

# Symmetry-Adapted Ro-vibrational Basis Functions for Variational Nuclear Motion Calculations: TROVE Approach

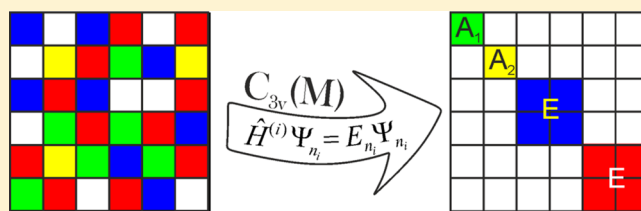
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**ABSTRACT:** We present a general, numerically motivated approach to the construction of symmetry-adapted basis functions for solving ro-vibrational Schrödinger equations. The approach is based on the property of the Hamiltonian operator to commute with the complete set of symmetry operators and, hence, to reflect the symmetry of the system. The symmetry-adapted ro-vibrational basis set is constructed numerically by solving a set of reduced vibrational eigenvalue problems. In order to assign the irreducible representations associated with these eigenfunctions, their symmetry properties are probed on a grid of molecular geometries with the corresponding symmetry operations. The transformation matrices are reconstructed by solving overdetermined systems of linear equations related to the transformation properties of the corresponding wave functions on the grid. Our method is implemented in the variational approach TROVE and has been successfully applied to many problems covering the most important molecular symmetry groups. Several examples are used to illustrate the procedure, which can be easily applied to different types of coordinates, basis sets, and molecular systems.

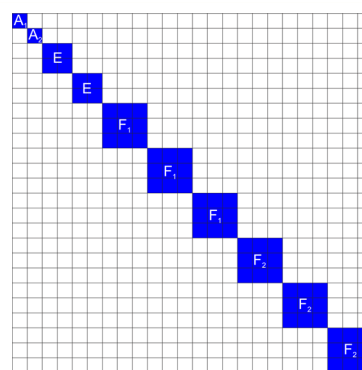


Symmetry adaptation without symmetry operations

## 1. INTRODUCTION

Symmetry plays an important role in computing ro-vibrational spectra of polyatomic molecules, particularly in variational solutions of the Schrödinger equation. Using a symmetry-adapted basis set can considerably reduce the size of the Hamiltonian matrix, depending on the symmetry group. For example, in low  $C_s$  symmetry (with inversion being the only nontrivial symmetry operation), the use of symmetric and antisymmetric basis functions reduces the matrix by a factor of 2. In higher  $\mathcal{T}_d$  symmetry, the Hamiltonian matrix is split into 10 independent blocks, of which only 5 are needed to determine the unique energies and wave functions of the molecular system (see Figure 1). For methane, which is a five-atom molecule, this is a huge advantage, considering the complexity and size of the ro-vibrational computations.<sup>1–3</sup>

If calculating only the energy levels of a molecule, a symmetry-adapted basis set is not essential and any sensible basis should lead to a physically meaningful solution. However, knowledge of the symmetry properties of the eigenvectors is vital for generating spectra, mainly due to the selection rules imposed by the nuclear spin statistics associated with different irreducible representations. Nuclear spin statistical weights give the degeneracy of the ro-vibrational states and contribute to the intensity of a transition. Importantly, some energy levels have zero weights and do not exist in nature. Without knowledge of how the eigenvectors transform under the symmetry operations, it is impossible to describe the molecular spectrum correctly. From a practical perspective, intensity calculations are also much more efficient in a symmetry-adapted representation.



**Figure 1.** Block-diagonal structure of a Hamiltonian matrix in the  $\mathcal{T}_d$  irreducible representation. The empty (white) cells indicate vanishing matrix elements. Only 5 blocks of the irreducible representations  $A_1$ ,  $A_2$ ,  $E$ ,  $F_{1a}$  and  $F_{2a}$  are needed as the other five matrices ( $E_b$ ,  $F_{1b}$ ,  $F_{1c}$ ,  $F_{2b}$ ,  $F_{2c}$ ) contain degenerate solutions.

The most common symmetry-adapted representation is the Wang basis functions, which are simply symmetric and asymmetric combinations of primitive basis functions. Such combinations are sufficient for building symmetrized basis sets for Abelian groups, which consist of one-dimensional irreducible representations only, and this is routinely done in most ro-vibrational applications. However, it is more

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challenging to symmetrize the basis set for non-Abelian groups, where the result of the group transformations involve linear combinations of basis functions and cannot be described by simple permutations. There exist only a handful of ro-vibrational methods in the literature capable of dealing with multidimensional symmetry group representations. Some examples of the variational approaches include works by Nikitin et al.,<sup>3</sup> Čejchan and Spirko,<sup>4</sup> Boudon et al.,<sup>5</sup> Yurchenko et al.,<sup>6,7</sup> Pavlyuchko et al.,<sup>8</sup> Cassam-Chenai et al.,<sup>9</sup> and Fábri et al.<sup>10</sup>

TROVE (Theoretical ROVibrational Energies)<sup>7,11</sup> is a general method and an associated Fortran 2003 program for computing ro-vibrational spectra and properties of small to medium-size polyatomic molecules of arbitrary structure. It has been applied to a large number of polyatomic species,<sup>2,11–26</sup> most of which are characterized by a high degree of symmetry ( $C_{3v}$ ,  $D_{2h}$ ,  $D_{3h}$  and  $T_d$  symmetry groups). TROVE has proven very efficient for simulating hot spectra of polyatomic molecules and is one of the main tools of the ExoMol project.<sup>27</sup> The most recent updates of TROVE have been reported in refs 28 and 29. Because of the importance of symmetry in intensity calculations, TROVE uses an automatic approach for building the symmetry-adapted basis set. In this paper, we present the TROVE symmetrization approach, which is a variation of the matrix symmetrization method.

The matrix symmetrization can be traced back to the original works by Gabriel,<sup>30</sup> Morozova and Morozov,<sup>31,32</sup> and Moccia<sup>33</sup> and was later extensively developed in a series of papers by, for example, Dellepiane et al.,<sup>34</sup> Chung and Goodman,<sup>35</sup> Bouman and Goodman,<sup>36</sup> Jordanov and Orville-Thomas,<sup>37</sup> and Chen et al.<sup>38</sup> The main idea of these studies is to use a diagonalization of matrices representing specially constructed symmetry operators. Using this technique, a symmetry adaptation can be obtained without the use of symmetry operations.<sup>37</sup> For example, Moccia<sup>33</sup> used the nuclear attraction matrix to build symmetry-adapted molecular orbitals, or a Wilson  $\mathbf{G} + \mathbf{F}^{-1}$  matrix in symmetrized force constants calculations; Dellepiane et al.<sup>34</sup> used a kinetic  $\mathbf{G}$ -matrix to obtain symmetry-adapted representations of vibrational molecular modes; Chung and Goodman<sup>35</sup> used an overlap matrix of atomic orbitals to symmetrize them. Chen et al.<sup>38</sup> proposed an “eigenfunction” method based on eigenfunctions of a linear combination of symmetry operations from the so-called complete set of commuting operators (CSCO), which was then extensively employed for constructing symmetry-adapted representations of coordinates and basis functions for (ro-)vibrational calculations.<sup>39–42</sup>

Here, we apply the idea of matrix symmetrization to the numerical construction of symmetry-adapted ro-vibrational representations of a ro-vibrational Hamiltonian  $\hat{H}$  for a general polyatomic molecule. In our version of this method, the symmetry-adapted basis functions are generated as eigenvectors of some reduced ro-vibrational Hamiltonians. These operators ( $\hat{H}^{(\text{red})}$ ) are derived from  $\hat{H}$ , such that (i) they represent different vibrational or rotational modes and (ii) they are symmetrically invariant to  $\hat{H}$ . According to the matrix symmetrization method, the eigenvectors of  $\hat{H}^{(\text{red})}$  necessarily transform according to irreducible representations (irreps) of the symmetry group.

Not only does this allow us to construct the symmetry-adapted basis functions, but it also helps to contract the basis set via standard diagonalization/truncation procedures. The relative simplicity of this procedure means it can be

straightforwardly implemented in many existing nuclear motion programs. It may also be interesting to apply the method in quantum chemical approaches, where the initial set of symmetry-adapted atomic orbitals can, for example, be constructed by diagonalizing the bare nuclear Hamiltonian.

The explanation of our method will be given in the form of practical illustrative examples, rather than using rigorous group-theoretical formalism. The paper is structured as follows: The main idea of the TROVE symmetrization approach is described in Section 2. Sections 3.1 and 3.2 present illustrative examples for  $XY_2^-$  and  $XY_3$ -type molecules. Readers interested in implementation of the method should read Section 4, where the sampling technique for reconstructing the symmetry transformation properties of vibrational wave functions is introduced, and Section 5, which details the TROVE reduction method based on the projection operator approach. A nonrigid, ammonia-type molecule  $XY_3$  of  $D_{3h}$  ( $M$ ) molecular symmetry is used as an example to illustrate this part of the method implementation. As a very special case, the degenerate multidimensional isotropic harmonic oscillator basis functions are considered in Section 5.3, with an example shown in the Appendix. Symmetrization of the rotational and total ro-vibrational basis functions is realized using standard reduction techniques, and this is discussed in Sections 5.4 and 5.5.

## 2. GENERAL DESCRIPTION OF THE METHOD

In order to introduce the TROVE symmetrization approach, we consider a general multidimensional ro-vibrational Schrödinger equation,

$$\hat{H}\Psi^{\text{rv}} = E\Psi^{\text{rv}} \quad (1)$$

which is to be solved variationally using the ro-vibrational basis set in a product form:

$$\Phi_{k,\nu}^l(\theta, \phi, \chi, q_1, q_2, \dots, q_N) = |J, k, m\rangle \phi_{n_1}(q_1) \phi_{n_2}(q_2) \dots \phi_{n_N}(q_N) \quad (2)$$

where  $\phi_{n_i}(q_i)$  is a one-dimensional (1D) vibrational function,  $n_i$  is a vibrational quantum number,  $q_i$  is a generalized vibrational coordinate,  $N$  is the number of vibrational degrees of freedom,  $|J, k, m\rangle$  are the rigid-rotor wave functions,  $k = -J, \dots, J$ , and  $m = -J, \dots, J$  are the rotational quantum numbers (projections of the total angular momentum onto the molecule-fixed  $z$  and laboratory-fixed  $Z$  axes, respectively),  $\nu$  is a generalized vibrational multi-index ( $\nu = \{n_1, n_2, \dots, n_N\}$ ). The primitive basis functions  $\phi_{n_i}(q_i) \equiv |n_i\rangle$  are any vibrational one-dimensional (1D) functions from an orthonormal set (e.g., Harmonic oscillator wave functions). In the absence of external fields,  $m$  does not play any role and can be omitted.

Let us assume that the molecule belongs to a molecular symmetry group  $\mathbf{G}$ ,<sup>43</sup> consisting of  $g$  elements (group operations)  $R$ . We aim to construct symmetry-adapted basis set functions  $\Psi_{\mu}^{J_s}$ , which transform according to irreducible representations  $\Gamma_s$  ( $s = 1, \dots, r$ ) of  $\mathbf{G}$ . Here,  $\mu$  is a counting number and  $\Gamma_s$  will be referred to as a “symmetry” or an “irrep” of  $\mathbf{G}$ . For an  $l_s$ -fold degenerate irrep, and when we will need to refer to specific degenerate components of  $\Psi_{\mu}^{J_s}$ , an additional subscript  $n = 1, \dots, l_s$  will be used as, e.g.,  $\Psi_{\mu,n}^{J_s}$ . For example, for the 2-fold degenerate  $E$  symmetry,  $n = 1$  and 2 corresponds to the  $E_a$  and  $E_b$  symmetry components, while, in case of the 3-fold degenerate  $F$  symmetry, these are  $F_a$ ,  $F_b$ , and  $F_c$ . In addition, we will require that the transformation properties of multifold irreps (e.g.,  $E$  or  $F$  representations) are known.

