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An efficient method for energy levels calculation using full symmetry and exact kinetic energy operator: Tetrahedral molecules

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A simultaneous use of the full molecular symmetry and of an exact kinetic energy operator (KEO) is of key importance for accurate predictions of vibrational levels at a high energy range from a potential energy surface (PES). An efficient method that permits a fast convergence of variational calculations would allow iterative optimization of the PES parameters using experimental data. In this work, we propose such a method applied to tetrahedral AB_4 molecules for which a use of high symmetry is crucial for vibrational calculations. A symmetry-adapted contracted angular basis set for six redundant angles is introduced. Simple formulas using this basis set for explicit calculation of the angular matrix elements of KEO and PES are reported. The symmetric form (six redundant angles) of vibrational KEO without the $\sin(q)^{-2}$ type singularity is derived. The efficient recursive algorithm based on the tensorial formalism is used for the calculation of vibrational matrix elements. A good basis set convergence for the calculations of vibrational levels of the CH_4 molecule is demonstrated. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4913520]

I. INTRODUCTION

The theory and computational modeling of molecular vibrations is of a major interest for molecular spectroscopy, theoretical chemistry and related fields. A progress in calculation of potential energy surfaces (PES) and vibration-rotation spectra of three-atomic molecules (see Refs. 1–7 and references therein) have been followed by advances in computational methods for nuclear motion in larger molecules including high symmetry polyatomics.[8–20] Some mathematical aspects have been reviewed in Ref. 21.

For ABC_3 type molecules, variational calculations have been applied to CH_3F[22] and CH_3Cl[23] molecules using finite basis representations and full C_{3v} symmetry. The same computational codes implementing symmetry properties of the C_{3v} sub-group have been applied to methane molecule.[24,25] Other methods of vibration-rotation spectra computation for AB_4 type molecules have been developed by Schwenke[8,26] and by Wang and Carrington[27–30] also using exact kinetic energy operator (KEO). In spite of a considerable number of publications in this domain, most of those that used exact KEO did not completely account for the full tetrahedral molecular symmetry. An accurate convergence in a moderate energy range can be achieved with a partial account of the symmetry,[8,29] this being also confirmed by the studies of symmetry breaking isotopic substitutions.[31,32] However, a full account of the symmetry properties involves smaller dimensions of basis sets and is beneficial for handling strict degeneracies and selection rules, particularly in case of transitions among highly excited vibration-rotation states and high temperatures spectra. Variational methods specific for tetrahedral molecules have been considered by Xie and Tennison[33,34] using Radau coordinates and Jacobi polynomials as the basis functions, but for bending and stretching states separately.

Some different approaches relied on expansions of the nuclear KEO and PES in normal mode or symmetry adapted coordinates using MULTIMODE[35–37] or TROVE[38] program suits. Rey *et al.*[39,40] have developed a computational method for rovibrational calculations using an expansion of Eckart-Watson Hamiltonian[41,42] in terms of irreducible normal mode T_d tensors. Calculations of methane energy levels using perturbative or iterative methods have also been reported.[43–48] The advances in the dipole moment theory[11,49] permitted full quantum-mechanical methane spectra predictions.[40,50,51] A common challenge for all variational methods is the basis set convergence of multi-dimensional vibration-rotation calculations for high energy states.

The aim of the present work is to develop an efficient method using both full tetrahedral symmetry of AB_4 molecules and the exact KEO in order to achieve a fast convergence of variational nuclear motion calculations. When using bending internal coordinates, such as six q_{ij} angles between four radial vectors, one-dimensional basis functions of these coordinates are generally not independent and non-orthogonal. If one considers the full T_d (M) point group as isomorphic one to a finite

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permutation group (permutations of four identical B atoms), the construction of the symmetry adapted basis set using the q_{ij} angles becomes a trivial task. However, a non-trivial issue is to work out an efficient technique for calculations of multidimensional integrals using this basis. In this study, a symmetry adapted approach using finite basis representations is applied to tetrahedral pentatomic molecules to derive straightforward techniques of matrix elements calculation both for the exact KEO and for the PES model. A fast spectrum computation would allow in turn increasing basis sets and accessing higher energies. Here, we mostly focus on the angular part of the matrix elements, because the symmetry properties of the radial part are quite simple and have been worked out in many previous studies. We also assume that the molecule has a deep PES minimum corresponding to the r_e-equilibrium configuration.

Tennyson and Sutcliffe,[52] Gatti, Iung, Nauts, Chapuisat *et al.*,[53,54] Mladenovic'[55,56] and Schwenke[57] have reported derivations of kinetic energy operators for treating rotations and vibrations of polyatomic molecules using polyspherical type coordinates. In these coordinates, the N nuclear position vectors are transformed to $N-1$ internal vectors and the nuclear center of mass vector, whereas the internal displacements are parametrized by spherical polar coordinates: R_i, θ_i, φ_i, $I = 1,\ldots,N-1$, where $(\theta_1 = 0, \varphi_1 = 0, \varphi_2 = 0)$. The symmetric form of vibration KEOs is known.[33,34,58] Instead of using the torsion angles, the symmetric form uses additional angles between molecular bonds. This form of KEO is more suitable for the representation of basis functions, which we use in the present work. The use of the symmetric form is particularly interesting because this does not involve the $\sin(q)^{-2}$ singularity which appears in the KEO of Ref. 55 in polar coordinates. In some formulations of the theory, the vibration basis set constructed as a product of one dimensional functions depending on the bending q and torsion t angles has to be constrained in a way that $f_n(q)$ are vanishing at $\sin(q) = 0$. From a physical point of view, such a choice of $f_n(q)$ is not always relevant as in certain vibrational displacements, a molecule could access geometric configurations corresponding to the angle $q = \pi$ with rather high probability.

In this work, we use mass-dependent orthogonal coordinates,[55] which in case of AB_4 molecules can be defined via four vectors $\{\vec{r}_i\}$,

$$\vec{r}_i = \vec{r}_{AB_i} + d\sum_{j=1}^{4}\vec{r}_{AB_j}, \text{ where } d = -\frac{1}{4} + \frac{1}{4\sqrt{1-4\mu_c}}$$

$$\text{with } \mu_c = \frac{m_H}{4m_H + m_C}, \tag{1}$$

where $\vec{r}_{AB_i}$ are the vectors linking the A atom with B_i atoms (I = 1, 2, 3, 4). Using Eq. (1), one can define ten salar coordinates including four vector lengths $\{r_1, r_2, r_3, r_4\}$ and six angles $\{q_{12}, q_{13}, q_{14}, q_{23}, q_{24}, q_{34}\}$, where q_{ij} is the angle between the vectors $\vec{r}_i$ and $\vec{r}_j$. It is well known that for a pentatomic non-linear molecule, six angles are redundant (Ref. 59 and references therein) since total number of vibrational degrees of freedom should be nine. However, such redundant coordinates represent certain advantage as they keep obvious permutation symmetry of identical B_i atoms and permit quite simple symmetrized expression for the KEO.[34,58]

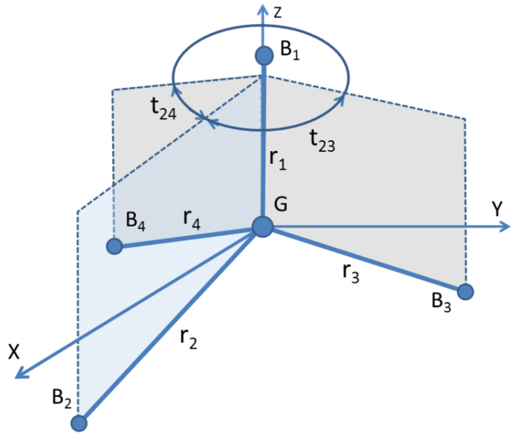

FIG. 1. Definition of torsional coordinates t_{23}, t_{24} corresponding to "radial" coordinates r_i.

For this reason, we use a redundant basis set of six angles hereafter, referred to as "6A-basis" in our algorithm of variational calculations. Such basis set is non-orthogonal and requires solving a generalised eigenvalue problem which is implemented in standard mathematical libraries like LAPACK and MKL. A similar approach has been already used for PH_3 type molecules.[20] Redundant vibrational coordinates have been also considered in Refs. 60–62 (see also references therein).

When calculating the matrix elements of PES whenever possible, we try to keep advantage of the symmetrical form with respect to six angles. At the final phase of the calculations, the angular matrix elements are expressed in terms of five non-redundant "polar" angular coordinates involving three bending coordinates $\{q_{12}, q_{13}, q_{14}\}$ and two torsion angles $\{t_{23}, t_{24}\}$ (Fig. 1) and thus resulting to five-dimensional integrals. Similarly, when calculating the matrix elements of the KEO in symmetric form, we first calculate the derivatives with respect to angles using full permutational symmetry, and only after this, we calculate the matrix element by using polar coordinates.

The present paper comprises seven sections. Section II describes an algorithm for constructing a contracted angular basis set that uses six angles q_{ij} between four radial vectors pointing identical atoms, and the scalar product calculation for this basis set. Sections III and IV are devoted to the algorithm of calculations of the angular matrix elements of PES and KEO in contracted angular basis set. Section V briefly outlines the general tree-like coupling scheme for the PES and for basis functions, a construction of the symmetry-adapted angular basis set, and the algorithm for calculation of vibrational matrix elements for AB_4 molecules. In Sec. VI, we report the basis convergence tests for calculated vibrational CH_4 levels in the 0-7660 cm^{-1} range. Section VII is devoted to discussion and conclusions.

