{\epsilon}$ , a rotation of an arbitrary angle  $\epsilon$  about the  $a$  axis. In the resulting EMS groups  $C_{\text{ov}}(\text{EM})$  and  $D_{\text{oh}}(\text{EM})$  the vibrational basis function  $|v_1, v_2, \dots, v_{N-1}; v_N^{\ell_N}, v_{N+1}^{\ell_{N+1}}, v_{N+2}^{\ell_{N+2}}, \dots, v_{2N-3}^{\ell_{2N-3}}\rangle$  generates a  $\Sigma, \Pi, \Delta, \Phi \dots$ . Similarly,  $|J, k, m\rangle$  generates a  $\Sigma, \Pi, \Delta, \Phi \dots$  symmetry for  $k = 0, 1, 2, 3, \dots$ . See Tables 17-1 and 17-2 of Ref. [2]. The introduction of  $C_{\text{ov}}(\text{EM})$  and  $D_{\text{oh}}(\text{EM})$  was, in principle, motivated by the same ideas that inspired the present work. These groups are more closely related to actual symmetries than the results presented here, since they utilise the near-symmetry of arbitrary rotations about the  $a$  axis; the ideas of the present work are more abstract.

Despite those benefits, the present approach was taken, as it proved challenging to practically utilize  $C_{\text{ov}}(\text{EM})$  and  $D_{\text{oh}}(\text{EM})$ . Moreover, although more physically relevant, the  $C_{\text{ov}}(\text{EM})$  and  $D_{\text{oh}}(\text{EM})$  have the disadvantage that they involve the degenerate irreps  $\Pi, \Delta, \Phi \dots$ . The double degeneracy is a simple consequence of the fact that any rotation about the  $a$  axis exists in two equivalent forms, which we can call clockwise and anti-clockwise, respectively. The  $2 \times 2$  transformation matrices of these irreps are not uniquely determined and more complicated to apply than the characters of non-degenerate representations.

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## Appendix A. TROVE Calculation Details Used in the CO<sub>2</sub> Example

To construct the full ro-vibrational basis functions, first  $J = 0$  (vibrational) 1D Hamiltonians are formed for each vibrational mode by setting the other coordinates in the Hamiltonian  $\hat{H}$  at their equilibrium values. The eigenfunctions of these Hamiltonians are obtained while using the Numerov–Cooley approach [49–51] for the stretches and using an associated Legendre or Laguerre polynomial-based basis set  $L_n^{(\ell)}$  for the bend, with the number  $\ell$  having the same role as the  $\ell$  in Section 1.3. Thus, one obtains functions of the form  $\Phi_{v_1}(r_1)$ ,  $\Phi_{v_2}(r_2)$ , and  $\Phi_{v_3}^{(\ell)}(\rho)$  for the two stretching and the bending functions, respectively, and combinations of these are used as the primitive basis set. A detailed explanation can be found in Yurchenko and Mellor [19].

Once we have the 1D basis set, we can use it to ‘build up’ multi-mode basis sets. For a triatomic molecule, we diagonalize the Hamiltonian for a simplified molecule that only carries out stretching motion, described by the bond lengths  $r_1$  and  $r_2$ , in a basis of products  $\Phi_{v_1}(r_1)\Phi_{v_2}(r_2)$ , producing the symmetry-adapted eigenfunctions  $\Psi_{i_1}^{\Gamma_1}(r_1, r_2)$ . The Hamiltonian for a simplified molecule that bends and rotates about the  $a$  axis is diagonalized in a basis of functions  $\Phi_{v_3}^{(\ell=k)}(\rho)\exp(ik\chi)$ , producing the symmetry-adapted eigenfunctions  $\Psi_{i_2}^{\Gamma_2}(\rho)\exp(ik\chi)$ .

The full ro-vibrational basis functions are now of the form

$$\Psi_{i_1}^{\Gamma_1}(r_1, r_2)\Psi_{i_2}^{\Gamma_2}(\rho)|J, k, m, \pm\rangle$$

where  $|J, k, m, \pm\rangle$  are rigid symmetric-top wavefunctions (that contain the factor  $\exp(ik\chi)$ ; see Ref. [2] and the references therein), with  $k$  having the same role here as in Section 1.3.