We now assume that the symmetry-adapted basis functions  $\Psi_{\mu,n}^{J,\Gamma_s}$  can be represented by linear combinations of the sum-of-product primitive functions from eq 2 by

$$\Psi_{\mu,n}^{J,\Gamma_s} = \sum_{k,\nu} T_{k,\nu}^{\mu,J,\Gamma_s} \Phi_{k,\nu}^J \quad (3)$$

where  $T_{k,\nu}^{\mu,J,\Gamma_s}$  are symmetrization coefficients. The important advantage of the symmetry-adapted basis set is that the corresponding Hamiltonian matrix has a block-diagonal form (see Figure 1):

$$\langle \Psi_{\mu,n}^{J,\Gamma_s} | H^{rv} | \Psi_{\mu',n'}^{J,\Gamma_s} \rangle = H_{\mu,\mu'} \delta_{s,t} \delta_{n,n'} \quad (4)$$

In practice, this means that each  $(J,\Gamma_s,n)$ -block can be diagonalized independently with  $J$  and  $(\Gamma_s,n)$  as good quantum “numbers” (i.e., constants of motion). The main goal of this work is to present a general numerical algorithm for constructing symmetrization coefficients  $T_{k,\nu}^{\mu,J,\Gamma_s}$  for a molecule of general structure and symmetry.

According with the matrix symmetrization method (see, for example, Jordanov and Orville-Thomas<sup>37</sup>), symmetry-adapted set of wave functions can be constructed by diagonalizing matrices representing some operators  $\hat{A}$ . These operators are chosen to be invariant to the symmetry operations  $R \in \mathbf{G}$ . Our approach is based on the realization that, in principle,  $\hat{H}$  itself would be an ideal choice for  $\hat{A}$ , as it has the right property to commute with any  $R$  from  $\mathbf{G}$ . [Here, we assume that there exists isomorphism between the elements  $R$  of  $\mathbf{G}$  and the corresponding representations, and use the same symbol  $R$  in both cases.]

$$[\hat{H}, R] = 0 \quad (5)$$

Indeed, the eigenfunctions of  $\hat{H}$  are also eigenfunctions of  $R$  (up to a linear combination of degenerate states) and, hence, transform as one of the irreps of the system (see, for example, the textbook by Hamermesh<sup>44</sup>). Obviously, it makes no sense to use the ro-vibrational Hamiltonian operator  $\hat{H}$  for this purpose. Instead, we define a set of reduced Hamiltonian operators  $\hat{H}^{(i)}$  derived from  $\hat{H}$  as follows:

- (i) All ro-vibrational degrees of freedom are divided into  $L$  symmetrically independent subspaces, which form subgroups of  $\mathbf{G}$ .
- (ii) For each  $i$ th subspace ( $i = 1, \dots, L$ ), a reduced Hamiltonian operator  $\hat{H}^{(i)}$  is constructed by neglecting or integrating over all other degrees of freedom.
- (iii) The symmetry-adapted wave functions for each  $i$ th subspace are obtained by diagonalizing the corresponding  $\hat{H}^{(i)}$ .
- (iv) The total basis set is built as a direct product of the subspace bases and then transformed to irreps, using standard reduction approaches.

Symmetrically independent subspaces of coordinates are selected such that each subspace contains only the coordinates related by symmetry operations of the group. For example, the vibrational motion of a molecule  $XY_2$  spanning the molecular symmetry group  $C_{2v}(\mathbf{M})$  can be described by two stretching and one bending mode, which transform independently and can thus be separated into two subspaces. More specifically, the bond lengths  $r_1$  ( $X-Y_1$ ) and  $r_2$  ( $X-Y_2$ ) are two stretching vibrational modes connected through symmetry transformations of the group  $C_{2v}(\mathbf{M})$ , which form subspace 1, while the

interbond angle  $\alpha$  ( $Y_1-X-Y_2$ ) belongs to subspace 2, with the transformation properties shown in Table 1.

**Table 1. Transformation Properties of the Internal Coordinates  $r_1$ ,  $r_2$ , and  $\alpha$  of an  $XY_2$ -Type Molecule and the Characters of the Irreps of the  $C_{2v}(\mathbf{M})$  Group**

coordinate	$E$	(12)	$E^*$	(12)*
$r_1$	$r_1$	$r_2$	$r_1$	$r_2$
$r_2$	$r_2$	$r_1$	$r_2$	$r_1$
$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$
irrep $\Gamma$	characters $\chi$			
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	-1	1
$B_2$	1	-1	1	-1

To explore eq 5 for constructing a symmetry-adapted basis, we define and solve a set of eigenvalue problems for reduced Hamiltonian operators  $\hat{H}^{(i)}$ . For each subspace  $i$  ( $i = 1, \dots, L$ ), a reduced eigenvalue problem is given by

$$\hat{H}^{(i)}(\mathbf{Q}^{(i)})\Psi_{\lambda_i}^{(i)}(\mathbf{Q}^{(i)}) = E_{\lambda_i}\Psi_{\lambda_i}^{(i)}(\mathbf{Q}^{(i)}) \quad (6)$$

where  $\mathbf{Q}^{(i)}$  is a set of coordinates  $\{q_{i1}, q_{i2}, \dots\}$  from a given subspace  $i$ ,  $E_{\lambda_i}$  is an eigenvalue associated with the eigenfunction  $\Psi_{\lambda_i}^{(i)}$  and  $\lambda_i$  counts all the solutions from the subspace  $i$ . The resulting solutions  $\Psi_{\lambda_i}^{(i)}$  should transform according with an irrep  $\Gamma_s$  of  $\mathbf{G}$  and one of its degenerate components  $n$  (holds for  $l_s > 1$ ). To indicate the symmetry of the wave function where necessary the notation  $\Psi_{\lambda_i}^{(i),\Gamma_s}$  will be used, or even  $\Psi_{\lambda_i,n}^{(i),\Gamma_s}$  to further specify its degenerate components.

The reduced Hamiltonian  $\hat{H}^{(i)}$  is constructed by averaging the total vibrational ( $J = 0$ ) Hamiltonian  $\hat{H}$  on the “ground state” primitive vibrational basis functions  $\phi_n(q_s) = |n_s\rangle$  from other subspaces ( $\{s\} \notin \{i\}$ ), as given by

$$\hat{H}^{(i)}(\mathbf{Q}^{(i)}) = \langle 0_p | \langle 0_q | \dots \langle 0_r | \hat{H} | 0_r \rangle \dots | 0_q \rangle | 0_p \rangle \quad (7)$$

where  $|0_s\rangle$  is a primitive basis function  $\phi_n(q_s)$  with  $n_s = 0$  and  $\{p,q,r\}$  are coordinates from other subspaces, i.e.,  $\{p,q,r\} \notin \{i\}$ .

For example, in the case of an  $XY_2$  molecule, the two reduced Hamiltonian operators can be formed as

$$\hat{H}^{(1)}(r_1, r_2) = \langle 0_3 | \hat{H} | 0_3 \rangle \quad (8)$$

$$\hat{H}^{(2)}(\alpha) = \langle 0_1 | \langle 0_2 | \hat{H} | 0_2 \rangle | 0_1 \rangle \quad (9)$$

where  $\mathbf{Q}^{(1)} = \{r_1, r_2\}$  and  $\mathbf{Q}^{(2)} = \{\alpha\}$  define the partitioning of the three coordinates into two subspaces  $i = 1$  and 2.

Equation 6 represents the main idea of the method, which will be referred to as TROVE symmetrization: since  $\hat{H}^{(i)}$  commutes with any  $R \in \mathbf{G}$ , the eigenfunctions  $\Psi_{\lambda_i}^{(i)}(\mathbf{Q}^{(i)})$  must necessarily span one of the irreducible representations  $\Gamma_s$  of the group  $\mathbf{G}$ . By solving eq 6, not only do we get a more compact basis set representation which can be efficiently contracted, following the diagonalization/truncation approach, it is also automatically symmetrized. The total vibrational basis set is then constructed as a direct product of  $L$  symmetrically adapted basis sets, followed by a reduction to irreducible representations using standard projection operator techniques (see, for example, ref 43). The major advantage of this

symmetrization approach is that it can be formulated as a purely numerical procedure, which is particularly valuable for handling the algebra of symmetry transformations to describe high vibrational excitations. The required components (Hamiltonian matrices and eigensolvers) are readily available in any variational program and thus the implementation of the present approach into a variational ro-vibrational calculation should be relatively straightforward.

However, there are two major problems to overcome: (i) Even though we know that  $\Psi_{\lambda}^{(i)}$  from eq 6 should transform as an irrep  $\Gamma_s$ , we do not automatically know which one, except for trivial one-dimensional subspaces; (ii) the degenerate solutions (e.g., for  $\Gamma_s = E, F, G, \Gamma_s, \dots$ ) are usually represented by arbitrary mixtures of the degenerate components and do not necessarily transform according to standard irreducible transformation matrices (see also examples below). The latter is a common problem of degenerate solutions, since any linear combination of degenerate eigenfunctions is also an eigenfunction. For example, when TROVE solves eq 6 by a direct diagonalization using one of the numerical linear algebra libraries (e.g., DSYEV from LAPACK), the degenerate eigenfunctions come out as unspecified mixtures of degenerate components. In Section 5, we will demonstrate that a general reduction scheme can be used to recast the degenerate mixtures, such that they follow the standard transformation properties upon the group operations. Note that the eigenvalue symmetrization method by Lemus,<sup>40,42</sup> can, in principle, be used to resolve the degenerate components by constructing a proper complete set of commuting operators.

### 3. EXAMPLES

**3.1. Vibrational Basis Set for  $XY_2$ -Type Molecules.** In order to demonstrate how TROVE symmetrization based on eq 6 works, we again consider an  $XY_2$  triatomic molecule. It spans the Abelian group  $C_{2v}(\mathcal{M})$  with well-known symmetry-adapted combinations of vibrational basis functions given by

$$\Phi_{n_1, n_2, n_3}^{A_1} = \frac{1}{\sqrt{2}} [\phi_{n_1}(r_1)\phi_{n_2}(r_2) + \phi_{n_2}(r_1)\phi_{n_1}(r_2)]\phi_{n_3}(\alpha) \quad n_1 \neq n_2 \quad (10)$$

$$\Phi_{n_1, n_2, n_3}^{B_2} = \frac{1}{\sqrt{2}} [\phi_{n_1}(r_1)\phi_{n_2}(r_2) - \phi_{n_2}(r_1)\phi_{n_1}(r_2)]\phi_{n_3}(\alpha) \quad n_1 \neq n_2 \quad (11)$$

$$\Phi_{n, n, n_3}^{A_1} = \phi_n(r_1)\phi_n(r_2)\phi_{n_3}(\alpha) \quad n_1 = n_2 \equiv n \quad (12)$$

where  $A_1$  and  $B_2$  are two irreducible representations of  $C_{2v}(\mathcal{M})$  (see Table 1). The “irreducible” functions  $\Phi_{n_1, n_2, n_3}^{A_1}$  and  $\Phi_{n_1, n_2, n_3}^{B_2}$  are also eigenfunctions of the group operators  $R = \{E, (12), E^*, (12)^*\}$ , e.g.,

$$(12)\Phi_{\nu}^{A_1} = \Phi_{\nu}^{A_1} \quad (13)$$

$$(12)\Phi_{\nu}^{B_2} = -\Phi_{\nu}^{B_2} \quad (14)$$

Here,  $\nu$  stands for  $\{n_1, n_2, n_3\}$ . The transformation of the “reducible” primitive functions  $|n_1\rangle|n_2\rangle|n_3\rangle = \phi_{n_1}(r_1)\phi_{n_2}(r_2)\phi_{n_3}(\alpha)$  (for  $n_1 \neq n_2$ ), that are not eigenfunctions of  $R = (12)$ , involves two different states:

$$(12)|n_1\rangle|n_2\rangle|n_3\rangle = |n_2\rangle|n_1\rangle|n_3\rangle \quad (15)$$

$$(12)|n_2\rangle|n_1\rangle|n_3\rangle = |n_1\rangle|n_2\rangle|n_3\rangle \quad (16)$$

