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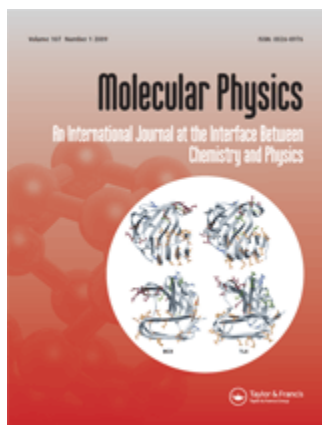
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**New efficient algorithm for the calculation of energy levels of AB₃
type molecules**

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representation, vibration energy levels

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ABSTRACT

This paper illustrates a method for the construction of a symmetry-adapted contracted angular basis set for AB₃ molecules. Simple formulas that use this basis set for calculations of the angular matrix elements of the kinetic energy (KE) operator and angular matrix elements of potential energy surface (PES) are reported. The efficient recursive algorithm based on the tensorial formalism is used for the calculation of vibrational matrix elements. The symmetric form of vibration KE operators without the $\sin(q)^{-2}$ type singularity is applied. A good basis set convergence for the calculations of vibrational levels of the PH₃ molecule is demonstrated.

I. INTRODUCTION

The theory and computational modeling of molecular vibrations is on the top of interest in the molecular spectroscopy and related fields. Advances in computation of vibration-rotation spectra of three-atomic molecules (see ref. 1-3 and references therein) resulted in an interest to computations of spectra for polyatomic molecules [4-31]. For more information on this subject, the reader is referred to the recent review [21]. An important part of polyatomic molecules are high symmetry molecules [4-14,18-27]. For the ABC_3 type molecules variational calculations using a finite basis representations and full C_{3v} symmetry have been applied to CH_3F [10,11] and CH_3Cl [27] molecules. In this paper C_{3v} and T_d point groups are considered to be isomorphic to finite permutation groups (permutations of three or four atoms). In spite of a considerable number of publications devoted to computation of vibration-rotation spectra of the AB_4 and the AB_3 type molecules, they often do not completely use the molecular symmetry [4,5,8,9,19,25,26]. One variational method for calculating excited bending states of symmetric tetrahedral pentaatomic molecules based on the use of Radau coordinates and Jacobi polynomials as the basis functions has been presented in [30,31]. Only the technique based on the normal or symmetry coordinates does not result in special difficulties related to a construction of the symmetry basis [13,17,18,21]. See also rovibration calculations by Rey *et al.* [24] using rectilinear normal coordinates and the normal mode Hamiltonian expressed in terms of irreducible tensor operators.

When using the internal coordinates, such as three angles between the H-P-H bonds in PH_3 , in the general case, the basis functions constructed on the base of these coordinates are not orthogonal, even though those angles are independent. The construction of the symmetry basis using the q_{ij} angles is a trivial task, but a problem is to work out an effective technique for calculations of multidimensional integrals using this basis. In the present work, a finite basis representations approach was applied for the AB_3 type molecules and simple formulas for calculations of the matrix elements of the KE operator and PES are reported. As a rule, we will consider only the angular part of the matrix elements, because the symmetry properties of radial part are obvious. Here we also assume that the molecule has only one deep minimum.

Tennyson *et al.* [32], Gatti *et al.* [33,34], Mladenovic' [35-36] have presented derivations of kinetic energy operators for treating rotations and vibrations of polyatomic molecules using polyspherical coordinates. In these coordinates, the N nuclear position vectors are transformed to

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3 $N-1$ internal vectors and the nuclear center of mass vector, and the internal vectors are
4 parametrized by spherical polar coordinates: $R_i, \theta_i, \varphi_i, i=1, \dots, N-1$. Then, a body-fixed coordinate
5 system is introduced, defined by aligning the body-fixed z axis along the first vector, and placing
6 the second vector in the body-fixed xz plane. The remaining angles θ_i, φ_i are either referenced
7 with respect to the body-fixed z axis, or other vectors.
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15 At the same time, the symmetric form of vibration KE operators is known [30,31,37,38].
16 Instead of using the torsion angle, symmetric form use additional angles between molecular
17 bonds. This form of KE operators is more tailored to our basis functions, and so we use it in the
18 present work. Symmetric form is especially interesting because it has no $\sin(q)^{-2}$ singularity
19 while the KE operator of Ref. [35] contains this singularity. When constructing the vibration
20 basis set using the products of functions that depend on the bending q and torsion t angles, the
21 angular basis $f_n(q)$ must be chosen to be vanishing at $\sin(q)=0$. From a physical point of view,
22 this choice of $f_n(q)$ is not always correct because in some vibration states, a molecule can be in a
23 geometric configuration with the angle $q=\pi$ with rather high probability.
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36 Described in this work algorithm of calculation of vibrational energy levels uses non-
37 orthogonal basis set of three interbond angles q_{ij} . Of course, the non-orthogonal basis is not
38 always easy-to-use, but this type of basis is used, for example, in the chemical reactions theory
39 [39]. When calculating the matrix elements of PES, whenever possible, we try to keep the
40 symmetrical form with respect to three angles. We transform to polar coordinates only at the final
41 phase of the calculations. Similarly, when calculating the matrix elements of the KE operator in
42 symmetric form, we first calculate the derivatives with respect to angles using matrix element
43 symmetry, and only after this, we calculate the matrix element by using polar coordinates.
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55 The present paper comprises seven sections. Section II describes an algorithm for
56 constructing contracted angular basis set that uses three angles q_{ij} between three identical atoms,
57 and the norm calculation for this basis set. Sections III and IV are devoted to algorithm of
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calculations of the angular matrix elements of PES and KE in contracted angular basis set. Section V briefly outlines the general tree-like coupling scheme of PES and basis functions, a construction of the symmetry-adapted angular basis set, and algorithm for calculation of vibrational matrix elements for AB₃ molecules. In section VI we report the tests of the convergence of calculated vibrational PH₃ levels in the 0-7000 cm⁻¹ range. Section VII is devoted to discussion and conclusion.

II. CONTRACTED ANGULAR BASIS FOR THREE IDENTICAL ATOMS AND NORM CALCULATION

In the present work, the following coordinates were chosen as independent ones: three bond lengths $\{r_1, r_2, r_3\}$ and three interbond angles $\{q_{12}, q_{13}, q_{23}\}$. For one-dimensional basis functions, the following functions were used: $f_n(q) = \sqrt{2\pi} \sum_l c_{nl} Y_{l,s}(q,0)$, where Y are spherical harmonics

written in the form of Ref. [40] that ensures that $Y_{0,0}(q,0) = \frac{1}{\sqrt{4\pi}}$ and $2\pi \int_0^\pi Y_{l,s}^2(q,0) d \cos(q) = 1$.