## References

1. Tarczay, G.; Császár, A.G.; Leininger, M.L.; Klopper, W. The barrier to linearity of hydrogen sulphide. *Chem. Phys. Lett.* **2000**, *322*, 119–128. [\[CrossRef\]](#)
2. Bunker, P.R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Research Press: Ottawa, ON, Canada, 1998.
3. Hirano, T.; Nagashima, U.; Jensen, P. Bending Wavefunctions for Linear Molecules. *J. Mol. Spectrosc.* **2018**, *343*, 54–61. [\[CrossRef\]](#)
4. Watson, J.K.G. Vibration-rotation hamiltonians of linear-molecules. *Mol. Phys.* **1993**, *79*, 943–951. [\[CrossRef\]](#)
5. Carter, S.; Handy, N. On the calculation of vibration-rotation energy levels of quasi-linear molecules. *J. Mol. Spectrosc.* **1982**, *95*, 9–19. [\[CrossRef\]](#)
6. Mátyus, E.; Czakó, G.; Sutcliffe, B.T.; Császár, A.G. Vibrational energy levels with arbitrary potentials using the Eckart-Watson Hamiltonians and the discrete variable representation. *J. Chem. Phys.* **2007**, *127*, 084102. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Bowman, J.M.; Carter, S.; Huang, X.C. MULTIMODE: A code to calculate rovibrational energies of polyatomic molecules. *Intern. J. Quantum Chem.* **2003**, *22*, 533–549. [\[CrossRef\]](#)
8. Schroeder, B.; Sebald, P. High-level theoretical rovibrational spectroscopy beyond fc-CCSD(T): The C<sub>3</sub> molecule. *J. Chem. Phys.* **2016**, *144*, 044307. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Bunker, P.; Papoušek, D. The symmetry groups of linear molecules. *J. Mol. Spectrosc.* **1969**, *32*, 419–429. [\[CrossRef\]](#)
10. Chubb, K.L.; Jensen, P.; Yurchenko, S.N. Symmetry Adaptation of the Rotation-Vibration Theory for Linear Molecules. *Symmetry* **2018**, *10*, 137. [\[CrossRef\]](#)
11. Hougen, J.T.; Bunker, P.R.; Johns, J.W.C. Vibration-rotation problem in triatomic molecules allowing for a large-amplitude bending vibration. *J. Mol. Spectrosc.* **1970**, *34*, 136–172. [\[CrossRef\]](#)
12. Carter, S.; Handy, N.C. A variational method for the calculation of vibrational levels of any triatomic molecule. *Mol. Phys.* **1982**, *47*, 1445–1455. [\[CrossRef\]](#)
13. Jensen, P. The nonrigid bender Hamiltonian for calculating the rotation-vibration energy levels of a triatomic molecule. *Comp. Phys. Rep.* **1983**, *1*, 1–55. [\[CrossRef\]](#)
14. Estes, D.; Secrest, D. The vibration-rotation hamiltonian—A unified treatment of linear and nonlinear molecules. *Mol. Phys.* **1986**, *59*, 569–578. [\[CrossRef\]](#)
15. Sutcliffe, B.T.; Tennyson, J. A generalised approach to the calculation of ro-vibrational spectra of triatomic molecules. *Mol. Phys.* **1986**, *58*, 1053–1066. [\[CrossRef\]](#)
16. Sayvetz, A. The kinetic energy of polyatomic molecules. *J. Chem. Phys.* **1939**, *7*, 383–389. [\[CrossRef\]](#)
17. Hougen, J.T. Rotational energy levels of a linear triatomic molecule in a 2II electronic state. *J. Chem. Phys.* **1962**, *36*, 519–534. [\[CrossRef\]](#)
18. Howard, B.J.; Moss, R.E. The molecular hamiltonian. *Mol. Phys.* **1971**, *20*, 147–159. [\[CrossRef\]](#)