Now we derive irreducible combinations of  $|n_1\rangle|n_2\rangle|n_3\rangle$ , using the numerical approach of eq 6. As an example, here, we use the vibrational wave functions of the  $H_2S$  molecule obtained variationally with TROVE based on the potential energy surface from ref 45. However, note that any computational approach using the same coordinates would essentially give equivalent expansions. We construct the matrix representations of the reduced Hamiltonians in eqs 8 and 9 based on the 1D functions  $\phi_{n_1}(r_1)$ ,  $\phi_{n_2}(r_2)$ , and  $\phi_{n_3}(\alpha)$  determined using the Numerov–Cooley approach,<sup>46,47</sup> as described in ref 7. For the sake of simplicity, we use a small basis set limited by the polyad number  $P_{\max} = 2$ , as given by

$$P = n_1 + n_2 + n_3 \leq P_{\max}$$

After solving the reduced eigenvalue problem for  $\hat{H}^{(1)}$  (eq 8), the following variational wave functions were obtained:

$$\Psi_1^{(1)}(r_1, r_2) = 0.999999|0, 0\rangle + 0.0000548(|0, 1\rangle + |1, 0\rangle) + \dots \quad (17)$$

$$\Psi_2^{(1)}(r_1, r_2) = 0.0000775|0, 0\rangle - 0.7071066(|0, 1\rangle + |1, 0\rangle) + \dots \quad (18)$$

$$\Psi_3^{(1)}(r_1, r_2) = -0.7071068(|0, 1\rangle - |1, 0\rangle) + \dots \quad (19)$$

where we have used a shorthand notation  $|n_1, n_2\rangle = |n_1\rangle|n_2\rangle$ . When compared to eqs 10 and 11, the eigenfunctions  $\Psi_{\lambda}^{(1)}$  have the expected symmetrized form and are classified according to the  $A_1$  and  $B_2$  irreps, i.e., as  $\Psi_1^{(1), A_1}$ ,  $\Psi_2^{(1), A_1}$ , and  $\Psi_3^{(1), B_2}$ . Thus, the expansion coefficients  $T_{k, \nu, n}^{j, \Gamma_s} = T_{\{n_1, n_2\}}^{j, \Gamma_s}$  in eq 3 are obtained numerically without any assumption on the symmetries. Here,  $J, k = 0$  (rotational indices) and  $n = 1$  (degenerate component) are omitted for simplicity and  $\nu = \{n_1, n_2\}$ . The numerical error of the symmetrization can be assessed by comparing eqs 17–19 to eqs 10 and 11. For example, the differences between  $T_{\{1, 0\}}^{1, A_1}$  and  $T_{\{0, 1\}}^{1, A_1}$ , between  $T_{\{1, 0\}}^{2, A_1}$  and  $T_{\{0, 1\}}^{2, A_1}$ , and between  $T_{\{1, 0\}}^{3, B_2}$  and  $-T_{\{0, 1\}}^{3, B_2}$  are found to be within  $10^{-15}$ .

Increasing the size of the basis set (using larger  $P_{\max}$ ) will lead to analogous expansions involving symmetrized contributions from higher excitations  $|n_1, n_2\rangle$ . The new reduced wave functions  $\Psi_{\lambda}^{(1), \Gamma_s}(r_1, r_2)$ , together with  $\Psi_{\lambda}^{(2), \Gamma_s}(\alpha)$  (eigenfunctions of  $H^{(2)}$  in eq 9) are utilized to build the new contracted and symmetrized basis set, which is then used to diagonalize the complete Hamiltonian  $\hat{H}$ . In this simple example, the symmetry properties of the expansion coefficients, as well as of the corresponding wave functions, are trivial. However, our goal is to develop a general numerical symmetrization algorithm applicable to arbitrary basis sets, coordinates, symmetries or molecules, which is also consistent with the TROVE ideology of a general, black-box like program. As will be demonstrated below, the advantage of our automatic symmetry classification method becomes more pronounced for larger molecules with more complicated symmetry, especially for those containing degenerate representations.

**3.2. Tetratomics of the  $XY_3$ -type,  $C_{3v}$  Symmetry.** Here we present another example of a rigid pyramidal tetratomic molecule  $XY_3$ , characterized by the  $C_{3v}(\mathcal{M})$  molecular symmetry group. We choose six internal coordinates as  $\Delta r_1, \Delta r_2, \Delta r_3$  (bond length displacements) and  $\Delta \alpha_{12}, \Delta \alpha_{13}, \Delta \alpha_{23}$  (the interbond angle displacements). The associated permutation symmetry operations and characters of  $C_{3v}(\mathcal{M})$  are collected in Table 2. These coordinates, as well as the

**Table 2.** Character Table and Transformation of the Internal Coordinates of an XY<sub>3</sub>-Type Molecule by the Symmetry Operations of the Molecular Symmetry Group C<sub>3v</sub>(M)<sup>43</sup>

variable	<i>E</i>	(123)	(321)	(23)*	(13)*	(12)*
<i>r</i> <sub>1</sub>	<i>r</i> <sub>1</sub>	<i>r</i> <sub>3</sub>	<i>r</i> <sub>2</sub>	<i>r</i> <sub>1</sub>	<i>r</i> <sub>3</sub>	<i>r</i> <sub>2</sub>
<i>r</i> <sub>2</sub>	<i>r</i> <sub>2</sub>	<i>r</i> <sub>1</sub>	<i>r</i> <sub>3</sub>	<i>r</i> <sub>3</sub>	<i>r</i> <sub>2</sub>	<i>r</i> <sub>1</sub>
<i>r</i> <sub>3</sub>	<i>r</i> <sub>3</sub>	<i>r</i> <sub>2</sub>	<i>r</i> <sub>1</sub>	<i>r</i> <sub>2</sub>	<i>r</i> <sub>1</sub>	<i>r</i> <sub>3</sub>
<i>α</i> <sub>23</sub>	<i>α</i> <sub>23</sub>	<i>α</i> <sub>12</sub>	<i>α</i> <sub>13</sub>	<i>α</i> <sub>23</sub>	<i>α</i> <sub>12</sub>	<i>α</i> <sub>13</sub>
<i>α</i> <sub>13</sub>	<i>α</i> <sub>13</sub>	<i>α</i> <sub>23</sub>	<i>α</i> <sub>12</sub>	<i>α</i> <sub>12</sub>	<i>α</i> <sub>13</sub>	<i>α</i> <sub>23</sub>
<i>α</i> <sub>12</sub>	<i>α</i> <sub>12</sub>	<i>α</i> <sub>13</sub>	<i>α</i> <sub>23</sub>	<i>α</i> <sub>13</sub>	<i>α</i> <sub>23</sub>	<i>α</i> <sub>12</sub>
Characters						
Irrep Γ	<i>E</i>	(123)	(23)*			
A <sub>1</sub>	1	1	1			
A <sub>2</sub>	1	1	-1			
<i>E</i>	2	-1	0			

corresponding 1D primitive basis functions  $|n_i\rangle$  ( $i = 1, \dots, 6$ ), form two subspaces that transform independently: subspace 1 is  $\{\Delta r_1, \Delta r_2, \Delta r_3\}$  and subspace 2 is  $\{\Delta\alpha_{12}, \Delta\alpha_{13}, \Delta\alpha_{23}\}$ . We assume that  $|n_1\rangle, |n_2\rangle$ , and  $|n_3\rangle$  are the 1D stretching basis functions of  $\Delta r_1, \Delta r_2$ , and  $\Delta r_3$ , respectively, and  $|n_4\rangle, |n_5\rangle$ , and  $|n_6\rangle$  are the 1D bending functions of  $\Delta\alpha_{12}, \Delta\alpha_{13}$ , and  $\Delta\alpha_{23}$ , respectively. The two reduced Schrödinger equations for subspaces 1 and 2 are given by

$$\begin{aligned}\hat{H}_{\text{str}}^{(1)}\Psi_{\lambda_1}^{(1)} &= E_{\lambda_1}\Psi_{\lambda_1}^{(1)} \\ \hat{H}_{\text{bnd}}^{(2)}\Psi_{\lambda_2}^{(2)} &= E_{\lambda_2}\Psi_{\lambda_2}^{(2)}\end{aligned}\quad (20)$$

where the reduced 3D Hamiltonian operators  $\hat{H}_{\text{str}}^{(1)}$  and  $\hat{H}_{\text{bnd}}^{(2)}$  are obtained by vibrationally averaging the total vibrational Hamiltonian  $\hat{H}^{\text{6D}}$  over the ground-state basis functions from subspace 2 and subspace 1, respectively:

$$\begin{aligned}\hat{H}_{\text{str}}^{(1)}(\Delta r_1, \Delta r_2, \Delta r_3) &= \langle 0_4 | \langle 0_5 | \langle 0_6 | \hat{H}^{\text{6D}} | 0_6 \rangle | 0_5 \rangle | 0_4 \rangle \\ \hat{H}_{\text{bnd}}^{(2)}(\Delta\alpha_{12}, \Delta\alpha_{13}, \Delta\alpha_{23}) &= \langle 0_1 | \langle 0_2 | \langle 0_3 | \hat{H}^{\text{6D}} | 0_3 \rangle | 0_2 \rangle | 0_1 \rangle\end{aligned}\quad (21)$$

The C<sub>3v</sub>(M) group spans the  $\Gamma_s = A_1, A_2$ , and *E* representations, where *E* is 2-fold. Following the discussion above, we expect the resulting wave functions  $\Psi_{\lambda_i}^{(i)}$  to be eigenfunctions of all six symmetry operators *R* of C<sub>3v</sub>(M) from Table 2, i.e., to transform according to A<sub>1</sub>, A<sub>2</sub>, or *E*.

The illustration below is based on the TROVE program again; however, it should be transferable, at least in principle, to any method (i.e., any basis set, kinetic energy operator or potential energy function), as long as a similar choice of vibrational coordinates and a product basis of 1D wave functions are used. We choose the PH<sub>3</sub> molecule and construct the symmetrized basis set in TROVE using a polyad number cutoff, given by

$$P = 2(n_1 + n_2 + n_3) + n_4 + n_5 + n_6 \leq P_{\text{max}} = 10$$

in conjunction with the potential energy surface (PES) of Sousa-Silva et al.<sup>15</sup> The 1D basis set functions are generated using the Numerov-Cooley procedure as described in ref. 15, where the details on the kinetic energy expansion and the vibrational coordinates can also be found. In practice, we usually choose the maximal polyad number  $P_{\text{max}}$  in the order of 14–20 (see, for example, refs 15 and 48–50).