The normalized eigenfunctions $\int_0^\pi f_n^2(q_{23}) d \cos(q_{23}) = 1$ of one-dimensional angular problem can be used to obtain f_n . Initial angular basis can be written in the form:

$$|n_1 n_2 n_3\rangle = f_{n_1}(q_{12}) f_{n_2}(q_{13}) f_{n_3}(q_{23}). \quad (1)$$

This basis is not orthogonal one. The norm is calculated using the following three-dimensional integral:

$$\langle n_1 n_2 n_3 | k_1 k_2 k_3 \rangle = \int_0^\pi \int_0^\pi \int_0^{2\pi} f_{n_1}(q_{12}) f_{k_1}(q_{12}) f_{n_2}(q_{13}) f_{k_2}(q_{13}) f_{n_3}(q_{23}) f_{k_3}(q_{23}) d \cos(q_{12}) d \cos(q_{13}) dt_{23}$$

where t_{23} is the torsion angle.

$$\text{To calculate the integral } \int_0^{2\pi} f_n^*(q_{23}) f_m(q_{23}) dt_{23} = 2\pi \int_0^{2\pi} \sum_{l_1, l_2} c_{nl_1} c_{ml_2} Y_{l_1, s}^*(q_{23}, s) Y_{l_2, s}(q_{23}, s) dt_{23}$$

the following expressions [40] were used:

$$Y_{l_1, s_1}(q_{23}, 0) Y_{l_2, s_2}(q_{23}, 0) = \sum_{LM} \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} C(l_1, 0, l_2, 0, L, 0) C(l_1, s_1, l_2, s_2, L, M) Y_{LM}(q_{23}, 0) \quad (2)$$

and

$$Y_{l,0}(\cos(q_{12}))\cos(q_{13}) + \sin(q_{12})\sin(q_{13})\cos(t_{23}) = \sqrt{\frac{4\pi}{2l+1}} \sum_m Y_{lm}(q_{12},0)Y_{lm}(q_{13},t_{23}) \quad (3)$$

Therefore, from Eqs. (2, 3), we get:

$$Y_{l_1,0}(q_{23},0)Y_{l_2,0}(q_{23},0) = \sum_L K_{l_1 l_2 L} \sum_m Y_{Lm}(q_{12},0)Y_{Lm}(q_{13},t_{23}), \quad (4)$$

where $K_{l_1 l_2 L} = \frac{\sqrt{(2l_1+1)(2l_2+1)}}{2L+1} C(l_1,0,l_2,0,L,0)^2$, and $C(l_1 m_1, l_2 m_2, LM)$ is Clebsch-Gordan coefficient. Using Eq. (4) we get

$$\begin{aligned} \langle n_1 n_2 n_3 | k_1 k_2 k_3 \rangle = & \int_0^\pi \int_0^\pi f_{n_1}(q_{12}) f_{k_1}(q_{12}) f_{n_2}(q_{13}) f_{k_2}(q_{13}) \\ & (2\pi)^2 \sum_{l_1 l_2} c_{n_1 l_1} c_{k_3 l_2} \sum_L K_{l_1 l_2 L} Y_{L0}(q_{12},0) Y_{L0}(q_{13},0) d \cos(q_{12}) d \cos(q_{13}) \end{aligned} \quad (5)$$

Let us denote the one-dimensional integral by

$$J_{n_1, k_1, L, \nu} = \int_0^\pi f_{n_1}(q_{12}) f_{k_1}(q_{12}) Y_{L\nu}(q_{12},0) d \cos(q_{12}) = 2\pi \sum_{l_1 l_2} c_{n_1 l_1} c_{k_1 l_2} \int_0^\pi Y_{l_1,0}(q_{12},0) Y_{l_2,0}(q_{12},0) Y_{L\nu}(q_{12},0) d \cos(q_{12})$$

Using Eq. (2) and taking into account that spherical harmonics Y_{lm} with the same m are orthogonal we get:

$$J_{n_1, k_1, L, 0} = \sum_{l_1 l_2} c_{n_1 l_1} c_{k_1 l_2} \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} C(l_1,0,l_2,0,L,0)^2 = \frac{1}{\sqrt{4\pi}} \sqrt{(2L+1)} \sum_{l_1 l_2} c_{n_1 l_1} c_{k_1 l_2} K_{l_1 l_2, L} \quad (6)$$

Using Eqs. (5, 6), one can derive

$$\langle n_1 n_2 n_3 | k_1 k_2 k_3 \rangle = (2\pi)^3 \sum_L \frac{1}{\sqrt{\pi(2L+1)}} J_{n_1, k_1, L, 0} J_{n_2, k_2, L, 0} J_{n_3, k_3, L, 0} \quad (7)$$

For example, if $c_{nl} = \delta_{nl}$ we get: $\langle 000 | 000 \rangle = \pi$, $\langle 111 | 111 \rangle = \frac{33\pi}{25}$, $\langle 112 | 112 \rangle = \frac{43\pi}{35}$.

III. CALCULATION OF MATRIX ELEMENTS OF PES FOR THREE IDENTICAL ATOMS

For majority of molecules, the angular PES can be expressed in terms of a sum of product functions: $\cos^{P_{12}}(q_{12})\cos^{P_{13}}(q_{13})\cos^{P_{23}}(q_{23})$. Due to simple recursive formulas [40] for $\cos(q)Y_{n,0}(q)$, this considerably facilitates the calculation of matrix elements. Therefore,

$$\cos^P(q)f_k(q) = \sqrt{2\pi} \sum_{l_2 l_3} c_{kl_2} \langle l_3 s | \cos^P(q) | l_2 s \rangle Y_{l_3, s}(q, 0).$$