II. SYMMETRY ADAPTED ANGULAR FUNCTIONS

For the symmetrisation of the angular part, the following concise notation will be used for the elementary terms:

$\varphi(q_{13})^{l_1}\varphi(q_{24})^{l_2}\varphi(q_{14})^{m_1}\varphi(q_{23})^{m_2}\varphi(q_{12})^{n_1}\varphi(q_{34})^{n_2} = (l_1,l_2;m_1,m_2;n_1,n_2)$, where φ is any smooth function. Because the transformation properties induced by atoms permutations do not depend on the explicit form of φ functions in this section, for the sake of simplicity we set $\varphi(x) = x$. Six numbers, l_1,l_2,m_1,m_2,n_1,n_2, are grouped into three couples of numbers which are denoted as l,m,n. The 24 permutations of four atoms H lead to permutations of l,m,n (6 permutations), and to even number of permutations inside of every couple (4 permutations). Let us denote $\mathrm{p_l}$, $\mathrm{p_m}$, $\mathrm{p_n}$ the permutation of numbers $(l_1, l_2), (m_1, m_2), (n_1, n_2)$. The full group could be represented as direct product of two sets of permutations $\{(lmn), (lnm), (mln), (mnl), (nml), (nlm)\}$ and $\{e, p_{l^*}p_m, p_{l^*}p_n, p_{n^*}p_m\}$, where e stands for identity operation. In general case, for six unequal numbers l_1, l_2, m_1, m_2, n_1, n_2 there are two independent 24-dimensional subsets corresponding to schemes $(l_1,l_2;m_1,m_2;n_1,n_2)$ and $(l_1,l_2;m_1,m_2;n_2,n_1)$. Two couples (l_1,l_2), (m_1, m_2) with $l_1 = m_1$ and $l_2 = m_2$ or $l_1 = m_2$ and $l_2 = m_1$ are considered as the "same" couples.

For tetrahedral AB_4 molecules, the following projection operators[63] are used:

$$
\begin{aligned}
P_{A_1} &= (e + (13) + (14) + (23) + (24) + (13)(24)) \\
&\quad \times (e + (12))(e + (34)), \\
P_{A_2} &= (e - (13) - (14) - (23) - (24) + (13)(24)) \\
&\quad \times (e - (12))(e - (34)), \\
P_{1E_b} &= ((13) - (14) - (23) + (24))(e + (12))(e + (34)), \\
P_{2E_b} &= (2e + (13) + (14) + (23) + (24) + 2(13)(24)) \\
&\quad \times (e - (12))(e - (34)), \\
P_{1F_{1z}} &= (e - (13)(24))(e - (12))(e - (34)), \\
P_{2F_{1z}} &= ((13) - (14) + (23) - (24))(e - (12))(e + (34)), \\
P_{3F_{1z}} &= ((13) + (14) - (23) - (24))(e + (12))(e - (34)), \\
P_{1F_{2z}} &= (e - (13)(24))(e + (12))(e + (34)), \\
P_{2F_{2z}} &= ((13) + (14) - (23) - (24))(e - (12))(e + (34)), \\
P_{3F_{2z}} &= ((13) - (14) + (23) - (24))(e + (12))(e - (34)).
\end{aligned}
\tag{2}
$$

Here, the notation (ij) stands for the permutation of identical nuclei $\mathrm{B_i}$ and $\mathrm{B_j}$. Using the projection operators (2), the explicit form of angular basis function could be found unambiguously for all cases except for the case where two F_2-symmetry functions occur. In the latter case, additional orthogonalisation was necessary. The action of projection operator $\mathrm{P_{1F2z}}$ on elementary terms $(n_1 \le l_1 \le m_1 \le l_2 \le m_2 \le n_2)$ is always not zero. The action of projection operator $\mathrm{P_{2F2z}}$ or $\mathrm{P_{3F2z}}$ could be zero, but one of four projection operators $\mathrm{P_{2F2z}}$, $\mathrm{P_{2F2z} + P_{1F2z}}$, $\mathrm{P_{3F2z}}$, $\mathrm{P_{3F2z} + P_{1F2z}}$ is always not zero and gives function orthogonal to $\mathrm{P_{1F2z}}$ function. Other way is to choose the second projection operator in the form $\mathrm{P_{2F2z} + P_{3F2z}}$. For example, in case of (0,1; 0,0; 0,1) there are initially three linear dependent F_2-symmetry functions: $\mathrm{f_1 = (q_{24}q_{34} + q_{23}q_{34} + q_{14}q_{34} + q_{13}q_{34} - q_{24}q_{12} - q_{14}q_{12} - q_{12}q_{23} - q_{12}q_{13})}$, $\mathrm{f_2 = (-2q_{23}q_{24} + 2q_{14}q_{24} + 2q_{13}q_{23} - 2q_{13}q_{14} - f_1)}$, $\mathrm{f_3 = (-2q_{23}q_{24} + 2q_{14}q_{24} + 2q_{13}q_{23} - 2q_{13}q_{14} + f_1)}$. Two functions $\mathrm{f_1}$ and $\mathrm{f_2 + f_3}$ (or $\mathrm{f_2 + f_1}$) are independent and orthogonal.

TABLE I. Decomposition of an elementary term $\varphi(q_{13})^{l_1}\varphi(q_{24})^{l_2}\varphi(q_{14})^{m_1}\varphi(q_{23})^{m_2}\varphi(q_{12})^{n_1}\varphi(q_{34})^{n_2} = (l_1,l_2;m_1,m_2;n_1,n_2)$ in irreducible T_d representations.

Number of equivalent couples	Number of couples $(\mathrm{l_1, l_2})$, $(\mathrm{m_1, m_2})$, $(\mathrm{n_1, n_2})$ with $l_1 = l_2$, $m_1 = m_2$, $n_1 = n_2$	A_1	A_2	E	F_1	F_2
0	0,1	1	1	2	3	3
	2	1	1	2	1	1
	3	1	1	2	0	0
1	0, 1	1	0	1	1	2
	2	1	0	1	0	1
	3	1	0	1	0	0
2,3	0	1	0	0	0	1
	3	1	0	0	0	0

The numbers of irreducible representations for every scheme $(l_1,l_2;m_1,m_2;n_2,n_1)$ are summarised in Table I.

Let us consider the matrix $\mathbf{M}$ composed of elements $M_{ij} = \cos(q_{ij})$. The determinant of the matrix $\mathbf{M}$ is always zero[59] and thus six interbond angles are redundant.

III. CONTRACTED ANGULAR WAVE FUNCTIONS AND SCALAR PRODUCTS CALCULATION

Calculation of matrix elements for the molecules of the type AB_4 is similar to that of the type AB_3. For one-dimensional basis functions, the following representation was used: $f_n(q) = \sqrt{2\pi}\sum_{l=s}^{LMax} c_{nl}Y_{l,s}(q,0)$, where Y are spherical harmonics written in the form of Ref. 64 that ensures $Y_{0,0}(q,0) = \frac{1}{\sqrt{4\pi}}$ and $2\pi\int_0^{\pi} Y^2_{l,s}(q,0)d\cos(q) = 1$. Here, $LMax$ is the maximum order of the expansion. The normalization condition $\int_0^{\pi} f_n^2(q)d\cos(q) = 1$ for the one-dimensional angular problem can be used to normalize f_n. Initial angular basis can be written in the form

$$
\begin{aligned}
&|n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}\rangle \\
&\quad = f_{n_{12}}(q_{12})f_{n_{13}}(q_{13})f_{n_{14}}(q_{14})f_{n_{23}}(q_{23})f_{n_{24}}(q_{24})f_{n_{34}}(q_{34}).
\end{aligned}
\tag{3}
$$

Taking into account the expression[64]

$$
f_n(q_{23}) = \sum_k c_{nk}\sqrt{\frac{4\pi}{2k+1}}\sum_m Y_{k,m}(q_{12},0)Y_{k,m}(q_{13},t_{23}),
\tag{4}
$$

the angular basis functions (3) could be written in terms of two torsion angles t_{23},t_{24} (Fig. 1) and three bending angles q_{12},q_{13},q_{14}. The expression (3) contains powers of t_{23},t_{24} up to $2 \times LMax$ and powers of q_{12},q_{13},q_{14} up to $3 \times LMax$. The scalar product of basis functions is calculated using the following five-dimensional integral with volume element $\mathrm{d\cos(q_{12})\, d\cos(q_{13})\, d\cos(q_{14}) dt_{23}dt_{24}}$:

$$\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle = \int_0^{\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} f_{n_{12}}(q_{12})f_{k_{12}}(q_{12})\ldots f_{n_{34}}(q_{34})f_{k_{34}}(q_{34})d\cos(q_{12})d\cos(q_{13})d\cos(q_{14})dt_{23}dt_{24}. \quad (5)$$