The basis set for subspace 1 (stretching) in this case contains only functions with  $n_1 + n_2 + n_3 \leq 5$  and  $n_4 = n_5 = n_6 = 0$ , while subspace 2 (bending) basis functions are constructed from the contributions  $n_4 + n_5 + n_6 \leq 10$  and  $n_1 = n_2 = n_3 = 0$ . The first four variational eigenfunctions of  $\hat{H}_{\text{str}}^{(1)}$  read (where the shorthand notation  $|n_1, n_2, n_3\rangle \equiv |n_1\rangle|n_2\rangle|n_3\rangle$  is used)

$$\begin{aligned}\Psi_1^{(1)} &= 0.9997|0, 0, 0\rangle - 0.128|1, 0, 0\rangle + |0, 1, 0\rangle + |0, 0, 1\rangle + \dots \\ \Psi_2^{(1)} &= 0.0223|0, 0, 0\rangle - 0.57689|1, 0, 0\rangle + |0, 1, 0\rangle + |0, 0, 1\rangle + \dots \\ \Psi_{3,1}^{(1)} &= 0.50667|0, 0, 1\rangle - 0.80753|0, 1, 0\rangle + 0.30086|1, 0, 0\rangle + \dots \\ \Psi_{3,2}^{(1)} &= 0.63993|0, 0, 1\rangle + 0.11883|0, 1, 0\rangle - 0.75875|1, 0, 0\rangle + \dots\end{aligned}\quad (22)$$

corresponding to the energy term values 0.0, 2317.86, 2328.28, and 2328.28 cm<sup>-1</sup>, respectively, relative to the zero-point-energy (ZPE) of 5222.59 cm<sup>-1</sup> (the actual coefficients are calculated in double precision). In fact, we find that high numerical accuracy is important for numerically reconstructing the symmetries of the eigensolutions. The first two wave functions  $\Psi_1^{(1)}$  and  $\Psi_2^{(1)}$  in eq 22 exhibit fully symmetric forms (to  $\sim 10^{-15}$ ) and thus belong to A<sub>1</sub>. The symmetry of the solutions  $\Psi_{3,1}^{(1)}$  and  $\Psi_{3,2}^{(1)}$  cannot be immediately recognized from their expansion coefficients, but the coinciding energy levels (within the numerical error of  $\sim 10^{-15}$ ) indicate a degenerate solution, which, for the case of C<sub>3v</sub>(M), can only mean the *E* symmetry. For these two states, we use the subscript notation  $\lambda, n$  to refer to two degenerate components ( $n = 1, 2$ ) of the degenerate state  $\lambda = 3$ .

Thus, all four wave functions (as well as other solutions not shown here) appear readily symmetrized. However, guessing the degenerate *E* symmetries based on the degeneracy of energies, which worked here, is not always reliable in actual numerical calculations. For example, accidentally close energies (accidental resonances) are common for high excitations. Moreover, some reduced Hamiltonian operators can lead to degenerate solutions of arbitrary order, such as, for example, harmonic oscillator or rigid rotor Hamiltonians. The A<sub>2</sub> states as single energy solutions can be also easily mixed up with A<sub>1</sub>.

Finally, the degenerate components are usually come out of diagonalizations as arbitrary degenerate mixtures. For example, the eigenfunctions  $\Psi_{3,1}^{(1)}$  and  $\Psi_{3,2}^{(1)}$  from eq 22 were obtained using the eigen-solver DSYEV (LAPACK). As a result, they do not necessarily obey the standard *E*-symmetry irreducible transformation rules: for example, the D[(123)] transformation (which represents the C<sub>3</sub> rotation about the axis of symmetry) does not transform the two *E*-symmetry components ( $\Psi_{3,1}^{(1)}, \Psi_{3,2}^{(1)}$ ), according to the transformation

$$D[(123)] = \begin{pmatrix} \cos \varepsilon & \sin \varepsilon \\ -\sin \varepsilon & \cos \varepsilon \end{pmatrix}$$

with  $\varepsilon = 2\pi/3$ , as one would expect. In principle, such functions with randomly mixed components would still lead to a block-diagonal representation of the Hamiltonian matrix, as in eq 4, and thus does not seem to be a problem. However, having the functions  $\Psi_{\lambda_i, n}^{(i)}$ , which transform according to standard transformation rules, is very useful for reducing the direct products of the corresponding irreducible representations. Therefore, these randomly mixed degenerate components must be further recast by a proper linear transformation to the standard form, which will be referenced as standard representations.

To conclude this section, the matrix symmetrization method based on reduced Hamiltonian operators can be efficiently used to produce a symmetry-adapted basis set in fully numerical fashion. However, the method does not indicate which irreps these functions belong to and, consequently, which symmetry properties they have; besides, the degenerate components are mixed by an arbitrary orthogonal transformation, which makes it difficult to use in subsequent calculations. This is where the second step of our symmetrization procedure—namely, the symmetry sampling—comes in.

#### 4. SYMMETRY SAMPLING OF THE EIGENFUNCTIONS

In this section, we show how to reconstruct the symmetries  $\Gamma_s$  of the eigenfunctions  $\Psi_{\lambda,n}^{(i)}$  from eq 6 by analyzing their transformation properties and also how to bring their degenerate components  $n$  into the “standard” form. Toward this end, we select a grid of  $N_{\text{grid}}^{(i)}$  instantaneous sampling geometries and use them to probe the values of the eigenfunctions  $\Psi_{\lambda,n}^{(i)}$ , as well as of their symmetry-related images. That is, for a given subspace  $i$  and selected instantaneous geometries  $\mathbf{Q}_k^{(i)}$  ( $k = 1, \dots, N_{\text{grid}}^{(i)}$ ), all symmetry-related images  $R\mathbf{Q}_k^{(i)}$  are generated. These are used to reconstruct the values of the wave functions  $\Psi_{\lambda,n}^{(i)}(R\mathbf{Q}_k^{(i)})$  at the new geometries, and to establish the transformation matrices  $\mathbf{D}[R]$  for each operation  $R$  of the group  $\mathbf{G}$ . This is different from the more common practice of directly exploring the permutational properties of the wave functions. At this point, it might appear that permuting the wave functions would be easier, at least for the case of  $|n_1\rangle |n_2\rangle |n_3\rangle$  in our example of the rigid  $XY_3$  molecule. However, as will be shown below, applying the group transformations to the coordinates instead of the basis functions provides a more general numerical approach applicable to complex cases when the permutation symmetry properties of the wave functions are not obvious.

Let us consider an  $l_\lambda$ -fold degenerate eigenstate  $\lambda$  with  $l_\lambda$  eigenfunctions  $\Psi_{\lambda,n}^{(i)}$  ( $n = 1, \dots, l_\lambda$ ) from a subspace  $i$ , and define a grid of randomly selected geometries  $\mathbf{Q}_k^{(i)}$  ( $k = 1, \dots, N_{\text{grid}}^{(i)}$ ). We assume that the transformation properties of the coordinates from a given subspace, with respect to  $R$ , are known at any specific point  $k$ . This can be expressed as

$$R\mathbf{Q}_k^{(i)} = \mathbf{Q}_k^{\prime(i)} \quad (23)$$

with each subspace being independent from the others by definition. Under the assumption that the eigenfunctions  $\Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)})$  can be evaluated at any grid point  $k$ , i.e., at any instantaneous geometry  $\mathbf{Q}_k^{(i)}$ , including their symmetry-related images  $\mathbf{Q}_k^{\prime(i)}$  (which is true for the TROVE program), we can evaluate

$$\Psi_{\lambda,n}^{(i)}(k) \equiv \Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)}) \quad (24)$$

$$\Psi_{\lambda,m}^{\prime(i)}(k) \equiv R\Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)}) = \Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{\prime(i)})$$

where  $\mathbf{Q}'$  and  $\Psi'$  are the transformed coordinates and functions, respectively. The eigenfunctions  $\Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)})$  and their symmetric images  $R\Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)})$  are also related via the transformation matrices, as given by

$$R\Psi_{\lambda,m}^{(i)}(\mathbf{Q}_k^{(i)}) = \sum_{n=1}^{l_\lambda} D[R]_{mn} \Psi_{\lambda,n}^{(i)}(\mathbf{Q}_k^{(i)}) \quad (25)$$

Note that we are using the convention by Bunker and Jensen<sup>43</sup> to define the operations  $R$  on the nuclear coordinates

and functions. This convention is also referred to as passive (see, e.g., a detailed discussion by Alvarez-Bajo et al.<sup>41</sup>). For instance, for the  $E$ -symmetry wave functions from eq 22, this expression reads

$$\begin{pmatrix} \Psi_{3,1}^{\prime(1)}(k) \\ \Psi_{3,2}^{\prime(1)}(k) \end{pmatrix} = R \begin{pmatrix} \Psi_{3,1}^{(1)}(k) \\ \Psi_{3,2}^{(1)}(k) \end{pmatrix} = \begin{pmatrix} D_{11}[R] & D_{12}[R] \\ D_{21}[R] & D_{22}[R] \end{pmatrix} \begin{pmatrix} \Psi_{3,1}^{(1)}(k) \\ \Psi_{3,2}^{(1)}(k) \end{pmatrix} \quad (26)$$

Note that the linear system in eq 25 does not impose the condition of unitariness of the solution. As a result, the matrices  $D[R]_{mn}$  can be nonorthogonal and must be orthogonalized, for which the Gram–Schmidt approach is employed.

Now, by combining eqs 24 and 25, we obtain

$$\sum_{n=1}^{l_\lambda} D[R]_{mn} \Psi_{\lambda,n}^{(i)}(k) = \Psi_{\lambda,m}^{\prime(i)}(k) \quad (27)$$

The  $(l_\lambda)^2$  elements  $D[R]_{mn}$  can be determined by solving eq 27 as a system of  $N_{\text{grid}}^{(i)}$  linear equations ( $k = 1, \dots, N_{\text{grid}}^{(i)}$ ) of the type

$$\sum_n A_{kn} x_n^{(m)} = b_k^{(m)} \quad (28)$$

Here, the matrix elements  $A_{kn} = \Psi_{\lambda,n}^{(i)}(k)$  and the vector coefficients  $b_k^{(m)} = \Psi_{\lambda,m}^{\prime(i)}(k)$  are known, while  $x_n^{(m)} = D[R]_{nm}$  are the unknown quantities. Once the system of  $N_{\text{grid}}^{(i)}$  linear equations given in eq 28 is solved for each  $R$  and all the  $g$  transformation matrices  $\mathbf{D}[R]$  are found ( $g$  is the group order), we apply the standard projection operator approach<sup>43</sup> to generate the irreducible representations (see Section 5).

The number of degenerate reducible states  $l_\lambda$  is simply taken as the number of states with the same energies. For nondegenerate wave functions ( $l_\lambda = 1$ ), the sampling procedure will always produce  $D[R]_{1,1} = \chi[R] = \pm 1$ . Accidental degeneracies (e.g.,  $A_1/A_2$  with identical energies) are processed as if they were normal degenerate components. In this case, the resulting matrices are diagonal,  $D[R]_{ii} = \pm 1$  and  $D[R]_{ij} = 0$  ( $i \neq j$ ).

At least  $N_{\text{grid}}^{(i)} = (l_\lambda)^2$  grid points are required to define the linear system (or even less due to the unitary property of the transformation matrices). In practice, it is difficult to find a proper set of geometries with all values of  $\Psi_{\lambda,n}^{(i)}(k)$  and  $\Psi_{\lambda,m}^{\prime(i)}(k)$  large enough to make the solution of the linear system numerically stable (i.e., with nonvanishing determinant). Therefore, we have a tendency to select more points ( $N_{\text{grid}}^{(i)} \gg (l_\lambda)^2$ ) and thus solve an overdetermined linear system using the singular value decomposition method implemented in the DGELSS (LAPACK) numerical procedure. We usually take  $N_{\text{grid}}^{(i)} = 10\text{--}200$  geometries  $\mathbf{Q}_k$  randomly distributed within the defined coordinate ranges around the equilibrium geometry of the molecule.

This symmetrization procedure can be applied to any primitive functions, provided their values can be calculated at any instantaneous geometry. For example, the commonly used basis functions in TROVE are 1D eigensolutions of a reduced 1D Hamiltonian determined, using the Numerov–Cooley procedure and defined on an equidistant grid of geometries, typically of  $\sim 1000$  points. In this case, the values of the primitive functions  $\phi_{n_k}(q_k)$  in eq 2 are obtained by interpolation using the POLINT procedure.<sup>51</sup> Other popular basis sets in TROVE are harmonic oscillator and rigid rotor wave functions,

for which the details of the symmetrization procedure are presented below.