If $s=0$, similarly to Eqs. (5, 6), we get the following expression for the matrix element:

$$\begin{aligned} \langle n_1 n_2 n_3 | \cos(q_{23})^P | k_1 k_2 k_3 \rangle &= (2\pi)^2 \int_0^\pi \int_0^\pi f_{n_1}(q_{12}) f_{k_1}(q_{12}) f_{n_2}(q_{13}) f_{k_2}(q_{13}) \\ &\sum_{l_1 l_2 l_3} c_{n_3 l_1} c_{k_3 l_2} \langle l_3 0 | \cos^P | l_2 0 \rangle \sum_L K_{l_1 l_3 L} Y_{L0}(q_{12}, 0) Y_{L0}(q_{13}, 0) d \cos(q_{12}) d \cos(q_{13}) \end{aligned}$$

In comparison with Eq. (5), this expression contains an additional summation over the l_3 index and the $\langle l_3 | \cos^P | l_2 \rangle$ matrix element. Using the expression

$$J_{n_3, k_3, L, 0}^P = 2\pi \sum_{l_1 l_2 l_3} c_{n_3 l_1} c_{k_3 l_2} \langle l_3 0 | \cos^P | l_2 0 \rangle K_{l_1 l_3 L} \sqrt{\frac{2L+1}{4\pi}} \quad (8)$$

one can write the matrix element in the form:

$$\begin{aligned} \langle n_1 n_2 n_3 | \cos(q_{23})^P | k_1 k_2 k_3 \rangle &= (2\pi)^2 \sum_{l_1 l_2 l_3} c_{n_3 l_1} c_{k_3 l_2} \langle l_3 0 | \cos^P | l_2 0 \rangle \sum_L K_{l_1 l_3 L} J_{n_1, k_1, L, 0} J_{n_2, k_2, L, 0} = \\ &(2\pi)^3 \sum_L \frac{1}{\sqrt{\pi(2L+1)}} J_{n_1, k_1, L, 0}^P J_{n_2, k_2, L, 0} J_{n_3, k_3, L, 0} \end{aligned}$$

Taking into account that q_{23} is independent of q_{12} and q_{13} , it is easy to obtain the following general expression for the PES matrix elements:

$$\langle n_1 n_2 n_3 | \cos(q_{12})^{P_{12}} \cos(q_{13})^{P_{13}} \cos(q_{23})^{P_{23}} | k_1 k_2 k_3 \rangle = (2\pi)^3 \sum_L \frac{1}{\sqrt{\pi(2L+1)}} J_{n_1, k_1, L, 0}^{P_{12}} J_{n_2, k_2, L, 0}^{P_{13}} J_{n_3, k_3, L, 0}^{P_{23}} \quad (9)$$

IV. CALCULATION OF MATRIX ELEMENTS OF KE

In this section, we use the mass-dependent orthogonal coordinates $\{r'_1, r'_2, r'_3, q'_{12}, q'_{13}, q'_{23}\}$. The polar coordinates are defined in a standard way via three vectors $\{\vec{r}_i\}$ ($i=1,2,3$) linking the centre of mass with three identical atoms. Three stretching coordinates r_i are the lengths of these vectors

and $\{q_{ij}\}$ are interbond angular coordinates. The mass-dependent orthogonal coordinates [35]

$\{r'_1, r'_2, r'_3, q'_{12}, q'_{13}, q'_{23}\}$ are defined in a similar way via three vectors $\{\vec{r}'_i\}$:

$$\vec{r}'_i = \vec{r}_i + d \sum_{j=1}^3 \vec{r}_j, \text{ where } d = -\frac{1}{3} + \frac{1}{3\sqrt{1-3\mu_c}} \text{ with } \mu_c = \frac{m_H}{3m_H + m_P}, \quad (10)$$

The most convenient expression for the kinetic energy can be obtained in terms of these coordinates, while the analytical representation using internal polar coordinates includes additional terms in the kinetic energy operator [35]. Mass-dependent coordinates (10) keep the same symmetry properties as initial polar coordinates. Let us use the KE operator in the form Ref. [30,31,37] where the KE operator does not comprise the singular terms of the $\sin(q)^2$ form.

Therefore one can use the $Y_{n,0}(q,0)$ spherical harmonics as basis functions that do not vanish at $q=\pi$. The kinetic energy of the AB_4 - and AB_3 -type molecules can be expressed in the form [37]:

$$T_V / (-\frac{1}{2}h^2) = \sum_{jk}^{3N-6} g^{jk} \frac{\partial^2}{\partial \mathcal{R}_j \partial \mathcal{R}_k} + \sum_j^{3N-6} h^j \frac{\partial}{\partial \mathcal{R}_j}. \quad (11)$$

For radial coefficients $g^{ij} = \frac{\delta_{ij}}{m_i}$. The angular diagonal coefficients of the g matrix are written in

the form: $\sin^2(q_{ij}) \left(\frac{1}{m_i r_i^2} + \frac{1}{m_j r_j^2} \right) \frac{\partial^2}{\partial^2 \cos(q_{ij})}$. For a pair of angles $q_{ij}q_{lk}$, the angular off-diagonal

elements of the g matrix vanish unless $i=l$ or $j=k$:

$$g^{\cos(q_{ij}), \cos(q_{jk})} = \frac{-\cos(q_{ij})\cos(q_{jk}) + \cos(q_{ik})}{m_j r_j^2} \frac{\partial^2}{\partial \cos(q_{ij}) \partial \cos(q_{jk})}. \text{ Note, that in the } g \text{ matrix, all}$$

off-diagonal radial-angular elements vanish. The radial and angular coefficients of the h matrix

are correspondingly $h^i = \frac{2}{m_i r_i}$ and $h^{\cos(q_{ij})} = -2 \cos(q_{ij}) \left(\frac{1}{m_i r_i^2} + \frac{1}{m_j r_j^2} \right) \frac{\partial}{\partial \cos(q_{ij})}$. For AB_4

molecules, the summation in (11) is performed over four radial coordinates r_i and six angles q_{ij} ,

while for AB_3 molecules, only three radial coordinates r_i and three angles q_{ij} are used. In this

paper, the sums over the diagonal and angular first derivative $h^i \frac{\partial}{\partial \mathfrak{R}_i}$ terms are referred to as a

diagonal term. It is easy to calculate the diagonal matrix element using the following equality

$$[40]: \left(\frac{\partial^2}{\partial^2 q_{ij}} + ctg(q_{ij}) \frac{\partial}{\partial q_{ij}} \right) Y_{l,0}(q_{ij}, 0) = -l(l+1)Y_{l,0}(q_{ij}, 0).$$