To calculate (5), the expression (4) was used for three couples of one dimensional functions depending on q_{23}, q_{24}, q_{34}. The details of the scalar product calculation are given in the Appendix. The final expression reads

$$\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle = (2\pi)^5 \sum_{L_{23}L_{24}L_{34}} \frac{8\pi^{3/2}}{\sqrt{(2L_{23}+1)(2L_{24}+1)(2L_{34}+1)}} J_{n_{23},k_{23},L_{23},0}J_{n_{24},k_{24},L_{24},0}J_{n_{34},k_{34},L_{34},0} \times \sum_{m=0}^{\min(L_{23},L_{24},L_{34})} J_{n_{12},k_{12},L_{23},L_{24},m}J_{n_{13},k_{13},L_{23},L_{34},m}J_{n_{14},k_{14},L_{24},L_{34},m} \times (2-\delta_{m,0}), \quad (6)$$

where $J_{n_1,k_1,L_1,0} = \sqrt{4\pi}J_{n_1,k_1,L_1,0,0}$ and $J_{n_1,k_1,L_1,L_2,\nu}$ are one dimensional integrals,

$$J_{n_1,k_1,L_1,L_2,\nu} = \int_0^{\pi} f_{n_1}(q_{12})f_{k_1}(q_{12})Y_{L_1,\nu}(q_{12},0)Y_{L_2,\nu}(q_{12},0)d\cos(q_{12})$$
$$= 2\pi\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\int_0^{\pi} Y_{l_10}(q_{12},0)Y_{l_20}(q_{12},0)Y_{L_1,\nu}(q_{12},0)Y_{L_2,\nu}(q_{12},0)d\cos(q_{12}). \quad (7)$$

The integral on the right hand side of Eq. (7) could be expressed as sum of Clebsch-Gordan coefficients of the rotation group (see the Appendix)

$$2\pi\int_0^{\pi} Y_{l_10}(q_{12},0)Y_{l_20}(q_{12},0)Y_{L_1,\nu}(q_{12},0)Y_{L_2,\nu}(q_{12},0)d\cos(q_{12})$$
$$= \sum_{L_a}\sqrt{\frac{(2l_1+1)(2L_1+1)}{4\pi(2L_a+1)}}\sqrt{\frac{(2l_2+1)(2L_2+1)}{4\pi(2L_a+1)}}C(l_10,L_10,L_a0)C(l_10,L_1v,L_av)C(l_20,L_20,L_a0)C(l_20,L_2v,L_av). \quad (8)$$

Only even values $l_1 + L_1 + L_a$ and $l_2 + L_2 + L_a$ contribute to the latter summation. Using Eqs. (7) and (8), $J_{n_1,k_1,L_1,L_2,\nu}$ can be easily calculated. In this work, the 6-dimensional angular wave function (3) is represented as a product of one dimensional angular eigen functions $f_n(\cos(q_{ij}))$ of partial bending Hamiltonians

$$h(q_{ij}) = -\frac{1}{\mu r_e^2}\left(\frac{\partial^2}{\partial {q_{ij}}^2} + ctg(q_{ij})\frac{\partial}{\partial q_{ij}}\right) + V(q_{ij}). \quad (9)$$

This does not result in a singularity as ctg(q) (d/dq) = cos (q) (d/dcos(q)) and spherical harmonics are expressed in terms of cos(q) as well. The behaviour of five one-dimensional functions f_0, f_1, f_5, f_{10}, f_{14} is shown in Fig. 2.

The expressions (6-8) are not only true for one dimensional eigen functions $f_n(q)$, but could be applied to other type of one dimensional functions. For *LMax* up to 20, it was possible to calculate the norm and the matrix elements without any contraction ($c_{nl} = \delta_{nl}$). In this particular case, if $c_{nl} = \delta_{nl}$, one has $J_{0,0,0,0,0} = J_{0,0,1,1,0} = J_{0,0,1,1,1} = 1/(4\pi)$, resulting to $\langle 0,0,0,0,0,0|0,0,0,0,0,0\rangle = \pi^2/2$, $\langle 1,0,0,0,0,0|1,0,0,0,0,0\rangle = \pi^2/2$, $\left\langle 1,1,0,0,0,0|1,1,0,0,0,0\right\rangle = \pi^2/2$, $\langle 1,1,1,0,0,0|1,1,1,0,0,0\rangle = \pi^2/2$, $\langle 2,0,0,0,0,0|2,0,0,0,0,0\rangle = \pi^2/2$, $\langle 0,0,0,1,1,0|0,0,0,0,0,1\rangle = \pi^2\sqrt{3}/6$.

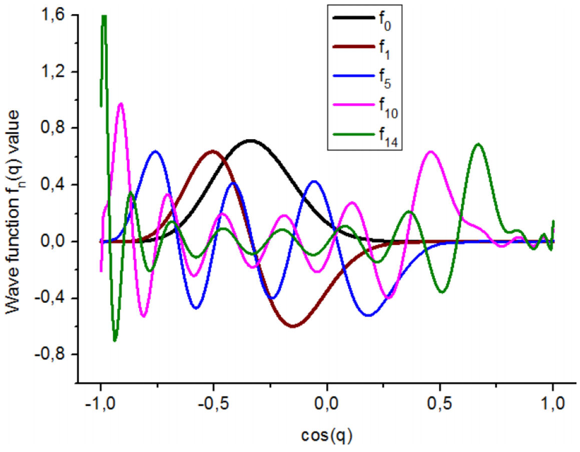

FIG. 2. The five one-dimensional angular basis functions f_0, f_1, f_5, f_{10}, f_{14}.

IV. CALCULATION OF MATRIX ELEMENTS FOR KINETIC AND POTENTIAL ENERGY TERMS

The replacement of the coefficient $J_{n_1,k_1,L_1,L_2,\nu}$ in Eq. (6) by the coefficient $J^P_{n_1,k_1,L_1,L_2,\nu}$ results in formula for matrix elements of the PES terms. This is similar to transformations involving Eqs. (7) and (9) of Ref. 20 previously discussed for AB_3 molecules,

$$J^{P}_{n_1,k_1,L_1,L_2,\nu} = \sum_{l_1l_2l_3} c_{n_1l_1}c_{k_1l_2} \int_0^{\pi} f_{l_1}(q)\,\langle l_30|\cos^P(q)|l_20\rangle\, f_{l_3}(q)Y_{L_1,\nu}(q,0)Y_{L_2,\nu}(q,0)d\cos(q)$$
$$= 2\pi \sum_{l_1l_2l_3} c_{n_1l_1}c_{k_1l_2}\langle l_30|\cos^P(q)|l_20\rangle \int_0^{\pi} Y_{l_10}(q,0)Y_{l_30}(q,0)Y_{L_1,\nu}(q,0)Y_{L_2,\nu}(q,0)d\cos(q). \tag{10}$$

$$\left\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}\left|\cos^{P_{12}}(q_{12})\cos^{P_{13}}(q_{13})\cos^{P_{14}}(q_{14})\cos^{P_{23}}(q_{23})\cos^{P_{24}}(q_{24})\cos^{P_{34}}(q_{34})\right| k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\right\rangle$$
$$= (2\pi)^5 \sum_{L_{23}L_{24}L_{34}} \frac{64\pi^3}{\sqrt{(2L_{23}+1)(2L_{24}+1)(2L_{34}+1)}} J^{P_{23}}_{n_{23},k_{23},L_{23},0,0} J^{P_{24}}_{n_{24},k_{24},L_{24},0,0} J^{P_{34}}_{n_{34},k_{34},L_{34},0,0}$$
$$\times \sum_{m=0}^{\min(L_{23},L_{24},L_{34})} J^{P_{12}}_{n_{12},k_{12},L_{23},L_{24},m} J^{P_{13}}_{n_{13},k_{13},L_{23},L_{34},m} J^{P_{14}}_{n_{14},k_{14},L_{24},L_{34},m} \times (2-\delta_{m,0}). \tag{11}$$

For example, in a particular case, if $c_{nl} = \delta_{nl}$, one obtains $\langle 0,0,0,0,0,0|\ \cos(q_{12})^2\,|0,0,0,0,0,0\rangle = \pi^2/6$, $\langle 0,0,0,0,0,0|\ \cos(q_{12})^2\ |1,1,0,1,0,0\rangle = \pi^2\sqrt{3}/10$, $\langle 0,0,0,0,0,0|\ \cos(q_{12})^2|\ 0,1,1,1,1,0\rangle = \pi^2/10$.

The calculation of large number of integrals (11, 10) is the most demanding part for the computational resources in our approach. The high permutational symmetry allows calculating only part of integrals (11). The integral (11) could be calculated only once and stored in memory to be further used iteratively in case of an empirical PES optimization.