## 5. PROJECTION TECHNIQUE AND SYMMETRY CLASSIFICATION

Because of the accidental degeneracies and, even more so, the intrinsic degeneracies imposed by some reduced Hamiltonians (e.g., Hamiltonian of isotropic Harmonic oscillators), it is common to address degenerate solutions of eq 6 of high order, which can be much higher than that of the corresponding irreducible representations. For example, the Hamiltonian of the 2D harmonic isotropic oscillator,<sup>43</sup>

$$\hat{H}^{2D} = \frac{1}{2}[P_a^2 + P_b^2 + \lambda(Q_a^2 + Q_b^2)]$$

has the eigenvalues

$$E_{v_a, v_b}^{2D} = \hbar\sqrt{\lambda}[v_a + v_b + 1]$$

which are  $(v_a + v_b + 1)$ -fold degenerate. As previously discussed, our numerical symmetrization approach often leads to arbitrarily mixed degenerate representations, which must be further transformed to the standard orthogonal form. In the following, we show how to use the standard projection technique to symmetrize such general cases in a fully numerical fashion.

In order to reduce a representation  $\Gamma_{\text{red}}$  to its irreducible components,

$$\Gamma_{\text{red}} = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus a_3\Gamma_3 \oplus \dots \oplus a_h\Gamma_h \quad (29)$$

the first step is to use the characters  $\chi[R]$  of the reducible representation as traces of the transformation matrices  $D[R]_{mm}$ :

$$\chi[R] = \sum_n D[R]_{nn}$$

and find the number of irreducible representations  $a_s$  (reduction coefficients) for each irreps  $\Gamma \in \mathbf{G}$ , as given by

$$a_s = \frac{1}{g} \sum_R \chi[R]^* \chi^{\Gamma_s}[R] \quad (30)$$

Remember that  $g$  is the order of the group,  $R$  runs over all the elements of the group, and  $\chi^{\Gamma}[R]$  are the group characters. To ensure the numerical stability of the symmetrization we usually check if these reduction coefficients are (i) integral and (ii) satisfy the reduction relations<sup>43</sup>

$$\chi[R] = \sum_s a_s \chi^{\Gamma_s}[R] \quad \text{and} \quad \sum_R |\chi^{\Gamma_s}[R]|^2 = g \quad (31)$$

If these conditions are not fulfilled (within some numerical thresholds, typically  $10^{-3}$ ), the grid points are reselected and the transformation matrices are rebuilt.

In principle, a projection onto a nondegenerate irrep  $\Gamma_s$  can be generated by the operator:<sup>43</sup>

$$P^{\Gamma_s} = \frac{1}{g} \sum_R \chi^{\Gamma_s}[R]^* R \quad (32)$$

However, a nondegenerate function  $\Psi_{\lambda}^{(i)}$ , obtained using eq 6, should already transform irreducibly as  $\Gamma_s$ , and therefore this projector  $P^{\Gamma_s}$  ( $\Gamma_s \in \mathbf{G}$ ) is not needed. For example, applying the reduction from eq 30 to the first two nondegenerate wave functions ( $\Psi_1^{(1)}$  and  $\Psi_2^{(1)}$ ) in eq 22 will give  $a_{A1} = 1$ ,  $a_{A2} = a_E = 0$ , which unambiguously defines their symmetries.

Degenerate solutions require special care. For the sake of generality, let us assume that degeneracy of the reducible solution  $l_{\lambda}$  can be higher than that of the irreducible representations  $l_s$ . The degenerate wave functions (both accidentally and intrinsically) can be selected simply based on the coincidence of energies within a specified threshold (usually  $0.001 \text{ cm}^{-1}$ ). The corresponding transformation  $l_{\lambda} \times l_{\lambda}$  matrices  $\mathbf{D}[R]$  are constructed using the sampling procedure of eq 25 and then symmetrized with eq 30, giving the reduction coefficients of irreps  $\Gamma_s$ .

In cases of multiple degenerate states ( $l_{\lambda} > 1$ ), the following transfer operator<sup>43</sup> is used:

$$P_{mn}^{\Gamma_s} = \frac{l_s}{g} \sum_R D^{\Gamma_s}[R]_{mn}^* R \quad (33)$$

where  $\mathbf{D}^{\Gamma_s}[R]$  is an irreducible orthogonal transformation matrix of  $\Gamma_s$  for an operation  $R$ , and  $l_s$  is the dimension (degeneracy) of  $\Gamma_s$ . Following the symmetrization protocol<sup>43</sup> and using the reducible  $D^{\Gamma_{\text{red}}}[R]_{mn}$  from eq 25 as a representation of  $R$ , the  $m$ th component of the irreducible wave function  $\Psi_{\lambda, m}^{\Gamma_s}$  is obtained by applying  $P_{mm}^{\Gamma_s}$  (diagonal element) to  $\Psi_{\lambda, n}^{\Gamma_{\text{red}}}$ . Here, we distinguish the reducible and irreducible representations by using the superscripts  $\Gamma_{\text{red}}$  and  $\Gamma_s$ , respectively. The off-diagonal elements of the transfer operator  $P_{m, n}^{\Gamma_s}$  are then used to recover other components of  $\Psi_{\lambda, n}^{\Gamma_s}$ .

Note that, generally, degenerate solutions  $\Psi_{\lambda, n}^{\Gamma_{\text{red}}}$  can span more than one representation. Besides, the projected vectors are not automatically orthogonal. Therefore, the symmetry classification procedure must include the following steps. (i) The projector  $P_{mm}^{\Gamma_s}$  ( $m = 1, \dots, l_{\lambda}$ ) is applied to  $\Psi_{\lambda, p}^{\Gamma_{\text{red}}}$  to form a trial irreducible solution  $\Psi_{\lambda, m}^{\Gamma_s}$ , which is then (ii) checked against already-found functions  $\Psi_{\lambda, n}^{\Gamma_s}$  ( $n < m$ ). The trial function is then either rejected (if it is already present in the set) or (iii) orthogonalized to this set using the Gram–Schmidt orthogonalization technique. This procedure is repeated until all  $a_s$  irreducible solutions are found.

**5.1. Tetratomics of the  $XY_3$ -Type,  $C_{3v}$  Symmetry (Continued).** Let us now return to the example above. Choosing 40 points and applying our sampling approach to the degenerate state  $\Psi_{3, n}^{(1)}$  in eq 22 for all six  $C_{3v}(M)$  group operations listed in Table 2, the following transformation matrices were determined:

$$\mathbf{D}[E] = \begin{pmatrix} 1.0000 & 0.0000 \\ 0.0000 & 1.0000 \end{pmatrix}$$

$$\mathbf{D}[(123)] = \begin{pmatrix} -0.5000 & 0.8660 \\ -0.8660 & -0.5000 \end{pmatrix} \quad (34)$$

$$\mathbf{D}[(321)] = \begin{pmatrix} -0.5000 & -0.8660 \\ 0.8660 & -0.5000 \end{pmatrix}$$

$$\mathbf{D}[(23)^*] = \begin{pmatrix} -0.5813 & -0.8137 \\ -0.8137 & 0.5813 \end{pmatrix} \quad (35)$$

$$\mathbf{D}[(13)^*] = \begin{pmatrix} 0.9953 & -0.0965 \\ -0.0965 & -0.9953 \end{pmatrix}$$

$$\mathbf{D}[(12)^*] = \begin{pmatrix} -0.4141 & 0.9102 \\ 0.9102 & 0.4141 \end{pmatrix} \quad (36)$$

**Table 3.** Term Energies ( $\tilde{E}_\lambda$ ), Symmetries ( $\Gamma$ ), Degeneracies ( $l_\lambda$ ), TROVE Assignments ( $\nu_i$ ), and Normal-Mode Assignments ( $\nu_i$ ) of the Eigensolutions for Each Subspace  $i$  ( $i = 1, 2$ )

subspace $i$	$\lambda_i$	$\tilde{E}_{\lambda_i}$ (cm $^{-1}$ )	$l_{\lambda_i}$	$\Gamma$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	state
1	1	0.0	1	$A_1$	0	0	0	0	0	0	0
1	2	2320.0950	1	$A_1$	0	1	0	0	0	0	$\nu_1$
1	3	2329.6856	2	$E$	1	0	0	0	0	0	$\nu_3$
2	1	0.0	1	$A_1$	0	0	0	0	0	0	0
2	2	1013.7488	1	$A_1$	0	0	0	1	0	0	$\nu_2$
2	3	1121.4813	2	$E$	0	0	0	1	0	0	$\nu_4$

In principle, only three matrices are unique, but TROVE currently computes matrices for all representations and does not take the advantage of generators. The characters  $\chi^\Gamma[R]$  of these transformations are 2.0,  $-1.0$ , and  $0.0$  ( $\pm 10^{-12}$ ), which, in conjunction with eq 30, leads to the following reduction coefficients  $a^E = 1$  and  $a^{A_1} = a^{A_2} = 0$  ( $\pm 10^{-12}$ ), as expected for a doubly degenerate solution.

Using the transformation matrices  $\mathbf{D}[R]$ , together with eq 33, we build a projection operator  $P_{11}^E$  and apply it to the degenerate components  $\Psi_a = \Psi_{3,1}^{(1)}$  and  $\Psi_b = \Psi_{3,2}^{(1)}$  to obtain a trial vector:

$$\tilde{\Psi}_a = 0.135862903\Psi_a - 0.342642926\Psi_b$$

which, after normalization, becomes

$$\tilde{\Psi}_a = 0.368595853\Psi_a - 0.929589747\Psi_b$$

The second component  $\tilde{\Psi}_b$  is found by applying the transfer operator in eq 33:

$$\tilde{\Psi}_b = \frac{2}{6} \sum_R D^{\Gamma_s}[R]_{12}^* \tilde{\Psi}_a$$

which, when normalized, reads  $\tilde{\Psi}_b = 0.92958974\Psi_a + 0.368595853\Psi_b$ .

Finally, by applying the transformation vectors to the original (reducible) representation  $\{\Psi_a, \Psi_b\}$  from eq 22, we obtain

$$\tilde{\Psi}_{3,1}^{(1)} = \tilde{\Psi}_{E_a}^{(1)} = -\frac{1}{\sqrt{6}}(|0\rangle|0\rangle|1\rangle + |0\rangle|1\rangle|0\rangle - 2|1\rangle|0\rangle|0\rangle) + \dots \quad (37)$$

$$\tilde{\Psi}_{3,2}^{(1)} = \tilde{\Psi}_{E_b}^{(1)} = \frac{1}{\sqrt{2}}(|0\rangle|0\rangle|1\rangle - |0\rangle|1\rangle|0\rangle) + \dots \quad (38)$$

which is the well-known form that transforms according to the standard  $E$ -symmetry representations of  $C_{3v}$  (see ref 4, for example). The expansion coefficients in eqs 37 and 38 are defined within a numerical error of  $10^{-14}$ .

We can check if the new vectors transform correctly, as in this case, i.e., according to the standard irreducible matrices  $\mathbf{D}^{\Gamma_s}[R]$ , as follows:

$$R\Psi_{\lambda,m}^{(i),\Gamma_s} = \sum_n D^{\Gamma_s}[R]_{m,n} \Psi_{\lambda,n}^{(i),\Gamma_s}$$

As previously mentioned, if the projection operator  $P_{mm}^{\Gamma_s}$  does not lead to a correct or independent combination, we would try a different component of  $P_{mm}^{\Gamma_s}$  until the correct solution is found (which is guaranteed).

With this procedure, symmetries of all eigenstates can be easily reconstructed. For the basis set  $P \leq P_{\max} = 10$  in this example (see Section 3.2), we computed 38 stretching  $\Psi_{\lambda_1}^{(1)}$  and 192 bending  $\Psi_{\lambda_2}^{(2)}$  eigenfunctions, with the symmetries and energies of the first three from each subspace shown in Table 3.