Note that only the full sum of all diagonal and off-diagonal angular terms results in symmetric matrix elements, while each of these sums, e.g. the summation only over the diagonal or off-diagonal terms, results in asymmetric matrix elements. In the present paper, to calculate matrix elements, we use the following property of the reduced matrix elements [41,42]:

$\langle F_L | \hat{O} | F_R \rangle = \langle PF_L | P\hat{O} | PF_R \rangle$ where P is an element of the molecular symmetry group. Due to this property, for AB_3 molecules, it is not mandatory to calculate all three diagonal and off-diagonal angular matrix elements. It is sufficient to calculate only one simplest diagonal and one off-diagonal angular matrix element. We calculate the matrix element for the sum of three diagonal operators using the expression:

$$\left\langle n_1 n_2 n_3 \left| \frac{\partial^2}{\partial q_{23}^2} + ctg(q_{23}) \frac{\partial}{\partial q_{23}} \right| k_1 k_2 k_3 \right\rangle = (2\pi)^3 \int_0^\pi \int_0^\pi \int_0^{2\pi} \sum_{l_1 l_1' l_2 l_2' l_3 l_3'} c_{n_1 l_1} c_{k_1 l_1'} c_{n_2 l_2} c_{k_2 l_2'} c_{n_3 l_3} c_{k_3 l_3'} \{l_3' (l_3' + 1)\} Y_{l_1,0}^*(q_{12}, 0) Y_{l_1,0}(q_{12}, 0) Y_{l_2,0}^*(q_{13}, 0) Y_{l_2,0}(q_{13}, 0) Y_{l_3,0}^*(q_{23}, 0) Y_{l_3,0}(q_{23}, 0) d \cos(q_{12}) d \cos(q_{13}) dt_{23}$$

Using the designation

$$J_{n_3, k_3, L, 0}^{D2} = \sum_{l_3 l_3'} c_{n_3 l_3} c_{k_3 l_3'} [l_3' (l_3' + 1)] K_{l_3 l_3' L} \sqrt{\frac{2L+1}{4\pi}}, \quad (12)$$

we can write the diagonal matrix element in the following form:

$$\left\langle n_1 n_2 n_3 \left| \frac{\partial^2}{\partial q_{23}^2} + ctg(q_{23}) \frac{\partial}{\partial q_{23}} \right| k_1 k_2 k_3 \right\rangle = (2\pi)^3 \sum_L \frac{1}{\sqrt{\pi(2L+1)}} J_{n_1, k_1, L, 0}^0 J_{n_2, k_2, L, 0}^0 J_{n_3, k_3, L, 0}^{D2} \quad (13)$$

It is more convenient to calculate the off-diagonal matrix element using the polar coordinates.

Let us show, that the off-diagonal matrix element can be expressed in the following form:

$$\left\langle n_1 n_2 n_3 \left| \cos(t_{23}) \frac{\partial}{\partial q_{12}} \frac{\partial}{\partial q_{13}} \right| k_1 k_2 k_3 \right\rangle = (2\pi)^3 \sum_L J_{n_1, k_1, L, 1}^{D1} J_{n_2, k_2, L, 1}^{D1} J_{n_3, k_3, L, 0} \frac{1}{\sqrt{\pi(2L+1)}}, \quad (14)$$

where $J_{n_i k_i L, 1}^{D1}$ is a coefficient similar to the coefficients used in Eqs. (6), (8), (12).

To prove the formula (14), we use Eq. (4) for product of J functions depending on q_{23} , integrate Eq. (14) over t_{23} , and using the known formula for spherical harmonics [40]

$Y_{l,-m}(q, \varphi) = (-1)^m Y_{l,m}(q, -\varphi)$, we get:

$$\int_0^\pi \int_0^\pi \int_0^{2\pi} f_{n_1}(q_{12}) f_{n_2}(q_{13}) f_{n_3}(q_{23}) \left(\cos(t_{23}) \frac{\partial}{\partial q_{12}} \frac{\partial}{\partial q_{13}} \right) f_{k_1}(q_{12}) f_{k_2}(q_{13}) f_{k_3}(q_{23}) d \cos(q_{12}) d \cos(q_{13}) dt_{23} = (2\pi)^2 \times$$

$$\sum_{l_1 l_2} c_{n_1 l_1} c_{k_1 l_1} c_{n_2 l_2} c_{k_2 l_2} \int_0^\pi \int_0^\pi f_{n_1}(q_{12}) f_{n_2}(q_{13}) \sum_L K_{l_1 l_2 L} \left(\frac{\partial}{\partial q_{12}} \frac{\partial}{\partial q_{13}} f_{k_1}(q_{12}) f_{k_2}(q_{13}) \right) Y_{L,1}(q_{12}, 0) Y_{L,1}(q_{13}, 0) d \cos(q_{12}) d \cos(q_{13})$$

If we denote the one-dimensional integrals in the right-hand member of this expression *via*

$$J_{n_1 k_1 l_1, 1}^{D1} = \int f_{n_1}(q_{12}) \left(\frac{\partial}{\partial q_{12}} f_{k_1}(q_{12}) \right) Y_{L,1}(q_{12}, 0) d \cos(q_{12}), \text{ we get Eq. (14).}$$

One can simplify the expression for the $J_{n_1 k_1 l_1, 1}^{D1}$ coefficient using the following formula [40]:

$$\frac{\partial}{\partial q} Y_{l,m}(q) = m \cot q Y_{l,m}(q) + \sqrt{l(l+1) - m(m+1)} Y_{l,m+1}(q), \text{ we get:}$$

$$J_{n_1 k_1 l_1, 1}^{D1} = (2\pi) \sum_{l_1 l_2} c_{k_1 l_1} c_{k_2 l_2} \int Y_{l_1 0}(q_{12}, 0) \sqrt{l_2(l_2+1)} Y_{l_2 1}(q_{12}, 0) Y_{L,1}(q_{12}, 0) d \cos(q_{12}). \text{ Using Eq. (2) with } s_1=0, s_2=1,$$

and taking into account the orthogonality of spherical harmonics, we get

$$J_{n_1 k_1 l_1, 1}^{D1} = \sum_{l_1 l_2} c_{k_1 l_1} c_{k_2 l_2} \sqrt{l_2(l_2+1)} \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} C(l_1, 0, l_2, 0, L, 0) C(l_1, 0, l_2, 1, L, 1)$$