The algorithm of calculation of KEO matrix elements for AB$_4$ is similar to that of AB$_3$ molecules.[20] In case of AB$_4$ molecules, there are 6 diagonal and 12 off-diagonal terms in orthogonal coordinates.[58] These 18 terms could be represented as sum of four terms T$_1$, T$_2$, T$_3$, T$_4$,

$$T_1 = \frac{1}{m_1{r_1}^2}\left(-\frac{\partial^{2+}}{\partial q_{12}^2} - \frac{\partial^{2+}}{\partial q_{13}^2} - \frac{\partial^{2+}}{\partial q_{14}^2} + \cos(t_{23})\frac{\partial^2}{\partial q_{12}\partial q_{13}}\right.$$
$$\left. + \cos(t_{24})\frac{\partial^2}{\partial q_{12}\partial q_{14}} + \cos(t_{34})\frac{\partial^2}{\partial q_{13}\partial q_{14}}\right), \tag{12}$$

where $\frac{\partial^{2+}}{\partial q^2} = \frac{\partial^2}{\partial q^2} + ctg(q)\frac{\partial}{\partial q}$. Other terms T$_k$ could be obtained from T$_1$ by permutations T$_k$ = (1k)T$_1$. The kinetic energy operator could be rewritten in a tensorial form as

$$T = \sum_{k=1}^{4} T_k = (T_R^{A1}T_Q^{A1})^{A_1} + \sqrt{3}(T_R^{F2}T_Q^{F2})^{A_1}, \tag{13}$$

where T_R^{A1},$T_{R,}^{F2,x}$,$T_{R,}^{F2,y}$,$T_{R,}^{F2,x}$ are symmetrized forms for the "radial" part $\frac{1}{m_kr_k^2}$ and T_Q^{A1}, $T_{Q,}^{F2,x}$,$T_{Q,}^{F2,y}$, $T_{Q,}^{F2,z}$ are symmetrized forms for the angular part (expression in parenthesis of T_k in Eq. (12)). The definition of the symmetrized form is the same as that usually written in the standard symmetric coordinates.[65] For example, the $F_{2,z}$ component for the radial coordinate reads $S_{R,}^{F2,z} = \frac{1}{2}(r_1 + r_2 - r_3 - r_4)$. Consequently, we have the similar form for the $F_{2,z}$ component of the kinetic radial and angular terms

$$T_{R,}^{F2,z} = \frac{1}{2}\left(\frac{1}{m_1{r_1}^2} + \frac{1}{m_2{r_2}^2} - \frac{1}{m_3{r_3}^2} - \frac{1}{m_4{r_4}^2}\right),$$
$$T_Q^{F2,z} = \frac{1}{2}(T_1 + T_2 - T_3 - T_4).$$

The details of matrix elements calculation could be found in the Appendix. Due to symmetry properties, it is sufficient calculating only one diagonal and one off-diagonal matrix element. The diagonal matrix element is similar to the scalar product calculation where one of the coefficients J is replaced by the coefficient J^{D2},

$$J^{D2}_{n_1,k_1,L_1,L_2,\nu} = \int_0^{\pi} f_{n_1}(q)\left(\left(\frac{\partial^2}{\partial q^2} + ctg(q)\frac{\partial}{\partial q}\right)f_{k_1}(q)\right)$$
$$\times Y_{L_1,\nu}(q,0)Y_{L_2,\nu}(q,0)d\cos(q)$$
$$= 2\pi\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}(l_2(l_2+1))\int_0^{\pi} Y_{l_10}(q,0)Y_{l_20}$$
$$\times (q,0)Y_{L_1,\nu}(q,0)Y_{L_2,\nu}(q,0)d\cos(q). \tag{14}$$

In order to calculate the off-diagonal terms of KEO, the following coefficients are necessary:

$$J^{D1}_{n_1,k_1,L_1,L_2,\nu,\pm} = \sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\int_0^{\pi} f_{l_1}(q)\left(\frac{\partial}{\partial q}f_{l_2}(q)\right)$$
$$\times Y_{L_1,\nu\pm1}(q,0)Y_{L_2,\nu}(q,0)d\cos(q). \tag{15}$$

The positive and negative values of ν are possible in Eq. (15) $J^{D1}_{n_1,k_1,L_1,L_2,-v,\pm} = J^{D1}_{n_1,k_1,L_1,L_2,v,\mp}$. The J^{D1} coefficient could be calculated (see Appendix) according to the formula

$$J^{D1}_{n_1,k_1,L_1,L_2,-v,\pm} = \pm\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\sum_{L_a}\sqrt{l_2(l_2+1)}\sqrt{\frac{(2l_1+1)(2L_1+1)}{4\pi(2L_a+1)}}\sqrt{\frac{(2l_2+1)(2L_2+1)}{4\pi(2L_a+1)}}$$
$$\times C(l_10,L_10,L_a0)C(l_1,0,L_1,-v\pm1,L_a,-v\pm1)C(l_20,L_20,L_a0)C(l_2,\pm1,L_2,-v,L_a,-v\pm1). \tag{16}$$

The final expression for the off-diagonal matrix elements can be written as follows:

$$\begin{aligned}
&\left\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}\left|\cos(t_{23})\frac{\partial^2}{\partial q_{12}\partial q_{13}}\right|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\right\rangle\\
&\quad=(2\pi)^5\sum_{L_{23}L_{24}L_{34}}\frac{4\pi^{3/2}}{\sqrt{(2L_{23}+1)(2L_{24}+1)(2L_{34}+1)}}J_{n_{23},k_{23},L_{23},0}J_{n_{24},k_{24},L_{24},0}J_{n_{34},k_{34},L_{34},0}\\
&\quad\times\sum_{m=0}^{\min(L_{23},L_{24},L_{34})}\left(J^{D1}_{n_{12},k_{12},L_{23},L_{24},m,-}J^{D1}_{n_{13},k_{13},L_{23},L_{34},m,-}+J^{D1}_{n_{12},k_{12},L_{23},L_{24},m,+}J^{D1}_{n_{13},k_{13},L_{23},L_{34},m,+}\right)(2-\delta_{m,0})J_{n_{14},k_{14},L_{24},L_{34},m}.
\end{aligned}$$

In a particular case, if $c_{nl}=\delta_{nl}$ this gives $\left\langle 000000\right|\cos(t_{23})\frac{\partial^2}{\partial q_{12}\partial q_{13}}\left|110011\right\rangle=\frac{(\pi)^2}{3}$.

V. FULL SYMMETRY BASIS SET AND CALCULATION OF VIBRATIONAL LEVELS

The initial angular basis (1) can be easily symmetrized using the technique of projector operators (2) as described in Sec. II.

$$|n_{12}n_{13}n_{14}n_{23}n_{24}n_{34};k_AC_A\sigma_A\rangle=\hat{P}_{kC\sigma}\,|n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}\rangle\,,$$

where C and σ are irreducible representation and row of T_d(M) point group, and k is the ranking number. The symmetrisation of the radial part can be done in terms of explicit rules of Refs. 66 and 67. Another way is construction of radial functions from symmetric coordinates.[68–70] For the radial basis functions, we apply in this work the symmetrisation procedure using projection operators[60] given by Eq. (2),

$$|m_1m_2m_3m_4;k_RC_R\sigma_R\rangle=\hat{P}_{kC\sigma}\,|m_1m_2m_3m_4\rangle\,,$$

where m_i are quantum numbers corresponding to primitive eigen functions $\phi_{m_i}(r_i)$ of radial equations. The full symmetry vibrational basis set is obtained as direct product of both

$$|n_{12}n_{13}n_{14}n_{23}n_{24}n_{34};k_AC_A\sigma_A\rangle\times|m_1m_2m_3m_4;k_RC_R\sigma_R\rangle\,.$$

The vibrational basis functions and the PES expansion terms can be expressed via irreducible tensors.[68,69] Each tensor is associated to a binary tree,[70] where every branch of the tree is characterized by its symmetry. The PES and kinetic energy operators are of A_1 symmetry type. For AB_4 (as for AB_3[20]) molecules, it is necessary to consider only one coupling of stretching basis functions and of bending basis functions. For the direct product of irreducible tensors,[68,69] the following standard definition is used:

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

where C, C′, C″ are irreducible representations, σ, σ′, σ″ 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 T_d symmetry group. Here, $[C]$ stands for the dimension of C irreducible representation. The recoupling scheme used for calculations of matrix elements is similar to one described in Ref. 70. Using the standard definition of the reduced matrix elements[68,69]

$$\left\langle\psi'^{(C')}\right\|\left|V^{(C)}\right\|\left|\psi''^{(C'')}\right\rangle=\frac{\left\langle\psi'^{(C')}_{\sigma'}\right\|\left|V^{(C)}_{\sigma}\right\|\left|\psi''^{(C'')}_{\sigma''}\right\rangle}{F\begin{pmatrix}C'&C&C''\\\sigma'&\sigma&\sigma''\end{pmatrix}}\qquad(17)$$

and the recoupling matrix elements formula

$$\begin{aligned}
&\left\langle(\psi_1^{C_1'}\psi_2^{C_2'})^{C'}\right\|\left|(V_1^{\Gamma_1}V_2^{\Gamma_2})^{\Gamma}\right\|\left|(\psi_1^{C_1''}\psi_2^{C_2''})^{C''}\right\rangle\\
&\quad=\sqrt{[C'][\Gamma][C'']}\begin{pmatrix}C_1'&C_2'&C'\\\Gamma_1&\Gamma_2&\Gamma\\C_1''&C_2''&C''\end{pmatrix}\\
&\quad\times\left\langle\psi_1^{C_1'}\right\|\left|V_1^{\Gamma_1}\right\|\left|\psi_1^{C_1''}\right\rangle\left\langle\psi_2^{C_2'}\right\|\left|V_2^{\Gamma_2}\right\|\left|\psi_2^{C_2''}\right\rangle,\qquad(18)
\end{aligned}$$

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

The use of a non-orthogonal angular basis set[20] does not complicate the procedure for eigenvalues calculations. 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 computational resources because the matrix $N=[\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle]$ of the scalar products does not depend on the PES parameters and could be calculated only once during iterations of a PES fit. The eigenvalues can be evaluated using the $(T+V)N^{-1}$ matrix. As a rule, the use of the full symmetry properties allows one to considerably decrease the dimension of the blocks in the Hamiltonian matrix. The fast algorithm for $9G$ symbols[71] was used for the matrix elements (17,18) calculations. Details of calculations together with the application to the methane molecule are given in Sec. VI .

