

# Algorithm for calculation of energy levels of molecules of ABC<sub>3</sub> and AB<sub>4</sub> types from the potential energy surface

A.V. Nikitin

*Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk*

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Algorithms for calculation of energy levels for symmetric molecules of ABC<sub>3</sub> and AB<sub>4</sub> types in internal orthogonal coordinates are discussed. The symmetric basis of two torsion coordinates is considered in detail. An advantage of the described technique for determination of vibration states consists in the possibility of localizing basic functions near the minimum, which decreases the sensitivity to errors in the potential energy surface far from the minimum. Low vibration energy levels of the <sup>12</sup>CH<sub>3</sub><sup>35</sup>Cl molecule are calculated.

## Introduction

In recent years, many papers devoted to calculation of methane vibrational energy levels have been published.<sup>1-4</sup> The analysis of high-excited energy levels and methane transitions is a complicated problem due to the localized structure of levels and a rather large dimension of the problem.<sup>5,6</sup> The aim of this paper is to describe the algorithm of determination of energy levels from the potential energy surface (PES) in internal coordinates for more complicated molecules of the ABC<sub>3</sub> type. From here on, the internal coordinates are specified by four vectors  $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4$ , each being a linear combination of radius vectors of a pentatomic molecule in some coordinate system. Permutation of three vectors  $\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4$  reduces to permutation of equivalent atoms. As internal coordinates, we use four distances  $r_1, r_2, r_3, r_4$ , three angles  $q_2, q_3, q_4$ , and two torsion angles  $t_3, t_4$ .

This paper describes the technique of symmetrization of the wave function of two torsion angles and additional potentials needed for correct localization of wave functions and considers numerical examples of solution of the torsion problem, a general algorithm for determination of matrix elements of a nine-dimensional problem, and an example of calculation of the <sup>12</sup>CH<sub>3</sub><sup>35</sup>Cl vibrational energy levels.

## Symmetric torsion basis

Table 1 summarizes the rules of transforming two torsion angles  $t_3, t_4$  upon permutations of three identical atoms 2, 3, and 4 [Refs. 7 and 8]; the fourth column presents the rules of transforming the coefficients  $m_3$  and  $m_4$  in the function  $e^{i(m_3 t_3 + m_4 t_4)}$  induced by the permutations of identical atoms. From here on, the permutations are defined as  $(abc) = (ab)(ac)$ ,  $(abcd) = (ab)(ac)(ad)$ , and, consequently,  $(13)(23) = (123)$ ,  $(12)(23) = (132)$ .

**Table 1. Transformation of torsion coordinates**

Permutation	Permutation-induced transformation of torsion coordinates	$e^{i(m_3 t_3 + m_4 t_4)} \equiv \{m_3, m_4\}$ , $m_+ = m_3 + m_4$
$e$	$\tilde{t}_3 = t_3 \quad \tilde{t}_4 = t_4$	$\{m_3, m_4\}$
(23)I	$\tilde{t}_3 = t_3 \quad \tilde{t}_4 = t_3 - t_4$	$\{m_+, -m_4\}$
(34)I	$\tilde{t}_3 = -t_4 \quad \tilde{t}_4 = -t_3$	$\{-m_4, -m_3\}$
(234)=(34)(23)	$\tilde{t}_3 = -t_4 \quad \tilde{t}_4 = t_3 - t_4$	$\{m_4, -m_+\}$
(243)=(23)(34)	$\tilde{t}_3 = t_4 - t_3 \quad \tilde{t}_4 = -t_3$	$\{-m_+, m_3\}$
(24)I=(34)(243)	$\tilde{t}_3 = t_4 - t_3 \quad \tilde{t}_4 = t_4$	$\{-m_3, m_+\}$

Let us define the projecting operators of the  $C_{3v}$  group as

$$\begin{aligned}
 P_{A_1} &= (e + (23) + (24)(e + (34)))/\sqrt{6}, P_{A_2} = \\
 &= (e - (23) - (24)(e - (34)))/\sqrt{6}, \\
 P_{1E_a} &= ((24) + (23) - 2e)(e + (34))/\sqrt{12}, P_{1E_b} = \\
 &= ((24) - (23)(e + (34)))/2, \\
 P_{2E_a} &= ((24) - (23)(e - (34)))/2, \\
 P_{2E_b} &= (-(23) - (24) - 2e)(e - (34))/\sqrt{12}. \quad (1)
 \end{aligned}$$