19. Yurchenko, S.N.; Mellor, T.M. Treating linear molecules in calculations of rotation-vibration spectra. *J. Chem. Phys.* **2020**, *153*, 154106. [[CrossRef](#)]
20. 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. [[CrossRef](#)]
21. 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. [[CrossRef](#)]
22. Yurchenko, S.N.; Barber, R.J.; Yachmenev, A.; Thiel, W.; Jensen, P.; Tennyson, J. A Variationally Computed  $T = 300$  K Line List for  $\text{NH}_3$ . *J. Phys. Chem. A* **2009**, *113*, 11845–11855. [[CrossRef](#)] [[PubMed](#)]
23. Yachmenev, A.; Yurchenko, S.N.; Jensen, P.; Thiel, W. A new “spectroscopic” potential energy surface for formaldehyde in its ground electronic state. *J. Chem. Phys.* **2011**, *134*, 11. [[CrossRef](#)]
24. 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. [[CrossRef](#)]
25. 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. [[CrossRef](#)]
26. Underwood, D.S.; Yurchenko, S.N.; Tennyson, J.; Jensen, P. Rotational spectrum of  $\text{SO}_3$  and theoretical evidence for the formation of sixfold rotational energy-level clusters in its vibrational ground state. *J. Chem. Phys.* **2014**, *140*. [[CrossRef](#)]
27. Al-Refaie, A.F.; Yachmenev, A.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists—VIII. A variationally computed line list for hot formaldehyde. *Mon. Not. R. Astron. Soc.* **2015**, *448*, 1704–1714. [[CrossRef](#)]
28. 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. [[CrossRef](#)]
29. Al-Refaie, A.F.; Ovsyannikov, R.I.; Polyansky, O.L.; Yurchenko, S.N.; Tennyson, J. A variationally calculated room temperature line-list for  $\text{H}_2\text{O}_2$ . *J. Mol. Spectrosc.* **2015**, *318*, 84–90. [[CrossRef](#)]
30. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Tennyson, J.; Thiel, W. Accurate ab initio vibrational energies of methyl chloride. *J. Chem. Phys.* **2015**, *142*. [[CrossRef](#)]
31. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Thiel, W. A global potential energy surface and dipole moment surface for silane. *J. Chem. Phys.* **2015**, *143*, 244317. [[CrossRef](#)] [[PubMed](#)]
32. Adam, A.Y.; Yachmenev, A.; Yurchenko, S.N.; Jensen, P. Ro-vibrational averaging of the isotropic hyperfine coupling constant for the methyl radical. *J. Chem. Phys.* **2015**, *143*, 244306. [[CrossRef](#)]
33. Owens, A.; Yurchenko, S.N.; Thiel, W.; Spirko, V. Accurate prediction of the ammonia probes of a variable proton-to-electron mass ratio. *Mon. Not. R. Astron. Soc.* **2015**, *450*, 3191–3200. [[CrossRef](#)]
34. Al-Refaie, A.F.; Polyansky, O.L.; Ovsyannikov, R.I.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists—XV. A new hot line list for hydrogen peroxide. *Mon. Not. R. Astron. Soc.* **2016**, *461*, 1012–1022. [[CrossRef](#)]
35. Underwood, D.S.; Tennyson, J.; Yurchenko, S.N.; Huang, X.; Schwenke, D.W.; Lee, T.J.; Clausen, S.; Fateev, A. ExoMol molecular line lists—XIV. The rotation-vibration spectrum of hot  $\text{SO}_2$ . *Mon. Not. R. Astron. Soc.* **2016**, *459*, 3890–3899. [[CrossRef](#)]
36. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Tennyson, J.; Thiel, W. A global ab initio dipole moment surface for methyl chloride. *J. Quant. Spectrosc. Radiat. Transf.* **2016**, *184*, 100–110. [[CrossRef](#)]
37. Owens, A.; Yurchenko, S.N.; Yachmenev, A.; Tennyson, J.; Thiel, W. A highly accurate ab initio potential energy surface for methane. *J. Chem. Phys.* **2016**, *145*. [[CrossRef](#)]
38. Owens, A.; Yachmenev, A.; Thiel, W.; Fateev, A.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists—XXIX. The rotation-vibration spectrum of methyl chloride up to 1200 K. *Mon. Not. R. Astron. Soc.* **2018**, *479*, 3002–3010. [[CrossRef](#)]
39. Mant, B.P.; Yachmenev, A.; Tennyson, J.; Yurchenko, S.N. ExoMol molecular line lists—XXVII. Spectra of  $\text{C}_2\text{H}_4$ . *Mon. Not. R. Astron. Soc.* **2018**, *478*, 3220–3232. [[CrossRef](#)]
40. Coles, P.A.; Yurchenko, S.N.; Kovacich, R.P.; Hobby, J.; Tennyson, J. A variationally computed room temperature line list for  $\text{AsH}_3$ . *Phys. Chem. Chem. Phys.* **2019**, *21*, 3264–3277. [[CrossRef](#)]
41. Mant, B.P.; Chubb, K.L.; Yachmenev, A.; Tennyson, J.; Yurchenko, S.N. The infrared spectrum of  $\text{PF}_3$  and analysis of rotational energy clustering effect. *Mol. Phys.* **2019**, *118*, e1581951. [[CrossRef](#)]
42. Tennyson, J.; Yurchenko, S.N. ExoMol: Molecular line lists for exoplanet and other atmospheres. *Mon. Not. R. Astron. Soc.* **2012**, *425*, 21–33. [[CrossRef](#)]
43. Tennyson, J.; Yurchenko, S.N. The ExoMol project: Software for computing large molecular line lists. *Int. J. Quantum Chem.* **2017**, *117*, 92–103. [[CrossRef](#)]
44. Al-Refaie, A.F.; Yurchenko, S.N.; Tennyson, J. GPU Accelerated INTensities MPI GAIN-MPI: A new method of computing Einstein-A coefficients. *Comput. Phys. Commun.* **2017**, *214*, 216–224. [[CrossRef](#)]
45. Owens, A.; Conway, E.K.; Tennyson, J.; Yurchenko, S.N. ExoMol line lists—XXXVIII. High-temperature molecular line list of silicon dioxide ( $\text{SiO}_2$ ). *Mon. Not. R. Astron. Soc.* **2020**, *495*, 1927–1933. [[CrossRef](#)]
46. Yurchenko, S.N.; Mellor, T.M.; Freedman, R.S.; Tennyson, J. ExoMol line lists—XXXIX. Ro-vibrational molecular line list for  $\text{CO}_2$ . *Mon. Not. R. Astron. Soc.* **2020**, *496*, 5282–5291. [[CrossRef](#)]
47. Campargue, A.; Solodov, A.M.; Solodov, A.A.; Yachmenev, A.; Yurchenko, S.N. Detection of electric-quadrupole transitions in water vapour near 5.4 and 2.5  $\mu\text{m}$ . *Phys. Chem. Chem. Phys.* **2020**, *22*, 12476–12481. [[CrossRef](#)]