VI. EXAMPLE OF APPLICATION TO THE CH_4 MOLECULE: CONVERGENCE TESTS

Accurate knowledge of methane absorption is necessary for the study of planetary systems because its spectral features are used to determine the physical properties of these atmospheres.[72–74] This is particularly true for Titan (Saturn's largest satellite) whose atmosphere is composed of 98.6% nitrogen with 1.4% of methane at temperatures ranging between 70 K and 200 K, the major part of the opacity in the infrared being due to methane absorption. Improving the methane spectroscopic parameters is essential[75–77] for full interpretation of near infrared observations returned by the ground-based and orbiting observatories. For this reason, methane is one of the most important molecular species for several spectroscopic databases.[78–81] However, the methane data are far from being complete and most of experimental spectra at high energy range[75,82–85] remain unassigned. Knowledge of methane bands is crucially important for high-temperature astrophysical applications, for interpretation of observed data for exoplanets and brown dwarfs.[86] Theoretical line lists for hot methane have been recently generated: ExoMol linelist in UCL London (Yurchenko *et al.*[87]) and Reims-Tomsk RNT linelist (Rey *et al.*[51]), the latter one being calculated up to 2000 K. Achieving an accurate basis set convergence is a great challenge for related variational methods.

The polyad structure of the methane molecule is essentially governed by the quasi coincidence of the stretching fundamental frequencies with the first overtones of the bending frequencies $\nu_1(A_1) \approx \nu_3(F_2) \approx 2\nu_2(E) \approx 2\nu_4(F_2)$.[68,69] The polyads P_n are defined by an integer n expressed in terms of the principal vibrational quantum numbers as $n = 2(v_1 + v_3) + v_2 + v_4$. Lower polyads: Ground state (GS) (from microwave to 1000 cm^{-1}), Dyad (1000-2000 cm^{-1}), Pentad (2000-3400 cm^{-1}), Octad (3400-4900 cm^{-1}) have been completely assigned, whereas Tetradecad (4900-6300 cm^{-1}) and Icosad (6300-7900 cm^{-1}) have been partly assigned (Refs. 82, 88–90 and references therein). The similar polyad approach was used for angular basis construction. It was possible because of nearly harmonic behavior of one dimensional angular eigen values $E^A = (n_A + 1/2)\omega_0$. The angular polyads are defined by an integer n_A expressed as the sum of six numbers n_{ij} (3).

In this work, we check the full symmetry vibrational basis convergence in orthogonal mass-dependent coordinates for $^{12}CH_4$ molecule using new technique of calculations described in Secs. III–V. For these convergence tests, we have used the methane PES in the following form:

$$V(S_i, Q) = V(S_i) + \Delta V. \tag{19}$$

Here, $S_i \in \{S_1^{A_1};\ S_{2a}^{E}, S_{2b}^{E};\ S_{3a}^{F_2}, S_{3b}^{F_2}, S_{3c}^{F_2};\ S_{4a}^{F_2}, S_{4b}^{F_2}, S_{4c}^{F_2}\}$ are nine symmetrized vibrational coordinates defined in Ref. 25 and $V(S_i)$ is the six-order PES expansion described in our previous work.[25] In this study, we include a supplementary term,

$$\Delta V = F^{(2)}(S_i) \cdot Q + const \cdot Q^2, \tag{20}$$

depending on the redundant coordinate Q which is defined as follows:

$$Q = (\cos(q_{12}) + \cos(q_{13}) + \cos(q_{14}) + \cos(q_{23}) + \cos(q_{24}) + \cos(q_{34}) + 2)\,/\sqrt{6}. \tag{21}$$

This additional totally symmetric coordinate Q satisfies the condition $Q = 0$ at the equilibrium nuclear configurations. Some mathematical aspects related to the introduction of such supplementary redundant coordinate have been discussed in Refs. 33, 34, and 59 (and references therein). In this study, we introduce Q containing terms because this allows obtaining a similar quality of the PES fit to *ab initio* points as for the $V(S_i)$ model, but with fewer number of adjusted parameters. Indeed, using few supplementary terms (20) added to $V^{(6)}(S_i)$ of the order 6, it was possible obtaining somewhat smaller root-mean-squares (rms) fit deviation than for $V^{(8)}(S_i)$ of our previous work[25] developed at order 8. Here, $F^{(2)}(S_i)$ is a second order totally symmetric polynomial containing 10 parameters only. For this purpose, we have taken exactly the same *ab initio* points as described in our previous work,[25] slightly extended in energy with the same *ab initio* method. The focus of the present work is the study of the basis convergence properties with new method of vibrational calculations. To have reliable conclusions, we have checked that the fitted PES did not possess spurious minima at least up to 31 000 cm^{-1} that was our energy cut-off. The details of the PES fit will be described elsewhere.

Five calculations with increasing vibrational basis sets denoted below as $X_1, X_2, \ldots, X_5$ were compared. The maximum order o in angular functions for these basis sets was chosen to be $o = 10, o = 11, o = 12, o = 13$, and $o = 14$, correspondingly. The basis energy cut-off was fixed progressively to 22 000, 23 500, 25 000, 27 000, and 31 000 cm^{-1}. In order to keep a reasonable size for X_5 basis, only selected angular functions in the range 27 000-31 000 cm^{-1} (corresponded to the angular polyad 14) were added to the X_4 basis set. We have checked that including 6 radial functions per each r_i bond is sufficient for a good convergence of vibrational energy levels up to the Icosad. The dimensions of these five basis sets are given in Table II. The number of basis functions for set X_{n+1} is about two times bigger than that for the set X_n (except for the highest basis set X_5).

TABLE II. Dimensions of five basis sets which were used for the convergence tests.

Basis sets		A1	A2	E	F1	F2	Full dimension of the space of wave functions
X_n	E_{max}/cm^{-1}	Dimensions D(C) of symmetry blocks					D(A1) + D(A2) + 2D(E) + 3D(F1) + 3D(F2)
X_1	22 000	2 538	1 713	4 214	5 634	6 445	48 916
X_2	23 500	4 120	2 916	6 985	9 518	10 706	81 678
X_3	25 000	6 630	4 948	11 518	15 925	17 589	135 156
X_4	27 000	13 273	10 549	23 748	33 519	36 221	280 538
X_5	31 000[a]	13 365	10 618	23 909	33 727	36 451	282 335

[a] Only selected pure angular functions in the range 27 000-31 000 cm^{-1} were added to the basis set X_5 with respect to X_4.

TABLE III. Basis set convergence: RMS_1 deviation[a] for band centers of six lower polyads.

Polyad/basis sets	X_4–X_5	X_3–X_5	X_2–X_5	X_1–X_5
P = 0, GS	4×10^{-6}	0.000 26	0.000 738	0.002 80
P = 1, dyad	5.7×10^{-5}	0.001 33	0.003 75	0.012 2
P = 2, pentad	0.000 56	0.006 06	0.022 7	0.070 5
P = 3, octad	0.004 3	0.033	0.12	0.37
P = 4, tetradecad	0.021	0.128	0.36	1.3
P = 5, icosad	0.071	0.497	2.18	5.9

[a] All values are in cm^{-1}.

As expected, in variational calculations the energy levels went down with increasing the basis set size. The root-mean-squares (RMS) deviations between energy levels computed using lower basis sets with respect to the largest X_5 basis set are calculated for six lower methane polyads and are given in Table III (denoted here as $RMS_1(X_n)$). The deviations between energy levels computed using successive basis sets X_n and X_{n+1} are given in Table IV (denoted as RMS_2 (X)).

By inspecting the behavior of the RMS_1 with increasing X_n in Table III, we derived an approximate formula $RMS(P,N) = \exp(7.2 + 1.6\times P - 1.32\times N_A)$ for the basis set convergence. Here, P is the polyad number (with $P = 0$ for the GS, $P = 1$ for the Dyad, $P = 2$ for the Pentad, …etc) and N_A is number of angular polyads ($N_A = 10, 11, 12, 13$ for $X_1, X_2, \ldots$) taken into account.

As both RMS_1 and RMS_2 deviations have similar trends, this formula could also be applied for an estimation of RMS_2. This resulted in the convergence precision estimation of ~0.02 cm^{-1} for our best calculations (X_5) in the tetradecad region (4800-6300 cm^{-1}). About 30% of the contribution to the RMS deviation in the tetradecad region comes from three energy levels of $4\nu_2$. Without these three energy levels, the RMS estimation for the basis convergence error in the tetradecad region is about 0.007 cm^{-1}. On the other hand, the $4\nu_2$ sub-bands are very weak,[89] an experimental determination of the corresponding upper state levels being less accurate and thus less useful for an empirical fit of PES parameters. In the Octad range, the RMS estimation for the basis convergence error is 0.005 cm^{-1} which is comparable with the accuracy of "experimental" energy levels determination.[88] For the Dyad and Pentad band centres, the basis set convergence approaches the experimental accuracy. In case of eight sub-bands of the $5\nu_4$ Icosad band system, for which a sufficiently compete analysis of experimental spectra is available,[90] the RMS_2 deviation between basis sets X_5 and X_4 is 0.034 cm^{-1} only.