For even values of l_1+l_2+L , it can be shown [40] that:

$$C(l_1, 0, l_2, 1, L, 1) = C(l_1, 0, l_2, 0, L, 0) \frac{l_2(l_2+1) + L(L+1) - l_1(l_1+1)}{2[L(L+1)l_2(l_2+1)]^{1/2}}$$

Since the $C(l_1, 0, l_2, 0, L, 0)$ coefficients are not equal to zero only at even values of l_1+l_2+L , one can simplify the expression obtained for J in the following way:

$$J_{n_1 k_1 l_1, 1}^{D1} = \sum_{l_1 l_2} c_{k_1 l_1} c_{k_2 l_2} K_{l_1 l_2 L} \frac{l_2(l_2+1) + L(L+1) - l_1(l_1+1)}{4[\pi L(L+1)]^{1/2}} [2L+1]^{1/2} \quad (15)$$

V. FULL SYMMETRY BASIS AND CALCULATION OF VIBRATIONAL LEVELS

The initial angular basis (1) can be easily symmetrized and tailored for calculations that use a symmetrical basis. Using the standard operators, one can construct the full symmetry basis set of functions:

$$|n_1 n_2 \dots n_S | kG\sigma \rangle = \hat{P}_{kG\sigma} |n_1 n_2 \dots n_S \rangle. \quad (16)$$

For example, for AB₃ molecules, we use the following six projection operators (17) to construct symmetrized three-dimensional angular $|n_{12}n_{13}n_{23}, k_A G_A \sigma_A\rangle$ and radial $|n_1 n_2 n_3, k_R G_R \sigma_R\rangle$ basis sets:

$$\begin{aligned} P_{A_1} &= (e + (12 + (13))(e + (23)))/\sqrt{6}, & P_{A_2} &= (e - (12) - (13))(e - (23))/\sqrt{6}, \\ P_{1E_a} &= ((13) + (12) - 2e)(e + (23))/\sqrt{12}, & P_{1E_b} &= ((13) - (12))(e + (23))/2, \\ P_{2E_a} &= ((13) - (12))(e - (23))/2, & P_{2E_b} &= (-(12) - (13) - 2e)(e - (23))/\sqrt{12} \end{aligned} \quad (17)$$

Note that in the present work, the angular $|n_{12}n_{13}n_{23}, k_A G_A \sigma_A\rangle$ and radial $|n_1 n_2 n_3, k_R G_R \sigma_R\rangle$ basis sets also are referred to as $f_{3D,BAB}^G(q_{12}, q_{13}, q_{23})$ and $f_{3D,AB}^G(r_1, r_2, r_3)$, respectively. The vibrational basis functions and the PES operators are expressed in terms of irreducible tensor operators [41,42]. Each tensor is associated to a binary tree [43]. The binary trees of vibrational coupling for AB₃ molecules are shown in Fig.1. Each branch of the tree is characterized by its symmetry. The binary tree of the PES parameters is shown in the left part of the figure while the binary tree of the vibrational basis coupling is shown in the right part of this figure. In order to determine the PES operators of the A₁ symmetry type, formed from the symmetrized coordinates [24,25] $SR_{A_1}, SR_{E_a}, SR_{E_b}, SA_{A_1}, SA_{E_a}, SA_{E_b}$ we used the two step procedure. In first step, we construct the symmetrized power of the coordinates $[SR_{A_1}]^{P_1}, [SR_{E_a}]^{P_2}, [SA_{A_1}]^{P_3}, [SA_{E_a}]^{P_4}$. In second step, we couple the symmetrized powers of different symmetrized coordinates into irreducible trees. A set of all possible trees of the A₁ symmetry type gives a final set of trees. The potential function was developed in power series of irreducible tensors $V(r_1, \dots, r_n) = \sum_i K_i R_i(r_1, \dots, r_n)$. The complete vibrational basis functions can be constructed by coupling the symmetrized basis functions of all coordinates into binary trees. For AB₃ and AB₄ molecules [26,27], it is necessary to perform only one coupling of stretching basis function and bending basis function $(|n_{12}n_{13}n_{23}, G_A\rangle)$ and

$|n_1 n_2 n_3, G_R\rangle$ in Fig 1). We used the following standard definition of the direct product of irreducible tensors [41,42]:

$$(T^{C'} \times T^{C''})^C_{\sigma} = \sqrt{[C]} \sum_{\sigma' \sigma''} F \begin{pmatrix} C' & C'' & C \\ \sigma' & \sigma'' & \sigma \end{pmatrix} T^{C'}_{\sigma'} T^{C''}_{\sigma''},$$

where C, C', C'' are irreducible representations, $\sigma, \sigma', \sigma''$ are their rows, and $F \begin{pmatrix} C' & C'' & C \\ \sigma' & \sigma'' & \sigma \end{pmatrix}$ are $3G$ symbols corresponding to Clebsch-Gordan coefficients of the C_{3v} symmetry group. Here $[C]$ stands for the dimension of C . The recoupling scheme used for calculations of matrix elements is similar to one described in ref. [43]. Using the standard definition of the reduced matrix elements [41,42]:

$$\langle \psi^{(C')}_{\sigma'} \| V^{(C)}_{\sigma} \| \psi^{(C'')}_{\sigma''} \rangle = \frac{\langle \psi^{(C')}_{\sigma'} \| V_{\sigma}^{(C)} \| \psi^{(C'')}_{\sigma''} \rangle}{F \begin{pmatrix} C' & C & C'' \\ \sigma' & \sigma & \sigma'' \end{pmatrix}} \quad (18)$$

and the recoupling matrix elements formula:

$$\langle (\psi_1^{C_1} \psi_2^{C_2})^{C'} \| (V_1^{\Gamma_1} V_2^{\Gamma_2})^{\Gamma} \| (\psi_1^{C_1} \psi_2^{C_2})^{C''} \rangle = \sqrt{[C'] [\Gamma] [C'']} \begin{pmatrix} C_1' & C_2' & C' \\ \Gamma_1 & \Gamma_2 & \Gamma \\ C_1'' & C_2'' & C'' \end{pmatrix} \langle \psi_1^{C_1} \| V_1^{\Gamma_1} \| \psi_1^{C_1} \rangle \langle \psi_2^{C_2} \| V_2^{\Gamma_2} \| \psi_2^{C_2} \rangle, \quad (19)$$

where the indices C and Γ denote point group irreducible representations (all other indices are omitted for the sake of simplicity) a multi-dimensional matrix element can be expressed as a sum of the one-dimensional matrix elements products.