48. Yurchenko, S.N.; Yachmenev, A.; Ovsyannikov, R.I. Symmetry adapted ro-vibrational basis functions for variational nuclear motion: TROVE approach. *J. Chem. Theory Comput.* **2017**, *13*, 4368–4381. [[CrossRef](#)] [[PubMed](#)]
49. Noumerov, B.V. A method of extrapolation of perturbations. *Mon. Not. R. Astron. Soc.* **1924**, *84*, 592–602. [[CrossRef](#)]
50. Noumeroff, B. Méthode nouvelle de la détermination des orbites et le calcul des éphémérides en tenant compte des perturbations. In *Trudy Glavnoi Rossiiskoi Astrofizicheskoi Observatorii*; Gosudarsvennoe Izdatel'stvo: Moscow, Russia, 1923; Volume 2, pp. 188–259.
51. Cooley, J.W. An Improved eigenvalue corrector formula for solving the Schrödinger equation for central fields. *Math. Comp.* **1961**, *15*, 363–374.
52. Kurzweil, H.; Stellmacher, B. *The Theory of Finite Group*; Springer: New York, NY, USA, 2004.
53. Mellor, T.M.; Yurchenko, S.N.; Mant, B.P.; Jensen, P. Transformation Properties under the Operations of the Molecular Symmetry Groups G36 and G36(EM) of Ethane H<sub>3</sub>CCH<sub>3</sub>. *Symmetry* **2019**, *11*, 862. [[CrossRef](#)]