TABLE IV. RMS_2 deviation[a] for band centers of six lower polyads between successive basis sets.

Polyad/basis sets	X_4–X_5	X_3–X_4	X_2–X_3	X_1–X_2
P = 0, GS	4×10^{-6}	2.58×10^{-4}	4.76×10^{-4}	0.002 07
P = 1, dyad	5.7×10^{-5}	0.001 28	0.002 43	0.008 45
P = 2, pentad	5.63×10^{-04}	0.005 58	0.016 74	0.047 86
P = 3, octad	0.0043	0.029 8	0.086 9	0.251 6
P = 4, tetradecad	0.021	0.128	0.361	1.290
P = 5, icosad	0.071	0.440	1.691	3.786
$5\nu_4 \in$ icosad	0.034	0.342	1.153	3.456

[a] All values are in cm^{-1}.

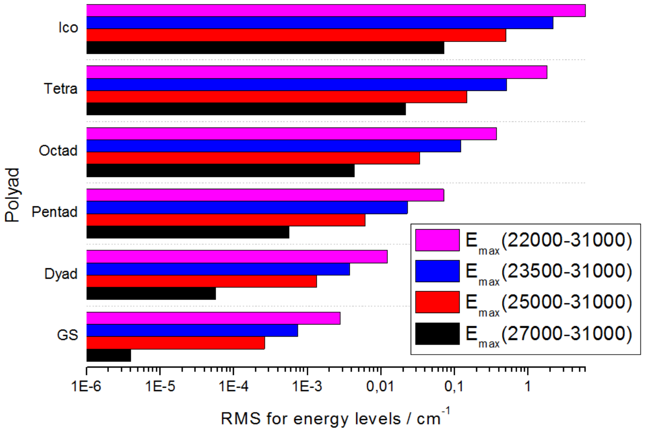

FIG. 3. Log scale convergence diagram presenting the RMS_1 for various polyads and basis sets. The cutoff E_{max}/cm^{-1} for various basis sets is given in parentheses.

The RMS_1 log-scale diagram of the vibration energy level convergence with increasing basis set for six lower polyads is given in Fig. 3. Fig. 4 shows the convergence up to the Icosad for individual levels. The above tests concern the convergence study with respect to increasing of number of basis functions. The shape of primitive functions has also an impact on final results, which was checked by comparing two rather closed forms of one dimensional functions for pure angular basis. The corresponding energy level variation was small for four lower polyads, whereas for Tetradecad and Icosad the difference becomes more significant. The influence of *LMax* value (see paragraph III) was also checked for the angular task with a simple trial PES of the order 2. The energy levels were calculated for three values *LMax* = 23, 25, 27 (basis sets with cutoff similar to X2 of Table II) that gave smaller discrepancies for lower polyads than those in Table V.

The important property of the presented algorithm is high speed of calculation. A comparison of the convergence for the eigenvalue calculations using the fully symmetrized 6*q*—basis described above with our previous calculations that used partial C_{3v} symmetry for the basis set[25] demonstrates that our new method allows for much faster convergence. The central processing unit (CPU) time of eigen functions and eigen values

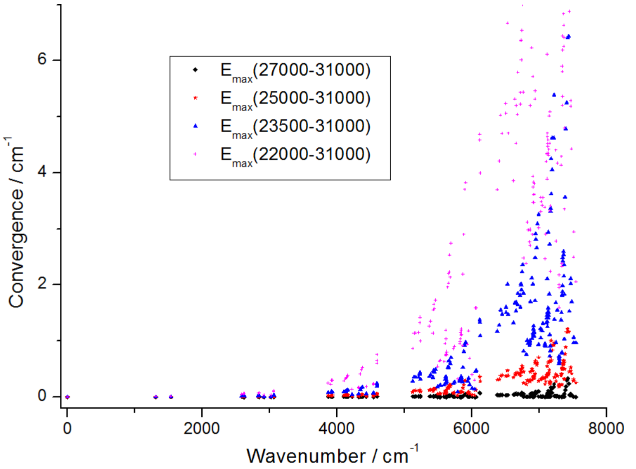

FIG. 4. Convergence of energy levels up to the Icosad range. Basis set cutoff E_{max}/cm^{-1} for various basis sets is given in parentheses.

TABLE V. Predicted vibrational $^{12}CH_4$ bands centers for the Icosad range: Comparison with the results of CT method using independent algebraic techniques.

This work	CT, Ref. 47	CT-TW[a]	Labels[b]
6378.04	6379.72	1.68	F2 (0005)
6406.24	6407.55	1.31	A1 (0005)
6429.69	6430.64	0.96	F1 (0005)
6450.65	6451.50	0.85	F2 (0005)
6507.36	6507.77	0.41	E (0005)
6507.59	6508.01	0.43	F2 (0005)
6529.93	6530.34	0.41	F1 (0005)
6539.38	6539.90	0.53	F2 (0005)
6618.66	6620.46	1.81	E (0104)
6639.49	6641.17	1.69	F1 (0104)
6657.19	6658.36	1.18	A1 (0104)
6657.69	6659.14	1.45	F2 (0104)
6681.47	6682.57	1.10	E (0104)
6683.50	6684.68	1.19	A2 (0104)
6718.41	6719.23	0.83	F2 (0104)
6722.17	6722.93	0.77	F1 (0104)
6730.35	6731.07	0.72	E (0104)
6733.60	6734.37	0.78	F2 (0104)
6737.96	6738.59	0.64	A1 (0104)
6746.57	6747.31	0.75	A2 (0104)
6755.50	6756.16	0.67	F1 (0104)
6766.40	6767.13	0.73	E (0104)
6769.36	6769.78	0.42	F2 (1003)
6809.33	6809.68	0.35	A1 (1003)
6822.27	6822.75	0.48	F1 (1003)
6833.30	6833.95	0.66	F2 (1003)
6858.85	6859.85	1.01	F2 (0013)
6862.76	6863.62	0.87	E (0013)
6862.77	6863.52	0.76	F1 (0013)
6863.41	6864.36	0.96	A1 (0013)
6871.16	6872.58	1.42	F2 (0203)
6890.76	6892.14	1.38	F1 (0203)
6897.35	6898.22	0.87	F2 (0013)
6906.52	6907.72	1.20	F2 (0203)
6908.66	6909.33	0.67	E (0013)
6910.28	6910.95	0.67	F2 (0013)
6914.91	6915.81	0.91	F1 (0013)
6918.45	6919.30	0.86	A2 (0013)
6921.54	6922.40	0.86	F1 (0013)
6922.19	6923.22	1.04	A1 (0013)
6924.93	6925.79	0.86	F2 (0013)
6925.83	6926.79	0.96	E (0013)
6938.90	6939.83	0.94	E (0203)
6940.64	6941.78	1.14	A1 (0203)
6941.06	6941.96	0.91	F2 (0203)
6946.10	6946.93	0.83	F1 (0203)
6950.42	6951.20	0.79	F1 (0203)
6962.78	6963.59	0.82	F2 (0203)
6973.01	6973.68	0.67	F1 (0203)
6990.44	6990.94	0.51	E (1102)
6992.92	6993.71	0.79	F2 (0203)
7020.71	7021.27	0.56	F1 (1102)
7024.48	7025.09	0.62	A1 (1102)
7035.21	7035.82	0.61	F2 (1102)
7045.74	7046.47	0.74	E (1102)
7056.58	7057.37	0.80	A2 (1102)
7085.42	7086.10	0.68	F1 (0112)
7085.59	7086.05	0.46	F2 (2001)
7098.05	7098.65	0.60	F2 (0112)
7107.57	7108.33	0.77	E (0112)
7114.94	7115.88	0.95	A2 (0112)
7116.51	7117.07	0.57	F2 (0112)
7117.94	7118.87	0.94	F1 (0112)
7119.77	7120.91	1.15	E (0302)
7121.52	7122.49	0.97	A1 (0302)
7121.85	7122.72	0.87	F2 (0112)
7131.04	7131.89	0.85	F1 (0112)
7131.25	7132.23	0.98	F2 (0112)
7133.05	7133.73	0.69	A1 (0112)
7134.02	7135.00	0.99	E (0112)
7134.88	7135.72	0.85	A2 (0302)
7139.34	7140.31	0.97	F1 (0112)
7141.68	7142.65	0.97	F2 (0112)
7151.05	7152.08	1.03	F1 (0112)
7155.02	7156.02	1.00	F1 (0302)
7156.96	7156.99	0.03	A1 (1011)
7158.03	7158.21	0.19	F2 (1011)
7164.84	7165.23	0.39	E (1011)
7166.31	7166.68	0.37	F1 (1011)
7169.22	7169.81	0.59	E (0302)
7169.36	7170.13	0.78	F2 (0302)
7177.42	7178.22	0.80	A1 (0302)
7180.93	7181.51	0.59	F1 (0302)
7192.08	7192.77	0.69	F2 (0302)
7192.72	7193.31	0.59	E (0302)
7218.13	7218.84	0.72	E (0302)
7221.91	7222.57	0.66	A2 (0302)
7225.94	7226.61	0.67	F2 (1201)
7246.30	7246.92	0.62	F1 (1201)
7250.55	7251.23	0.68	F2 (0021)
7269.57	7270.24	0.67	F2 (1201)
7294.82	7295.03	0.22	E (2100)
7295.89	7296.56	0.68	F1 (0021)
7296.55	7297.16	0.61	E (0021)
7299.47	7300.27	0.80	A1 (0021)
7299.52	7300.29	0.78	F2 (0021)
7326.57	7326.99	0.42	F1 (0211)
7331.42	7332.07	0.66	F2 (0211)
7337.75	7338.43	0.69	F2 (0021)
7338.27	7338.87	0.61	F1 (0021)
7342.51	7343.43	0.92	A1 (0211)
7342.78	7343.61	0.83	E (0211)
7346.29	7347.03	0.75	F2 (0211)
7346.76	7347.53	0.78	F1 (0211)
7349.33	7350.26	0.94	A2 (0211)
7352.65	7353.50	0.86	E (0211)
7361.20	7362.17	0.98	A1 (0211)
7362.11	7363.02	0.91	E (0211)
7365.73	7366.59	0.87	F2 (0211)
7369.18	7370.11	0.94	F1 (0211)
7373.34	7373.46	0.12	F1 (1110)
7374.80	7375.34	0.55	F2 (1110)
7385.16	7385.85	0.69	F2 (0401)
7395.71	7396.16	0.46	F1 (0401)
7409.60	7409.97	0.37	F2 (0401)
7423.64	7424.02	0.39	F1 (0401)
7437.82	7438.21	0.39	F2 (0401)
7448.24	7448.94	0.71	E (1300)