The use of a nonorthogonal angular basis does not complicate the procedure for obtaining eigenvalues. There are two methods of solution eigenvalue vibrational problem. In first method, one can solve the eigenvalue angular problem, and then use the resulting orthogonal eigenvectors to construct the symmetrized orthogonal angular basis. In second method, one can use a nonorthogonal vibrational basis set. To solve the symmetric-definite generalized eigenvalue problem, standard computational programs, such as programs available in LAPACK library can be applied. Note that this technique does not consume too much additional main memory because

the norm matrix is used only to transform the V(PES)+T(KE) matrix. The eigenvalues can be obtained then from the transformed V+T matrix. As a rule, the use of the full symmetry properties allows one to considerably decrease the dimension of the V+T matrices. The general technique used for the vibrational energy levels calculation includes several steps. Step 1: the solving of one-dimensional vibrational problems and calculation of the J coefficients like (6,8,12,15) for angular problem. Step 2: the symmetrization of wave functions and calculation of irreducible matrix elements for angular and radial trees in terms of a sum of products of one-dimensional integrals. Step 3: Eq. (19) is recursively used for obtaining sub trees of basis functions until the subsequent sub tree becomes a tree representing only the same type coordinates or a leaf. The 9G symbols are saved in the memory. Vibrational reduced matrix elements are stored on disk separately for each type of symmetry. Step 4: the solution of the generalized eigenvalue problem.

VI. EXAMPLE OF APPLICATION TO PH₃ MOLECULE

In the present work, we employ potential in the mass-dependent orthogonal coordinates that has been determined in the paper Ref. [25]. One-dimensional eigenfunctions were computed from the multi-dimensional PES by fixing all other coordinates to the equilibrium values. For the stretching coordinates, the following Morse type function was used:

$$f(r'; a) = 1 - \exp[-a(r'_i - r'_e)] \quad (20)$$

where $a=1.9$. This value of the a parameter ensures that the second order term of the potential provides a reliable representation for the one-dimensional stretching cut. The terms of higher orders result in relatively small corrections. For the interbond angular coordinates, the following functions were used:

$$\phi(q_{ij}) = \cos(q_{ij}) - \cos(q_e) \quad (21)$$

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3 The above defined elementary functions (20-21) were used to build six symmetrized
4 linear combinations of $SR_{A_1}, SR_{E_a}, SR_{E_b}, SA_{A_1}, SA_{E_a}, SA_{E_b}$ [24,25] by using three projection
5 operators $P_{A_1}, P_{1E_a}, P_{1E_b}$ from six existing projection operators (17) for the group of permutations
6 of three H-atoms. The subindices correspond to irreducible representations of the C_{3v} point
7 group. In order to determine the six-dimensional (6D) expansion terms of the A_1 symmetry type,
8 we applied the two step procedure [described above](#). First step corresponds to the construction of
9 the symmetrized powers, and second step to the coupling of the symmetrized powers of different
10 symmetrized coordinates in irreducible trees. A set of all possible trees of the A_1 representation
11 gives a final set of the 6D expansion terms. Two types of localized one-dimensional wave
12 functions were constructed: $Q_n(q_{ij})$ - functions of bending angles q_{ij} , and $R_n(r_i)$ - functions of
13 radial coordinates r_i . One can obtain the symmetrized vibrational basis set by coupling the
14 $|n_{12}n_{13}n_{23}, G_A\sigma_A\rangle$ and $|n_1n_2n_3, G_R\sigma_R\rangle$ basis functions using Clebsch-Gordan coefficients of the
15 C_{3v} symmetry group.

16 To ensure a rapid computation of the irreducible matrix elements, we applied the
17 following technique. We first calculate all J-coefficients (6,8,12,15). After this, we calculate
18 angular and radial three-dimensional matrix elements and store results into main memory. It is
19 not necessary to use an optimization of calculations to get the radial matrix elements. At the same
20 time, one needs to use an optimization of calculations to get the angular irreducible matrix
21 elements.

22 Several convergence tests involving calculated vibration levels have been already
23 performed using various analytical PES representations and C_{2v} symmetry [25]. A good
24 agreement between vibration levels calculated using two PES fitted in orthogonal mass-
25 dependent coordinates (10) and in internal mass-independent coordinates have been already
26 reported in Ref. [25]. In this section, we check only the full symmetry nonorthogonal vibrational
27 basis set convergence in orthogonal mass-dependent coordinates (10). Calculations with

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3 increasing dimensions for the basis cut-off suggest that our vibration energies up to 7000 cm^{-1} are
4 converged in average to 0.01 cm^{-1} or better. The corresponding residuals increase gradually with
5 energies. Similarly to Ref. [25], in the present paper, we use the nonsymmetrized vibrational
6 basis dimension as the basis dimension. All calculations have been performed using a full
7 symmetry-adapted set of basis functions. The used basis functions have been grouped into the A_1 ,
8 A_2 , and E symmetry classes. Let us consider four basis sets referred to as I, II, III, IV. The
9 dimensions of those basis sets are 14643, 16047, 17889, and 19230 functions, respectively. The
10 standard deviation between energy levels calculated using the basis sets I-IV, I-IV, III-IV is
11 0.034482 , 0.002616 , and 0.000571 cm^{-1} , respectively, up to 7000 cm^{-1} . Because all lower
12 calculated energy levels show a slight difference with respect to those obtained in Ref. [25] only
13 four observed band centers in the region $6700\text{-}7000\text{ cm}^{-1}$ were considered. Comparison of these
14 observed band centres of PH_3 molecule and calculated from PES[25] in four basis sets I, II, III,
15 IV given in Table 1. The deviations between vibration levels calculated using vibrational basis set
16 IV and basis sets I, II, and III are shown in Fig. 2. Similarly to the results of calculations using
17 internal coordinates [25], the main contribution to this standard deviation results from two levels
18 above 6500 cm^{-1} shifted to 0.3 and 0.5 cm^{-1} (these levels are not shown in Fig. 2) and without
19 these levels the standard deviation between all set is less 0.01 cm^{-1} . It is possible, that the
20 considerable deviation for these two levels is resulted from wrong asymptotic behavior of the
21 potential when the molecule is far from its equilibrium geometry. In general, one can come to the
22 conclusion that calculations using the nonorthogonal C_{3v} basis and the basis reported in the Ref.
23 [25] result in the similar convergence behavior. For example, according to results from Ref. [25],
24 the standard deviation between two vibrational calculations using 12000 and 15000 non-
25 symmetrised basis functions is 0.048 cm^{-1} . At the same time, the use of the full symmetry
26 provides that the computation speed of vibration levels is several times faster than for
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3 computations using the C_{2v} basis. In addition, the computations using the full symmetry require
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5 less memory space that allows us to work with big basis sets.
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10 VII. DISCUSSION AND CONCLUSION