Once all symmetry-adapted eigenfunctions for each subspace  $i$  (where  $i = 1, 2$ ) are found, the final vibrational basis set is formed as a direct product,

$$\Psi_{\lambda_1, \lambda_2}^{\Gamma_1, \Gamma_2} = \Psi_{\lambda_1}^{(1), \Gamma_1} \otimes \Psi_{\lambda_2}^{(2), \Gamma_2}$$

which is not irreducible and must be further symmetrized. We use the same projection/transfer operator approach described above (and even the same numerical subroutine) by eqs 32 and 33). The required transformation matrices are obtained as products of the standard irreducible transformation matrices,

$$\mathbf{D}^{\Gamma_1, \Gamma_2}[R] = \mathbf{D}^{\Gamma_1}[R] \mathbf{D}^{\Gamma_2}[R]$$

which are well-known and also programmed in TROVE for most symmetry groups. Using standard transformation matrices is numerically more stable, compared to the procedure based on the matrices  $\mathbf{D}[R]$  evaluated directly as solutions of eq 27. This is exhibited in significantly smaller errors in the computed coefficients  $a_i$ , which are very close to being integral.

To illustrate this point, it is informative to look at the product of two degenerate functions  $\Psi_3^{(1),E} \otimes \Psi_3^{(2),E}$  as an example (see Table 3). The four components of the product  $\Psi_{3,n}^{(1),E} \Psi_{3,m}^{(2),E}$  ( $n, m = 1, 2$ ) transform as a direct product of two  $E$ -representation matrices<sup>43</sup>

$$\mathbf{D}^{\Gamma_s}[R] = \mathbf{D}^E[R] \otimes \mathbf{D}^E[R]$$

The characters are defined by

$$\chi^{\Gamma_s}[R] = (\chi^E)^2$$

and give values of 4, 1, and 0 for  $E$ ,  $(123)$ , and  $(12)^*$ , respectively, which is the standard textbook example of a reduction of the  $E \otimes E$  product (see, for instance, ref 43). The reduction coefficients as obtained from eq 30 are 1, 1, 1 for  $A_1$ ,  $A_2$ , and  $E$ , respectively; i.e.,

$$E \otimes E = A_1 \oplus A_2 \oplus E$$

The irreducible representations determined using the numerical approach described above are

$$\Psi_{3,3}^{A_1} = \frac{1}{\sqrt{2}} [\Psi_{3,3}^{(E_a, E_a)} + \Psi_{3,3}^{(E_b, E_b)}] \quad (39)$$

$$\Psi_{3,3}^{A_2} = \frac{1}{\sqrt{2}} [\Psi_{3,3}^{(E_a, E_b)} - \Psi_{3,3}^{(E_b, E_a)}] \quad (40)$$

$$\Psi_{3,3}^{E_a} = \frac{1}{\sqrt{2}} [\Psi_{3,3}^{(E_a, E_a)} + \Psi_{3,3}^{(E_b, E_b)}] \quad (41)$$

$$\Psi_{3,3}^{E_b} = \frac{1}{\sqrt{2}} [\Psi_{3,3}^{(E_a, E_b)} - \Psi_{3,3}^{(E_b, E_a)}] \quad (42)$$

where the corresponding expansion coefficients  $\pm 1/\sqrt{2}$  are obtained numerically with double precision accuracy.



This completes the  $\text{PH}_3$  example, as well as the description of the TROVE numerical symmetrization procedure. The approach is very robust and is applicable to any product-type basis sets constructed from 1D functions provided the transformation rules for the coordinates are known. The most time-consuming part of our numerical implementation is the sampling procedure which relies on the random selection of points and can occasionally lead to poor solutions of eq 27 for the transformation matrices. Usually, the calculations are quick (seconds), but sometimes they can take hours (remember this is a basis set initialization part that must be done only once).

**5.2. An  $\text{XY}_3$  Molecule of  $\mathcal{D}_{3h}(\text{M})$  Symmetry: Degenerate and Redundant Coordinates.** Let us consider a more complicated example of coordinate choice, where some of the coordinates transform according to 2-fold irreducible representations. Such coordinates are commonly used to describe the vibrations of nonrigid molecules. For example, the nuclear coordinates of ammonia can be defined as

$$q_1 = \Delta r_1 \quad (43)$$

$$q_2 = \Delta r_2 \quad (44)$$

$$q_3 = \Delta r_3 \quad (45)$$

$$q_4 = \frac{1}{\sqrt{6}}[2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13}] \quad (46)$$

$$q_5 = \frac{1}{\sqrt{2}}[\Delta\alpha_{12} - \Delta\alpha_{13}] \quad (47)$$

$$q_6 = \tau \quad (48)$$

Here,  $r_1, r_2, r_3$  are the bond lengths,  $\alpha_{23}, \alpha_{12}$ , and  $\alpha_{13}$  are the corresponding interbond angles, and  $\tau$  is the inversion “umbrella” coordinate measuring the angle between a bond and the trisector (see ref 52, for example).

In this case, the vibrational modes span three subspaces, stretching  $\{q_1, q_2, q_3\}$ , bending  $\{q_4, q_5\}$ , and inversion  $\{q_6\}$ , which transform independently. The symmetry properties of the two bending modes are special, compared to those of the stretching and inversion modes, where the effect of the symmetry operations on the latter is just a permutation,

$$Rq_i = q_j \quad i, j = 1, 2, 3$$

or a change of sign,

$$Rq_6 = \pm q_6$$

However, the two asymmetric bending coordinates  $q_4$  and  $q_5$  (which are based on three redundant coordinates:  $\alpha_{23}, \alpha_{12}$ , and  $\alpha_{13}$ ) are mixed by the degenerate  $E$ -symmetry transformations:

$$R \begin{pmatrix} q_4 \\ q_5 \end{pmatrix} = \begin{pmatrix} D^E[R]_{11}q_4 + D^E[R]_{12}q_5 \\ D^E[R]_{21}q_4 + D^E[R]_{22}q_5 \end{pmatrix}$$

The product-type primitive basis set for  $\text{NH}_3$  ( $J = 0$ ) is

$$\phi_{\nu}(\mathbf{Q}) = \phi_{n_1}(q_1)\phi_{n_2}(q_2)\phi_{n_3}(q_3)\phi_{n_4}(q_4)\phi_{n_5}(q_5)\phi_{n_6}(q_6) \quad (49)$$

where  $\phi_{n_k}(q_k) \equiv |n_k\rangle$  ( $k = 1, \dots, 6$ ) are 1D primitive basis functions. Because of the 2D character of the transformations of  $q_4$  and  $q_5$ , the primitive bending functions  $\phi_{n_4}(q_4)$  and  $\phi_{n_5}(q_5)$  do not follow simple permutation symmetric properties. For

example, by applying the (123) permutation to the product  $\phi_{n_4}(q_4)\phi_{n_5}(q_5)$ , we get

$$(123)\phi_{n_4}(q_4)\phi_{n_5}(q_5) = \phi_{n_4}\left(-\frac{1}{2}q_4 + \frac{\sqrt{3}}{2}q_5\right)\phi_{n_5}\left(-\frac{\sqrt{3}}{2}q_4 - \frac{1}{2}q_5\right)$$

which cannot be expressed in terms of products of  $\phi_{n_4}(q_4)$  and  $\phi_{n_5}(q_5)$  only. Strictly speaking, an infinite primitive basis set expansion in terms of  $\phi_{n_4}(q_4)\phi_{n_5}(q_5)$  is required to represent  $R\phi_{n_4}(q_4)\phi_{n_5}(q_5)$  exactly, except for the special case of Harmonic oscillator functions (see section 5.3). In practice, we use expansions large enough to converge the symmetrization error below the defined threshold of  $10^{-14}$ . Unlike the two above examples of rigid molecules, the lack of the permutation character of the product-type basis set  $\phi_{n_1, \dots, n_6}(\mathbf{Q})$  in eq 49 also prevents its symmetrization using the transformation properties of the functions. However, our approach is based on the transformation properties of the coordinates  $\mathbf{Q}$ , not functions, which allows a symmetry-adapted representation to be constructed, even in this case.

The first step is to build three reduced Hamiltonian operators for each  $i = 1, 2, 3$  subspace of coordinates

$$\hat{H}^{(1)}(q_1, q_2, q_3) = \langle 0_4 | \langle 0_5 | \langle 0_6 | \hat{H} | 0_6 \rangle | 0_5 \rangle | 0_4 \rangle \quad (50)$$

$$\hat{H}^{(2)}(q_4, q_5) = \langle 0_1 | \langle 0_2 | \langle 0_3 | \langle 0_6 | \hat{H} | 0_6 \rangle | 0_3 \rangle | 0_2 \rangle | 0_1 \rangle \quad (51)$$

$$\hat{H}^{(3)}(q_6) = \langle 0_1 | \langle 0_2 | \langle 0_3 | \langle 0_4 | \langle 0_5 | \hat{H} | 0_5 \rangle | 0_4 \rangle | 0_3 \rangle | 0_2 \rangle | 0_1 \rangle \quad (52)$$

and solve the corresponding eigenvalue problems

$$\hat{H}^{(i)}(\mathbf{Q}^{(i)})\Psi_{\lambda_i}^{(i)}(\mathbf{Q}^{(i)}) = E_{\lambda_i}\Psi_{\lambda_i}^{(i)}(\mathbf{Q}^{(i)}) \quad (53)$$

As discussed above, we expect all eigenvectors of eq 53 to transform according to the irreducible representations  $\Gamma_s^{(i)}$  of  $\mathcal{D}_{3h}(\text{M})$ , despite the nonpermutative character of the bending primitive functions. Note that, in practical calculations, employing a finite basis set affects the accuracy with which the irreducible character of the eigenfunctions can be determined, which is particularly true for high vibrational excitations  $n_k$ .

To illustrate this, let us consider a generic variational calculation of several lower eigenstates for ammonia. Here, we use the PES from ref 12 and the primitive basis set defined by a polyad number  $P$  of

$$P = 2(n_1 + n_2 + n_3) + n_4 + n_5 + n_6/2 \leq P_{\text{max}} = 28 \quad (54)$$

The primitive basis functions  $\phi_{n_k}(q_k)$  ( $k = 1, \dots, 6$ ) are obtained as eigensolutions of the corresponding 1D reduced Hamiltonians using the Numerov–Cooley technique<sup>46,47</sup> with a computational setup as described in ref 12. The solution of the reduced stretching problem in eq 50 is equivalent to the example of the rigid  $\text{XY}_3$  example detailed above (see eqs 22) and is not discussed further. The first three solutions of the bending reduced problem in eq 50 are given by (where  $|n_4\rangle|n_5\rangle \equiv |n_4\rangle|n_5\rangle$ )

$$\Psi_1^{(2)} = 0.99995|0, 0\rangle - 0.00741(|2, 0\rangle + |0, 2\rangle) + \dots \quad (55)$$

$$\Psi_{2,1}^{(2)} = 0.00377|0, 1\rangle + 0.99988|1, 0\rangle + \dots \quad (56)$$

$$\Psi_{2,2}^{(2)} = -0.99988|0, 1\rangle + 0.00377|1, 0\rangle + \dots \quad (57)$$

with the energy term values of 0.0, 1679.6324, and 1679.6324  $\text{cm}^{-1}$ , relative to the ZPE = 1953.7381  $\text{cm}^{-1}$ .