TABLE V. (*Continued.*)

This work	CT, Ref. 47	CT-TW[a]	Labels[b]
7468.58	7469.08	0.50	A2 (1300)
7468.88	7469.42	0.54	A1 (1300)
7483.93	7484.49	0.57	E (1300)
7510.53	7511.10	0.57	F2 (0120)
7512.53	7513.16	0.63	F1 (0120)
7546.54	7546.92	0.38	A2 (0120)
7552.47	7552.97	0.50	E (0120)
7559.29	7559.86	0.57	A1 (0120)
7570.23	7570.94	0.71	F1 (0310)
7576.52	7577.25	0.74	F2 (0310)
7581.57	7582.32	0.75	F1 (0310)
7585.38	7586.32	0.94	F2 (0310)
7641.52	7642.29	0.78	E (0500)
7644.80	7644.93	0.14	A2 (0500)
7645.69	7646.21	0.53	A1 (0500)
7652.57	7652.45	−0.12	E (0500)

[a] All values in cm^{-1}; TW = this work; CT = contact transformation order eight calculations.[47]

[b] Vibration state labels include T_d symmetry types and principal vibrational quantum numbers: see Ref. 47 for more details.

TABLE VI. Comparison of $^{12}CH_4$ Icosad band centers with available empirical values.

This work	Emp[a]	TW-emp	Labels
6378.04	6377.53	0.51	F2 (0005)
6406.24	6405.97	0.27	A1 (0005)
6429.69	6429.24	0.45	F1 (0005)
6450.65	6450.06	0.59	F2 (0005)
6507.36	6507.39	−0.03	E (0005)
6507.59	6507.55	0.04	F2 (0005)
6529.93	6529.78	0.15	F1 (0005)
6539.38	6539.18	0.20	F2 (0005)
7158.03	7156.72[b]	1.31	F2 (1011)
7510.53	7510.97[b]	−0.44	F2 (0120)

[a] Empirically derived values from experimental spectra, first eight in Ref. 90, last two from Refs. 92 and 93. All values are given in cm^{-1}.

[b] These values may not be accurate.

calculation for our largest X$_5$ basis was 11 h on one 16-kernels Xeon node. This is to be compared with the time of previous calculations,[25] which took more than seven days on a comparable node.

The convergence remains better than that of Ref. 25 even for the basis set with similar number of non-symmetrized basis functions. The basis set used in Ref. 25 contained 131 524 non-symmetrized basis functions (see Ref. 25 for details). This is comparable in size to the set of primitive functions used to build the X$_3$ basis of the present work. For all considered polyads, the vibrational calculations using 6A-basis set X$_3$ converge better than those of Ref. 25. For four- and five-quanta band systems $4\nu_4$ and $5\nu_4$, the 6A-basis converged at least 20 times better than the C_{3v} basis.[25] At the same time, the use of the full T_d (M) symmetry in the present method allows significantly increasing the size of non-symmetrized set of primitive functions. Finally, the convergence achieved for the angular $4\nu_4$ and $5\nu_4$ states was more than 100 better than that with the previously used C_{3v} basis set.[25]

Converged variational predictions for methane vibrational levels have been reported by Nikitin *et al.*[25] up to the Tetradecad of $^{12}CH_4$ and by Rey *et al.*[32,40,51,91] for $^{12}CH_4$, $^{12}CD_4$, and $^{12}CH_3D$ up to 5000 cm^{-1}. Recently, Wang and Carrington[31] have published results of carefully converged variational calculations for several methane isotopologues using an empirically optimized Schwenke-Partridge PES[8] with 40 experimental vibrational levels included in the fit. For the Icosad of $^{12}CH_4$, Wang and Carrington[31] extended the comparison to 10 experimentally analyzed sub-bands centers for which theoretical values have been also previously reported by Tyuterev *et al.*[47] using algebraic method of Contact Transformations (CTs).

The full Icosad range of methane involving 134 Icosad sub-bands[47] covers the spectral interval up from 6300 to 7660 cm^{-1}. Though first-principles spectra predictions recently reported for this range for T = 80 K and for room temperature conditions T = 296 K are encouraging,[40] a detailed analysis of the complete Icosad range represents a challenge for the theory. Indeed, the major part of nearly 30 000 experimentally recorded rovibrational lines[83] using laser cavity-ring-down measurements still remains unassigned. The basis convergence for the corresponding band centers is an important part of this issue. Using the results of Tables III and IV, we estimate the basis set convergence as ∼0.05–0.2 cm^{-1} for our best X$_5$ calculations in the Icosad range. The corresponding results for vibrational band centers are given in Table V.

The RMS deviation between our band centers and experimentally known values (see Table VI) for 10 analysed bands is only 0.53 cm^{-1}. For the entire set of 134 band centers, the RMS deviation between our variational predictions and the results obtained with algebraic contact transformation method[47] using normal mode representation is 0.81 cm^{-1}. As these two methods are absolutely independent, this overall agreement confirms a good convergence of our variational approach.

VII. DISCUSSION AND CONCLUSION

The primary motivation for this study was to prove a good convergence of new 6A angular basis set and to develop the corresponding algorithm for the matrix elements calculation. To do this, we applied a solution of the generalized eigenvalues problem using orthogonal coordinates. The functional form of the angular basis involves cos(q_{ij}) products. The symmetrization of this basis functions can be easily achieved via the projector operators technique. The exact kinetic energy operator in redundant coordinates[33,58] was applied. This approach permits avoiding the sin(q)$^{-2}$ singularity (which was present in polar coordinates[55,56]) in the vibrational kinetic energy operator. Many of previously published methods for nuclear motion calculation for methane-type molecules either used some approximations for the KEO or did not employ the full symmetry of the molecule. For example, in Refs. 24, 27, and 28, only 6 of 24 permutations in T_d point group were used that corresponded to a C_{3v} symmetry, whereas 8 from 24 elements of T_d point group were used in Ref. 8 In the present work, full symmetry calculations with the exact KEO were developed and the efficiency of the algorithm for the basis set convergence was demonstrated for vibrational levels of CH_4. With quite moderate dimensions of matrices, this allowed achieving a good accuracy for the band centers in the Icosad range (up to 7660 cm^{-1}) that could be useful for analyses of corresponding complex experimental spectra.[83] Fast calculations of multi-dimensional angular integrals are appropriate for further accuracy improvement via iterative least-squares fits during empirical PES[8,25,31,94] optimizations. Keeping reasonable dimensionality with converged results is mandatory for an extension of accurate methane calculations to higher energy ranges where experimentally recorded spectra[82,85,92] still remain unassigned. This issue is of major importance for various atmospheric[72,77,82] and astrophysical[50,51,84] applications.