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12 The primary motivation for this study was to demonstrate a good convergence of new
13 angular basis and to check algorithm of the matrix elements calculation. To do this, we dealt only
14 with a solution of vibrational problem using orthogonal coordinates. At the same time, one can
15 calculate the matrix elements of the vibration-rotation and nonorthogonal terms of the
16 Hamiltonian in a similar way. For example, the matrix elements (14) have been calculated in
17 polar coordinates. The functions of the torsion angle used to write vibration-rotation and
18 nonorthogonal terms of the Hamiltonian can be expressed in terms of three angles q_{ij} . This allows
19 one to obtain a symmetrical form similar to (11). In addition, the dependence of the PES
20 functions used in Ref. [17] on $\sin(q_{ij})$ presents no essential difficulties.
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34 The form of angular basis set based on $\cos(q_{ij})$ product removes the $\sin(q)^{-2}$ singularity
35 from the vibrational kinetic energy operator in polar coordinates[35] also for AB_4 , ABC_3 type
36 molecules. However, the matrix elements calculations are complicated by the presence of a
37 redundancy among the six angles q_{ij} [19,10] for these molecules. On the other hand,
38 symmetrisation of these basis functions can be achieved easily *via* projector operators technique.
39 For the CH_4 molecule, the study of spectra in the range higher than 5400 cm^{-1} is of considerable
40 importance and it is difficult to obtain a good convergence of the calculated high energy levels
41 without using the T_d symmetry. The paper [8,9,26] uses the C_{3v} symmetry. This means that only 6
42 from 24 permutations in T_d point group are in use. In paper [22], only 8 from 24 elements of T_d
43 point group were used. Thus, the cited papers do not employ the full symmetry of the molecule.
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Of course, one can try to perform a numerical symmetrization of the angular basis, but it is a

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3 difficult task, because an accurate solution of the vibration problem requires the use of the high
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5 excited angular basis functions.
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8 The calculation of the angular matrix elements for AB_4 molecules is a rather difficult task.
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10 The calculation procedures for the AB_3 matrix elements employ only the $(l_1, 0, l_2, 0, l, 0)$
11 coefficients, while the calculations of the AB_4 matrix elements employ the $(l_1, 0, l_2, MIL, M)$
12 coefficients. For high values of L and M , the calculation of the $(l_1, 0, l_2, MIL, M)$ coefficients
13 becomes a difficult problem [45,46,29]. For the AB_4 type molecules the same coupling scheme
14 (Fig 1) as for the AB_3 type molecules could be applied. For ABC_3 molecules [27], the complete
15 angular basis function could be received by coupling the three-dimensional symmetrized angular
16 function $f_{3D,ABC}^G(q_{12}, q_{13}, q_{14})$ and the two-dimensional angular symmetrized function
17 $f_{2D,CBC}^G(q_{23}, q_{24}, q_{34})$ or two-dimensional wave function $f_{2D,CBC}^G(t_{23}, t_{24})$ of two torsion angles
18 [26,27]. The symmetrized form of the PES used in the present paper contains much less terms
19 than a nonsymmetrized form. For example, the 6th order PES expansion for AB_3 , AB_4 and ABC_3
20 molecules contains only 196, 287 and 967 parameters, respectively. At the same time, the
21 number of terms in nonsymmetrized forms [27] is 20-40 times greater than that in symmetrized
22 forms. This proves that computations using symmetry-adapted forms of PES are very important.
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42 In our future works, we will try to apply these computations to AB_4 and ABC_3 molecules.
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47 Acknowledgement

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Figure captions**Figure 1**

Binary tree of vibrational coupling for AB₃ molecules. In the left part: tree of the PES parameters.

In the right part: tree of the basis function coupling.

Figure 2

Deviations between vibration levels of PH₃ molecule calculated in various vibrational basis sets.

Table I. Comparison of some observed band centers of PH₃ and calculated from PES[25] in four basis sets I, II, III, IV. All values are in cm⁻¹.

PH ₃ band	Obs. †	I	II	III	IV
3v ₃ (E)	6714.60	6714.769	6714.771	6714.766	6714.766
2v ₁ +v ₃ (E)	6883.73	6886.345	6886.348	6886.344	6886.344
v ₁ +2v ₃ (E)	6890.86	6890.122	6890.125	6890.121	6890.120
3v ₃ (A ₁)	6971.16	6971.360	6971.362	6971.359	6971.358

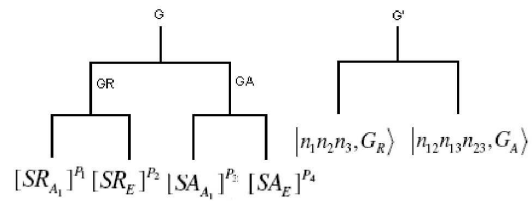
† See Ref [44].

Special characters

† footnote

v lower case nu

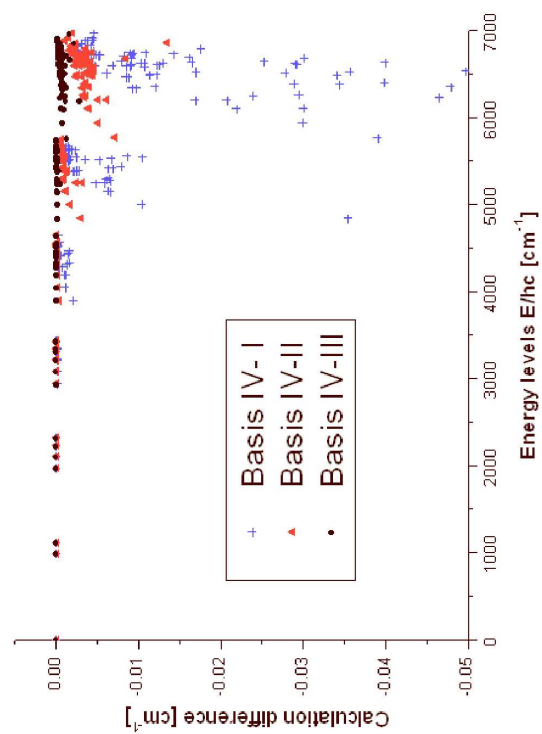
For Peer Review Only



Binary tree of vibrational coupling for AB₃ molecules. In the left part: tree of the PES parameters.