The wave functions  $\Psi_{2,1}^{(2)}$  and  $\Psi_{2,2}^{(2)}$  are recognized as degenerate ( $\lambda_2 = 2$ ), because of their very similar energies (we use a threshold of  $10^{-6} \text{ cm}^{-1}$ ) and should be processed together at the symmetrization step. The transformation matrices  $D[R]$  are determined by sampling the eigenfunctions on a grid of 40 points to give the reduction coefficients  $a_i = 0, 0, 1, 0, 0$ , and  $0$  ( $\pm 10^{-12}$ ) for  $A'_1, A'_2, E', A''_1, A''_2$ , and  $E''$ , respectively. The projection operator procedure leads to the symmetrized combinations given by

$$\Psi_{2,1}^{(2)} = -0.99989|1, 0\rangle - 0.00741|1, 2\rangle - 0.01283|3, 0\rangle + \dots \quad (58)$$

$$\Psi_{2,2}^{(2)} = -0.99989|0, 1\rangle + 0.00741|2, 1\rangle + 0.01283|0, 3\rangle + \dots \quad (59)$$

Reducing the basis set to  $P_{\max} = 2$ , i.e., taking only  $n_4, n_5 \leq 1$ , leads to similar solutions but with larger errors of  $\sim 10^{-8}$  for  $a_i$ , which is still rather small in this case. However, the wave functions corresponding to higher excitations will introduce larger errors and will require more basis functions for accurate symmetrization. We use a threshold of  $10^{-3}$ – $10^{-4}$  for reduction coefficients  $a_i$  to control the symmetrization procedure: the program will accept solutions if  $a_i$  differ from an integer by less than this value.

As a final and conclusive test, TROVE also checks the matrix elements of the total Hamiltonian  $\hat{H}$  between different symmetries, which should be vanishingly small to allow a block-diagonal form of the Hamiltonian matrix. TROVE uses an acceptance threshold of  $10^{-3}$ – $10^{-3} \text{ cm}^{-1}$  to control the quality of the symmetrization procedure. Failure to pass this test (usually small errors) indicates that the basis set is not large enough for an accurate symmetrization. Critical failure (huge errors) usually indicates problems with the model (e.g., in the potential energy function, coordinate transformation relations, kinetic energy operator, definition of the molecular equilibrium structure, etc.).

This example is a good illustration of how the redundant coordinates can be incorporated into a product-type basis of 1D functions. The redundant vibrational coordinates are very common; for example, they appear as part of multidimensional symmetrically adapted coordinates. The typical example are the bending modes used to represent vibrational modes of ammonia (eqs 46, 47) or methane (see, for example, ref 53). The TROVE symmetrization can still handle this situation, even at a cost of a larger basis set. As it will be shown in the next section, the harmonic oscillator basis functions have the property of their products to form symmetrized combinations from a finite size basis of functions, which holds also for the case of the redundant coordinates.

**5.3. Harmonic Oscillator Basis Sets.** Our most common choice of the primitive basis set is based on the Numerov–Cooley approach, where 1D functions are generated numerically on a large grid of 1000–5000 equidistantly placed points by solving a set of 1D reduced Hamiltonian problems for each mode. This provides a compact basis set optimized for a specific problem. However, as was discussed in the previous section, some types of degenerate coordinates require large expansions, in terms of products of 1D functions for accurate symmetrization. A very simple work-around of this problem is

to use 1D harmonic oscillators as a basis set. The (degenerate) harmonic oscillators have a unique property: one can always build an isotropic harmonic oscillator with proper symmetric properties as a finite sum of products of 1D harmonic oscillators  $\phi_{n_i}^{\text{HO}}(q_i)$  (see, for example, ref 43). This is also valid for higher multifold degeneracies. As an illustration, in the Appendix, we show how to construct a 2D symmetrized basis set using 1D harmonic oscillator functions to represent the asymmetric bending modes of the ammonia molecule, using our symmetrization procedure. In fact, this illustration can be reproduced without the TROVE program, since it is solely based on the properties of the harmonic wave functions. This makes up a good toy example to try our symmetrization approach without having to address TROVE implementation.

Note that the eigenfunction methods for many-particle harmonic oscillator wave functions was also explored by Novoselsky and Katriel.<sup>54</sup>

**5.4. Reduction of the Rotational Rigid Rotor Basis Functions.** TROVE uses the rigid rotor wave functions (Wigner  $D$ -functions) as the rotational basis set. In principle, for most of the groups (such as  $C_{nv}$ ,  $C_{nh}$ ,  $D_{nh}$ , or  $D_{nd}$ ), the symmetry properties of the rigid rotor wave functions  $|J, k, m\rangle$  are trivial and can be reconstructed based on the  $k$  value only.<sup>43</sup> This is possible because all symmetry operations from these groups can be associated with some equivalent rotations about the body-fixed axes  $x$ ,  $y$ , and  $z$  only (see, for example, the discussion in ref 55). Furthermore, symmetrized combinations of the rigid-rotor wave functions are trivial and can be given by the so-called Wang wave functions. For example, TROVE uses the following symmetrization scheme:<sup>6</sup>

$$|J, 0, \tau_{\text{rot}}\rangle = |J, k, m\rangle \quad (60)$$

$$|J, K, \tau_{\text{rot}}\rangle = \frac{i^\sigma}{\sqrt{2}} [|J, K, m\rangle + (-1)^{J+K+\tau_{\text{rot}}} |J, -K, m\rangle] \quad (61)$$

where  $K = |k|$ ,  $\tau_{\text{rot}}$  is the value associated with the parity of  $|J, K, \tau_{\text{rot}}\rangle$ ,  $\sigma = K \bmod 3$  for  $\tau_{\text{rot}} = 1$ ,  $\sigma = 0$  for  $\tau_{\text{rot}} = 0$ ,<sup>6</sup> and  $m$  is omitted on the left-hand side for simplicity's sake. The symmetry properties of  $|J, K, \tau_{\text{rot}}\rangle$  can be derived from the properties of  $|J, K, m\rangle$  under the associated rotations<sup>43</sup> and depend on  $J, K$  and  $\tau_{\text{rot}}$  only. Therefore, a more sophisticated symmetrization approach like the one presented above is not required in such cases. As an example, Table 4 lists the symmetries of  $|J, K, \tau_{\text{rot}}\rangle$  for a rigid  $\text{XY}_3$ -type molecule ( $C_{3v}(\text{M})$ ) described above.

However, some symmetry groups contain operations with equivalent rotations about other axes than  $x$ ,  $y$ , and  $z$ , such as  $\mathcal{T}_d$  and  $\mathcal{O}_h$ . Consider a rigid  $\text{XY}_4$  molecule spanning the  $\mathcal{T}_d(\text{M})$  symmetry group. The permutation (124) is associated with the

**Table 4.**  $C_{3v}(\text{M})$  Symmetries of the Rigid-Rotor Wavefunctions  $|J, K, \tau_{\text{rot}}\rangle$  ( $K \geq 0$ ) for the Case of a Rigid  $\text{XY}_3$  Molecule<sup>a</sup>

$\Gamma$	$K$	$\tau_{\text{rot}}$
$A_1$	$3n$	0
$A_2$	$3n$	1
$E_a$	$3n \pm 1$	0
$E_b$	$3n \pm 1$	1

<sup>a</sup> $K = 0$  is the special case with  $\tau_{\text{rot}} = 0$  (even  $J$ ) and  $\tau_{\text{rot}} = 1$  (odd  $J$ ).

equivalent rotation  $R_3(1,1,1)$ , which is a  $2\pi/3$  right-hand rotation about an axis from the origin to the point  $(x,y,z)$ - $(1,1,1)$ .<sup>55</sup> In this case, the symmetrized basis can only be formed from a linear combination of  $|J,K,m\rangle$  spanning a range of  $k$  values, as was also shown by Alvarez-Bajo et al.<sup>41</sup> This is where we use the TROVE symmetrization approach to build symmetry-adapted rotational basis functions  $|J,\Gamma\rangle$  (see also refs 2 and 56, where this approach was applied for  $J$  values up to 45). The formulation of the symmetrization scheme is given in the Appendix.

Once the  $\mathbf{D}^{\text{Wang}}[R]$  matrices are known, the numerically adapted reduction scheme described above is used to build the symmetrized representation for any  $J$ . The rotational quantum number  $K$  cannot be used for classification of these symmetrized rigid-rotor combinations anymore. Instead, we label them as  $|J,\Gamma,n\rangle$ , where  $n$  is a counting index.

**5.5. Constructing (Ro-)vibrational Basis Sets.** Following the subspace-based approach introduced for symmetrization of the vibrational part, the rotational modes are also treated as part of an independent, rotational subspace, which is referred in TROVE as subspace 0. The symmetry-adapted ro-vibrational basis set is then constructed as a direct product of the symmetrized components from different subspaces as  $\Psi_{\lambda_0}^{(0),\Gamma_0} \otimes \Psi_{\lambda_1}^{(1),\Gamma_1} \otimes \Psi_{\lambda_2}^{(2),\Gamma_2} \dots \otimes \Psi_{\lambda_L}^{(L),\Gamma_L}$ , where  $L$  is the number of vibrational subspaces. The product of irreducible representations must be further reduced, which is much easier when each component is transformed as one of the irreps of the group with standard transformation properties. In this case, the same projection operator symmetrization technique is used without further sampling of the symmetric properties of the corresponding components.

An efficient alternative to the vibrational basis set as a direct product of subspaces is the  $J = 0$  contraction scheme.<sup>12</sup> According to this scheme, the eigenfunctions of the vibrational problem ( $J = 0$ ) are used as contracted vibrational basis functions for  $J > 0$ . The  $J = 0$  eigenfunctions represent an even more compact basis set and can be further contracted (referred to as the  $J = 0$  contraction). The symmetry-adapted ro-vibrational basis set is then constructed exactly as described above (using the same numerical symmetrization subroutines), as a direct product of  $\Phi_{\lambda_0}^{(0),\Gamma_0} \otimes \Phi_{\lambda_1}^{(1),\Gamma_1}$ , where the subspace-index  $i$  in  $\Phi_{\lambda_i}^{(i),\Gamma_i}$  runs over 0 and 1 only, and the  $J = 0$  basis functions are combined into subspace 1.

## 6. CONCLUSION

A new method for constructing symmetry-adapted basis sets for ro-vibrational calculations has been presented. The method is a variation of the matrix (or eigenfunction) approaches and is based on solving eigenfunction problems for a set of reduced Hamiltonian operators without resorting to rigorous group-theoretical algebra. The advantage of using reduced Hamiltonians in the matrix symmetrization is that it also improves the properties of the basis sets by making them more compact and adjusted to the physics of the problem, thus allowing for efficient contraction. However, it lacks the automatic classification of the basis functions by the irreps, which is a useful feature of the CSCO-based eigenfunction approach by Chen et al.<sup>38</sup> To make up for this, the TROVE symmetrization procedure must be complemented by a sampling technique accompanied by a projection-based reduction.

Our symmetrization approach has been implemented in the TROVE program suite and has been extensively used for a

variety of tri-, tetra-, and penta-atoms covering the  $C_s(M)$ ,  $C_{2v}(M)$ ,  $C_{3v}(M)$ ,  $D_{2h}(M)$ ,  $D_{3h}(M)$ , and  $T_d(M)$  groups. TROVE symmetrization is general, in that it can be applied to any molecule with arbitrary selection of coordinates, provided the symmetry properties of the latter are known. We are now implementing a general numerical technique for  $C_{nh}(M)$ ,  $C_{nv}(M)$ , and  $D_{nh}(M)$  representations, where  $n$  is an arbitrarily large integer value. Although TROVE symmetrization was developed and used for building ro-vibrational basis sets, we believe it can be useful for many other applications in physics and chemistry. The symmetrization subroutines (Fortran 95) are written to be as general as possible and, in principle, can be interfaced with other variational codes, if there will be interest from the community. The illustration of the symmetrization approach applied to the harmonic oscillator wave functions (see the Appendix) is an example where using TROVE is not necessary and thus could be a good place to start.