APPENDIX: CALCULATION OF FIVE DIMENSIONAL INTEGRALS

In order to calculate the scalar products (5), the expression (4) was used for one-dimensional functions depending on q_{23}, q_{24}, q_{34},

$$
\begin{aligned}
&\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle \\
&\quad = (2\pi)^3 \sum_{l_{23}l_{23}^*l_{24}l_{24}^*l_{34}l_{34}^*} c_{n_{23}l_{23}}c_{k_{23}l_{23}^*}c_{n_{24}l_{24}}c_{k_{24}l_{24}^*}c_{n_{34}l_{34}}c_{k_{34}l_{34}^*} \sum_{L_{23}L_{24}L_{34}} K_{l_{23}l_{23}^*L_{23}}K_{l_{24}l_{24}^*L_{24}}K_{l_{34}l_{34}^*L_{34}} \\
&\qquad \times \int_0^{\pi}\int_0^{\pi}\int_0^{\pi} f_{n_{12}}(q_{12})f_{k_{12}}(q_{12})f_{n_{13}}(q_{13})f_{k_{13}}(q_{13})f_{n_{14}}(q_{14})f_{k_{14}}(q_{14})S_{L_{23}L_{24}L_{34}}(q_{12},q_{13},q_{14})d\cos(q_{12})d\cos(q_{13})d\cos(q_{14}),
\end{aligned}
$$

where $K_{l_1l_2L} = \frac{\sqrt{(2l_1+1)(2l_2+1)}}{2L+1}C(l_10,l_20,L0)^2$ and

$$
\begin{aligned}
&S_{L_{23},L_{24},L_{34}}(q_{12},q_{13},q_{14}) \\
&\quad = \int_0^{2\pi}\int_0^{2\pi} \sum_{m_{23},m_{24},m_{34}} Y_{L_{23}m_{23}}(q_{12},0)Y_{L_{23}m_{23}}(q_{13},t_{23})Y_{L_{24}m_{24}}(q_{12},0)Y_{L_{24}m_{24}}(q_{14},t_{24})Y_{L_{34}m_{34}}(q_{13},0)Y_{L_{34}m_{34}}(q_{14},t_{34})dt_{23}dt_{24}.
\end{aligned}
\tag{A1}
$$

The integral over torsional angles t_{23} and t_{24} in right part of (5) results in the factors $2\pi\delta(m_{23}-m_{34})$ and $2\pi\delta(m_{24}-m_{34})$.

This simplifies Eq. (A1) to give

$$
S_{L_{23},L_{24},L_{34}}(q_{12},q_{13},q_{14}) = (2\pi)^2\sum_m Y_{L_{23}m_{23}}(q_{12},0)Y_{L_{23}m}(q_{13},0)Y_{L_{24}m}(q_{12},0)Y_{L_{24}m}(q_{14},0)Y_{L_{34}m}(q_{13},0)Y_{L_{34}m}(q_{14},0).
$$

Using the expression (7). one can write the matrix element in the form

$$
\begin{aligned}
\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle = (2\pi)^5 &\sum_{l_{23}l_{23}{}^*l_{24}l_{24}{}^*l_{34}l_{34}{}^*} c_{n_{23}l_{23}}c_{k_{23}l_{23}{}^*}c_{n_{24}l_{24}}c_{k_{24}l_{24}{}^*}c_{n_{34}l_{34}}c_{k_{34}l_{34}{}^*} \\
&\times \sum_{L_{23}L_{24}L_{34}=0} K_{l_{23}l_{23}{}^*L_{23}}K_{l_{24}l_{24}{}^*L_{24}}K_{l_{34}l_{34}{}^*L_{34}} \\
&\times \sum_{m=0}^{\min(L_{23},L_{24},L_{34})} J_{n_{12},k_{12},L_{23},L_{24},m}J_{n_{13},k_{13},L_{23},L_{34},m}J_{n_{14},k_{14},L_{24},L_{34},m}.
\end{aligned}
\tag{A2}
$$

Using $J_{n_1,k_1,L,0} = \sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}}C(l_10,l_20,L0)^2 = \frac{1}{\sqrt{4\pi}}\sqrt{(2L+1)}\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}K_{l_1,l_2,L}$. Equation (6) can be obtained from (A2).

Taking into account $J_{n_1,k_1,L_1,0} = \sqrt{4\pi}J_{n_1,k_1,L_1,0,0}$, another form for the scalar products (6) could be derived,

$$
\begin{aligned}
\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\rangle = (2\pi)^5 &\sum_{L_{23}L_{24}L_{34}} \frac{64\pi^3}{\sqrt{(2L_{23}+1)(2L_{24}+1)(2L_{34}+1)}} \\
&\times J_{n_{23},k_{23},L_{23},0,0}J_{n_{24},k_{24},L_{24},0,0}J_{n_{34},k_{34},L_{34},0,0} \\
&\times \sum_{m=0}^{\min(L_{23},L_{24},L_{34})} J_{n_{12},k_{12},L_{23},L_{24},m}J_{n_{13},k_{13},L_{23},L_{34},m}J_{n_{14},k_{14},L_{24},L_{34},m}{}^*(2-\delta_{m,0}).
\end{aligned}
$$

Using successfully the relation

$$
Y_{l_1s_1}(q,0)Y_{l_2s_2}(q,0) = \sum_{LM}\sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}}C(l_10,l_20,L0)C(l_1s_1,l_2s_2,LM)Y_{LM}(q,0),
$$

($s_1 = 0, s_2 = 1$),[64] and the orthogonality of spherical harmonics, we obtain the integrals (8) in right part of (7).

In order to calculate the off-diagonal matrix elements of KEO, the coefficients (15) are necessary,

$$\begin{aligned}J^{D1}_{n_1,k_1,L_1,L_2,v,\pm} &= 2\pi\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\int_0^{\pi} Y_{l_10}(q,0)\left(\pm\sqrt{l_2(l_2+1)}\right)Y_{l_2\pm1}(q,0)Y_{L_1,\nu\pm1}(q,0)Y_{L_2,\nu}(q,0)d\cos(q)\\ &= \pm\sum_{l_1l_2} c_{n_1l_1}c_{k_1l_2}\sum_{L_a}\sqrt{l_2(l_2+1)}\sqrt{\frac{(2l_1+1)(2L_1+1)}{4\pi(2L_a+1)}}\sqrt{\frac{(2l_2+1)(2L_2+1)}{4\pi(2L_a+1)}}C(l_10,L_10,L_a0)\\ &\quad\times C(l_1,0,L_1,v\pm1,L_a,v\pm1)C(l_20,L_20,L_a0)C(l_2,\pm1,L_2,v,L_a,v\pm1).\end{aligned} \tag{A3}$$

Taking into account the relations for Clebsch-Gordan coefficient of Ref. 64 (page 210), one has

$$\begin{aligned}C(a,-\alpha,b,-\beta;c,-\gamma) &= (-1)^{a+b-c}C(a,\alpha,b,\beta;c,\gamma),\\ C(l_1,0,L_1,v\pm1,L_a,v\pm1) &= (-1)^{l_1+L_1-L_a}C(l_1,0,L_1,-v\mp1,L_a,-v\mp1),\\ C(l_2,\pm1,L_2,v,L_a,v\pm1) &= (-1)^{l_2+L_2-L_a}C(l_2,\mp1,L_2,-v,L_a,-v\mp1).\end{aligned}$$

The formula (16) for $J^{D1}_{n_1,k_1,L_1,L_2,-v,\pm}$ was derived by taking in account that L_a was integer and that only even $l_1+L_1+L_a$ and $l_2+L_2+L_a$ gave contributions to Eq. (A3). Using $C\big(l_1,0,L_1,-v\pm1,L_a,-v\pm1\big)C\big(l_2,\pm1,L_2,-v,L_a,-v\pm1\big) = C\,(l_1,0,L_1,v\mp1,L_a,v\mp1)\,C\,(l_2,\mp1,L_2,v,L_a,v\mp1)$, one obtains $J^{D1}_{n_1,k_1,L_1,L_2,-v,\pm} = J^{D1}_{n_1,k_1,L_1,L_2,v,\mp}$. To calculate $J^{D1}_{n_1,k_1,L_1,L_2,\nu,+}$, it is convenient expressing the derivatives in terms of $Y_{m,1}$, and in terms of $Y_{m,-1}$ for $J^{D1}_{n_1,k_1,L_1,L_2,\nu,-}$. In both cases, after recoupling, the products $Y_{k,v+1}Y_{m,v+1}$ or $Y_{k,v-1}Y_{m,v-1}$ are orthogonal with respect to the first index. Taking into account the formula for first derivatives of $Y_{m,l}$[64] and Eq. (A3), one can write the matrix elements for the off-diagonal KEO terms as

$$\begin{aligned}&\left\langle n_{12}n_{13}n_{14}n_{23}n_{24}n_{34}\left|\cos(t_{23})\frac{\partial^2}{\partial q_{12}\partial q_{13}}\right|k_{12}k_{13}k_{14}k_{23}k_{24}k_{34}\right\rangle\\ &\quad= (2\pi)^5\sum_{L_{23}L_{24}L_{34}}\frac{4\pi^{3/2}}{\sqrt{(2L_{23}+1)(2L_{24}+1)(2L_{34}+1)}}J_{n_{23},k_{23},L_{23},0}J_{n_{24},k_{24},L_{24},0}J_{n_{34},k_{34},L_{34},0}\\ &\quad\quad\times\sum_{m=-\min(L_{23},L_{24},L_{34})}^{\min(L_{23},L_{24},L_{34})}\left(J^{D1}_{n_{12},k_{12},L_{23},L_{24},m,-}J^{D1}_{n_{13},k_{13},L_{23},L_{34},m,-}+J^{D1}_{n_{12},k_{12},L_{23},L_{24},m,+}J^{D1}_{n_{13},k_{13},L_{23},L_{34},m,+}\right)J_{n_{14},k_{14},L_{24},L_{34},m}.\end{aligned}$$

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