In the right part: tree of the basis function coupling.

215x279mm (600 x 600 DPI)



Deviations between vibration levels of PH₃ molecule calculated in various vibrational basis sets.
215x279mm (600 x 600 DPI)

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3 Reply to the Reviewer 1 (R1) of the manuscript TMPH-2010-0349
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6 by A.V. Nikitin
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9 In the Introduction (and possibly later) the reference list [4-27] might include the papers
10 of Kozin et al (2003-5) which also consider and apply some of the topics considered in
11 this paper (orthogonal coordinates, contracted angular basis functions, efficient
12 calculation of matrix elements ...) in the context of 4-atomic molecules.
13

14 Reply> I added two references [28,29]
15

16 Also in the first paragraph of the Intro, references [34,35] could be cited in the context of
17 the symmetry of AB₄ systems.
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20 Reply> I added next sentence to the introduction: One variational method for calculating
21 excited bending states of symmetric tetrahedral pentaatomic molecules based on the use
22 of Radau coordinates and Jacobi polynomials as the basis functions has been presented in
23 [30,31].
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25
26 p4, line 43, which "New Algorithm"? The one to be described in This Work?

27 Reply> Replaced on "Described in this work algorithm"
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29 p5, line 54, has "t23" been defined?

30 Reply> I added the definition
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33 p7, line 8, insert "angular" before "PES"

34 Reply> OK
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36 p7, line 8, should "the power functions" read "a sum of product functions"?

37 Reply> OK
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41 p8 (and elsewhere), I think the symbol q is being used in too many different and
42 confusing ways: general coordinates with 1 subscript (as in equation 11) and also
43 interbond angles with 2 subscripts (as in line 3) or no subscripts (as in line 36).
44

45 Reply> OK, general coordinates changed to R
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47 p8, line 48, should "couple" be just "pair"?

48 Reply> OK
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50 p9, line 13, what are "linear in q_{ij} terms"?

51 Reply> Changed to 'first derivative'
52
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54
55 p9, why has "cos(q_{ij})" in line 18 become just "q_{ij}" in line 45?

56 Reply> My misprint! Line 18 changed to q
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6 p9, line 29, what are the "reduced matrix elements"? (They are defined later, but I think
7 need some explanation here or earlier).

8 Reply> I just added two references because there are explanation in next paragraph
9

10
11 p11, line 3, "The not symmetry-adapted" should be "The initial" (and I think everything
12 after "symmetrised" could be deleted in that sentence!).

13
14 Reply> OK, changed
15

16 p11, line 21, there are 2 closing brackets missing in the first formula.

17
18 Reply> OK, changed
19

20
21 p11 & fig 1, the "binary tree" seems trivial - maybe all is explained in ref [41] but
22 perhaps a further sentence of explanation here would make the significance of this
23 clearer?

24 Reply> I agree that figure 1 is trivial. But readers very often don't understand coupling
25 scheme. I added some details in the text. Figure 1 is also updated.
26
27

28 p11, line 46, "the symmetrized coordinates S_i " (as distinct from symmetrised basis
29 functions) appear suddenly and without definition - again some explanation might help
30 the reader.

31
32 Reply> S_i replaced and text is changed
33

34
35 p13, line 3, "In the sequel" is not clear (does it mean "next" or "in practice" ...?)

36
37 Reply> Text changed
38

39 p15, lines 20-27, apparently a sentence is repeated but with different numbers!

40
41 Reply> Deleted one sentence
42

43 p15 lines 27-9 and Table 1, why only compare with 4 observed band centres? What
44 makes these special? Are there no other observations?

45 Also, how do the calculated vibrational levels compare with other variational calculations
46 on this PES?

47 Reply> I added one sentence to text. Calculated levels are very closed to [25]. The
48 purpose of article just demonstrate that the algorithm work. Orthogonal and non
49 orthogonal surfaces [25] are a little different so direct comparing is not informative.
50
51

52
53 p15, the speculation about "some peculiarities of the potential" seems very vague - can
54 the author be more specific? Can he say at least how the two large deviations vary with
55 basis set?
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Reply> Potential don't adapted for calculation of high excited states ($>7000\text{cm}^{-1}$). Wrong asymptotic behavior of PES leads to problems with basis convergence. New PES is under construction now.

Other minor errors (but NOT an exhaustive list!):

p1, in the title, "of energy levels calculation for the AB₃ types molecules" should be "for the calculation of energy levels of AB₃ type molecules"

Reply> OK, changed

All through the text the author has trouble with articles ("the" and "a"); for example on p2, line 6, "the symmetry-adapted" should be "a symmetry-adapted"; line 10, insert "the" before "kinetic" and line 20, insert "the" before "PH₃".

Reply> Changed

p2, line 15, "vibrational matrix elements calculation" should be "the calculation of vibrational matrix elements".

Reply> OK, changed

p3, line 24, should "numbers" be "quantum numbers" or "atoms"?

Reply> OK, changed to atoms

p4, line 29, "has no the" should be "does not have the" or "has no"

Reply> OK, changed to has no

p4, line 43, "not orthogonal" should be "non-orthogonal"

Reply> OK, changed

p4, line 53, "completion" should be "final"

Reply> OK, changed

p5, line 39, insert "of" after "form"

Reply> OK, changed

p6, line 55, Should "In a particular case" be "In three particular cases" or "For example"?

Reply> OK, changed to for example

p7, line 11, the notation "n_{ij}" is used for the powers of the cos functions but it seems to be P_{ij} thereafter.

Reply> OK, changed

p11, line 51, "obtained" should be "resulting"

Reply> OK, changed

p15, line 31, delete "standard"

1
2
3 Reply> OK, changed
4

5
6 p15 line 22, "CM" should be lower case.

7 Reply> OK, changed
8

9
10 p16, line 13, "approve" should be "demonstrate"

11 Reply> OK, changed
12

13 p17, line 40, "prominent" should be "important."

14 Reply> OK, changed
15

16 p21, footnote to Table 1, why not give the original references here?

17 Reply> OK, added
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