## APPENDIX

### A. Symmetrized 2D Harmonic Oscillator Basis Sets

Here, we illustrate how to build a  $\mathcal{D}_{3h}(M)$  symmetrized vibrational basis set for ammonia-type molecules to represent the two asymmetric bending modes  $q_4$  and  $q_5$  from subspace 2 (see eqs 46 and 47) for the example from Section 5.2. The basis set will be formed from the products of the degenerate harmonic oscillator basis set functions, as given by

$$\phi_{n_4,n_5}^{\text{HO}}(q_4, q_5) = C_{n_4,n_5} H_{n_4}(q_4) e^{-\alpha q_4^2} H_{n_5}(q_5) e^{-\alpha q_5^2}$$

where  $H_n$  is a Hermite polynomial,  $\alpha$  is a parameter (the same for all degenerate components), and  $C_{n_4,n_5}$  is a normalization constant. These functions represent solutions of the 2D degenerate harmonic oscillator

$$H^{\text{HO}} \phi_{n_4,n_5}^{\text{HO}}(q_4, q_5) = \tilde{\omega}(n_4 + n_5 + 1) \phi_{n_4,n_5}^{\text{HO}}(q_4, q_5)$$

and can be combined to express a solution of the 2D isotropic harmonic oscillator (IHO):

$$\Psi_{N,l}^{\text{IHO}} = F_{N,l}(\rho) e^{i\phi}$$

where<sup>43</sup>

$$\rho = \sqrt{q_4^2 + q_5^2}, \quad \phi = \arctan \frac{q_5}{q_4}$$

$$N = n_4 + n_5, \quad l = N, N - 2, \dots, -N + 2, -N$$

Here,  $\Psi_{N,l}^{\text{IHO}}$  is an eigenfunction of the corresponding 2D IHO problem:

$$H^{\text{HO}} \Psi_{N,l}^{\text{IHO}} = \tilde{\omega}(N + 1) \Psi_{N,l}^{\text{IHO}}$$

which transforms as  $A_1/A_2$  (for  $l = 0, 3, 6, \dots$ ) and  $E$  (otherwise). That is, there exists a linear transformation that connects  $\Psi_{N,l}$  and  $\phi_{n_4,n_5}(q_4, q_5)$  subject to  $N = n_4 + n_5$ .

In order to determine such a transformation and, thus, build the symmetry-adapted functions  $\Psi_{N,b}$  we apply the TROVE numerical symmetrization procedure. For example, for a given polyad number  $N = 3$ , we need to combine the following four products  $\phi_{n_4}(q_4)\phi_{n_5}(q_5)$  satisfying  $n_4 + n_5 = 3$ :

$$\phi_3\phi_0, \quad \phi_2\phi_1, \quad \phi_1\phi_2, \quad \phi_0\phi_3 \quad (\text{A-1})$$

These four wave functions are degenerate and share the same Harmonic oscillator energy,<sup>43</sup>

$$\tilde{E}_{n_4, n_5}^{\text{HO}} = \tilde{\omega}(n_4 + n_5 + 1)$$

with  $\tilde{\omega} = 1679.380 \text{ cm}^{-1}$  and  $\alpha = 0.2241 \text{ rad}^{-2}$ . We use a sampling grid of 40 geometries ranging between  $-1.0 \leq q_4, q_5 \leq 1.0$  radians to probe the values of the wave functions and their symmetric replicas and to obtain the six  $4 \times 4$  transformation matrices  $\mathbf{D}[R]$  for each operation  $R$  in  $\mathcal{D}_{3h}(\text{M})$ .

Applying the group operations  $E$ , (123), (23),  $E^*$ , (132)\*, and (23)\* to the four selected degenerate wave functions  $\phi_1 = |0, 3\rangle$ ,  $\phi_2 = |1, 2\rangle$ ,  $\phi_3 = |3, 0\rangle$ ,  $\phi_4 = |2, 1\rangle$ , the following matrices  $\mathbf{D}[R]$  are obtained:

$$\mathbf{D}[E] = \mathbf{D}[E^*] = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{D}[(23)] = \mathbf{D}[(23)^*] = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{D}[(132)] = \mathbf{D}[(132)^*] = \begin{pmatrix} -\frac{1}{8} & -\frac{3}{8} & -\frac{3\sqrt{3}}{8} & -\frac{3\sqrt{3}}{8} \\ \frac{3}{8} & \frac{5}{8} & \frac{\sqrt{3}}{4} & -\frac{3\sqrt{3}}{8} \\ -\frac{3\sqrt{3}}{8} & -\frac{\sqrt{3}}{4} & \frac{5}{8} & -\frac{3}{8} \\ \frac{3\sqrt{3}}{8} & -\frac{3\sqrt{3}}{8} & \frac{3}{8} & -\frac{1}{8} \end{pmatrix}$$

where the matrix elements are given to  $10^{-15}$ . With the help of eq 31, we obtain the reduction coefficients  $a_i = 1, 1, 1, 0, 0, 0$  (within  $10^{-15}$ ) ( $i = A'_1, A'_2, E', A''_1, A''_2, E''$ ), i.e., only  $A'_1, A'_2, E'$  combinations can be formed. For the 1D representations  $A_1$  and  $A_2$ , the projection operators obtained using eq 32 are given by

$$P^{A_1} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \frac{3}{4} & 0 & -\frac{\sqrt{3}}{4} \\ 0 & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{4} & 0 & \frac{1}{4} \end{pmatrix} \quad (\text{A-2})$$

$$P^{A_2} = \begin{pmatrix} \frac{1}{4} & 0 & -\frac{\sqrt{3}}{4} & 0 \\ 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{4} & 0 & \frac{3}{4} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (\text{A-3})$$

These matrices contain a total of eight vectors that we can choose from to build the irreducible combinations of  $\phi_1, \phi_2, \phi_3$ , and  $\phi_4$ , four of which are trivial and only two pairs are linearly

independent. Choosing the second column vector from the  $P^{A_1}$  matrix, after normalization, we obtain

$$\Psi_1^{A_1}(q_4, q_5) = \frac{\sqrt{3}}{2}|1\rangle|2\rangle - \frac{1}{2}|3\rangle|0\rangle$$

where the index 1 indicates the counting number of this state. The only nontrivial and linearly independent choice is given by (after normalization)

$$\Psi_2^{A_2}(q_4, q_5) = \frac{1}{2}|0\rangle|3\rangle - \frac{\sqrt{3}}{2}|2\rangle|1\rangle$$

The projection operator for the  $E$ -symmetry component leads to the following matrices:

$$P_{11}^E = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \frac{1}{4} & 0 & \frac{\sqrt{3}}{4} \\ 0 & 0 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{4} & 0 & \frac{3}{4} \end{pmatrix} \quad (\text{A-4})$$

$$P_{22}^E = \begin{pmatrix} \frac{3}{4} & 0 & \frac{\sqrt{3}}{4} & 0 \\ 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{4} & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (\text{A-5})$$

From this space of eight possible vectors, we select the following trial vector, which is linear independent from  $\Psi_1^{A_1}$  and  $\Psi_2^{A_2}$ :

$$\phi^{\text{trial}} = \left(0, \frac{3}{4}, 0, \frac{\sqrt{3}}{4}\right)^T$$

This vector is then orthogonalized to  $\Psi_1^{A_1}$  and  $\Psi_2^{A_2}$ , using the Grand-Schmidt procedure to get

$$\Psi_{3,1}^{E_a}(q_4, q_5) = \frac{1}{2}|1\rangle|2\rangle + \frac{\sqrt{3}}{2}|3\rangle|0\rangle$$

The second component of the latter vector,  $E_b$ , is obtained by applying the corresponding transfer operator in eq 33 to  $\Psi_{3,1}^{E_a}$ , which after the Grand-Schmidt orthogonalization reads

$$\Psi_{3,2}^{E_b}(q_4, q_5) = -\frac{\sqrt{3}}{2}|0\rangle|3\rangle - \frac{1}{2}|2\rangle|1\rangle$$

In all of these above equations, the coefficients  $1/2, 3/4, \sqrt{3}/2$ , and  $\sqrt{3}/4$  are obtained numerically, and they coincide with the numerical values to within  $10^{-14}$ .

This completes the example of the reduction of degenerate wave functions in the basis of 2D isotropic harmonic oscillator functions. It is also a good illustration of how our method is applied to degeneracies of arbitrary order and dimensions. The only limitation is the memory and time required for sampling wave functions and inverting the transformation matrices via eq 25. For example, in ref 1, the highest degeneracy order used was 120, together with the 2D and 3D symmetries  $E, F_1$ , and  $F_2$ .

Note that, as an alternative to the orthogonalization with the Grand-Schmidt orthogonalization, one can impose the orthogonality conditions on the elements of matrix  $\mathbf{D}[R]$

during the solution of eq 27, for example, by utilizing the exponential ansatz:

$$\mathbf{D}[R] = \exp(-\boldsymbol{\kappa}[R]), \boldsymbol{\kappa}^T = -\boldsymbol{\kappa} \quad (\text{A-6})$$

with only one independent element  $\kappa_{12}$ , in case of a doubly degenerate irrep, three independent elements  $\kappa_{12}$ ,  $\kappa_{13}$ , and  $\kappa_{23}$ , in case of a triply degenerate irrep, etc. to be determined. Using this representation, the system of equations in eq 27 becomes nonlinear and can be easily solved using the iterative approach described in ref 11 for solution of the Eckart equations. We are planning to explore this approach in the future.

## B. Symmetrization of the Rotational Rigid Rotor Wave Functions

The symmetry transformation properties (i.e., transformation matrices  $\mathbf{D}[R]$ ) of the rigid-rotor wave functions required for our symmetrization scheme can be obtained directly from the Wigner  $D$ -functions, associated with the corresponding Euler angles of the particular equivalent rotation  $R(\alpha, \beta, \gamma)$ . These are given by

$$R(\alpha, \beta, \gamma)|J, k, m\rangle = \sum_{k'=-J}^J D_{k',k}^{(J)*}(\alpha, \beta, \gamma)|J, k', m\rangle$$

(also see ref 41).

Thus, the sampling procedure is not required for rotational basis functions. For example, the Euler angles for all equivalent rotations of a rigid  $\text{XY}_4$  molecule ( $\mathcal{T}_d(\text{M})$ ) are given in Table 4 of ref 41. The transformation properties of the Wang functions  $|J, K, \tau_{\text{rot}}\rangle$  in eqs 60 and 61) can then be deduced using the unitary transformation

$$\mathbf{D}^{\text{Wang}}[R] = \mathbf{U}^+ \mathbf{D}_{(J)}^*(\alpha, \beta, \gamma) \mathbf{U}$$

where the  $(2J + 1) \times (2J + 1)$  matrix  $U_{ij}$  is given by

$$U_{11} = \begin{cases} 1, & \text{even } J \\ -(i)^J & \text{odd } J \end{cases}$$

$$U_{n,n} = \frac{1}{\sqrt{2}} \quad (\text{B-1})$$

$$U_{n,n+1} = -i \frac{(-1)^\sigma}{\sqrt{2}} \quad (\text{B-2})$$

$$U_{n+1,n} = \frac{(-1)^{J+K}}{\sqrt{2}} \quad (\text{B-3})$$

$$U_{n+1,n+1} = i \frac{(-1)^{J+K+\sigma}}{\sqrt{2}} \quad (\text{B-4})$$

$$U_{n,n'} = 0 \quad \text{for } |n - n'| > 1 \quad (\text{B-5})$$

where  $n = 2K$ ,  $K = 1, \dots, J$ ,  $\sigma = K \bmod 3$  for  $\tau_{\text{rot}} = 1$ , and  $\sigma = 0$  for  $\tau_{\text{rot}} = 0$ . Once the transformation matrices are known, the standard projection technique described above is applied to obtain the symmetry-adapted rigid-rotor combinations used as rotational basis functions.<sup>2</sup>

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## Notes

The authors declare no competing financial interest.

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