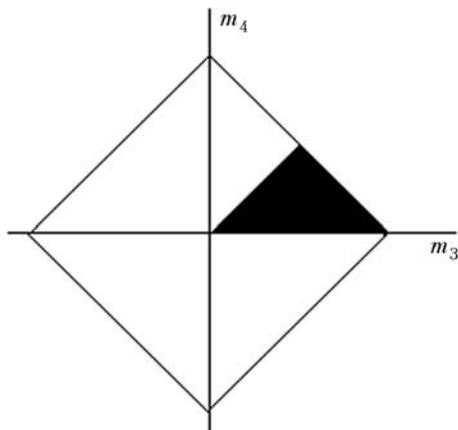
Acting by the projecting operators on the basis  $e^{i(m_3 t_3 + m_4 t_4)}$ , we obtain a set of symmetric torsion functions  $F_{m_3, m_4}^{n, G, \sigma}$ , where  $G$  is the representation;  $\sigma$  is the row of the representation;  $n = 1, 2$  for the representation  $E$ . The functions obtained are real only at  $m_3 = m_4$ . In place of the functions  $F_{m_3, m_4}^{n, G, \sigma}$ , at  $m_3 \neq m_4$  and  $m_3 \neq 0, m_4 \neq 0$ , it is possible to introduce the real functions:

$$F_{m_3, m_4}^{+, n, G, \sigma} = \frac{1}{\sqrt{2}} \left( F_{m_3, m_4}^{n, G, \sigma} + (F_{m_3, m_4}^{n, G, \sigma})^* \right)$$

and

$$F_{m_3, m_4}^{-, n, G, \sigma} = \frac{1}{\sqrt{2}i} \left( F_{m_3, m_4}^{n, G, \sigma} - (F_{m_3, m_4}^{n, G, \sigma})^* \right). \quad (2)$$

In particular cases  $m_3 = 0$  and  $m_4 = 0$ , only three of six functions (1) remain, and in this case the normalization of the functions differs from Eq. (1). Selecting all pairs of non-negative  $m_3$  and  $m_4$  so that  $m_3 + m_4 \leq m_{\max}$  and  $m_4 \leq m_3$ , we obtain the complete symmetric basis. The area of  $m_3$  and  $m_4$  values determining the complete basis (2) is marked in Fig. 1.



**Fig. 1.** Area of values determining the basis (2) (the square shows the range of all  $m_3$  and  $m_4$  values obtained through permutations).

An alternative method for constructing the symmetric basis is the numerical solution of the two-dimensional torsion problem followed by symmetrization. Fixing the coordinate  $t_4$  equal to its equilibrium value, we can find one-dimensional eigenfunctions  $T_n(t_3)$ . Solving the two-dimensional problem in the basis  $T_{n_3}(t_3)T_{n_4}(-t_4)$  with the kinetic energy operator

$$T = -\frac{\hbar^2}{mr_e^2} \left( \frac{\partial^2}{\partial t_3^2} + \frac{\partial^2}{\partial t_4^2} + \frac{\partial}{\partial t_3} \frac{\partial}{\partial t_4} \right),$$

we find eigenvectors and the corresponding energies. The eigenvectors obtained are not always transformed correctly upon permutations. Thus, double degenerate vectors with close energies can be linear combinations of vectors transformed by the representation  $E$ . Using the rules from Table 1, we can find how two eigenvectors transform upon the permutation (23) $I$ :

$$(23)I \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = \begin{pmatrix} -a & b \\ b & a \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \end{pmatrix}. \quad (3)$$

Let us find such rotation that the vector  $(f_1, f_2)$  is transformed into the vector  $(f'_1, f'_2)$ , being transformed similarly to Eq. (3) with  $a = 1/2$ ,  $b = \sqrt{3}/2$ . This rotation results in two vectors, which are then transformed by the representation  $E$ . The eigenvectors of the symmetry  $A_1$  and  $A_2$  do not require an additional rotation. A disadvantage of this approach is the fact that the high-excited functions not always can be easily

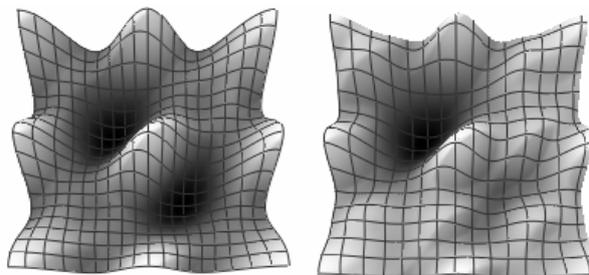
symmetrized, but it is easier to calculate contracted torsion matrix elements in this basis.

## Additional potentials

The introduction of additional potentials is reasonable, when the used potential behaves incorrectly at some points of the coordinate space or when additional localization of wave functions is necessary. For the two-dimensional torsion basis, we use the potential of the symmetry  $A_1$  in the form

$$V_{A_1}(t_3, t_4) = f(t_3) + f(-t_4) + f(-t_3 + t_4). \quad (4)$$

Figure 2 shows the two-dimensional torsion surface of the  $^{12}\text{CH}_4$  potential at the equilibrium coordinates  $r$  and  $q$ . Two deep minima correspond to the points  $(120, 240)$  and  $(240, 120)$  in the space  $t_3, t_4$ .



**Fig. 2.** Two-dimensional torsion PES (from 0 to 360°) in the coordinates  $t_3, t_4$  (left); two minima at  $(120, 240)$  and  $(240, 120)$ . The same surface with the additional potential removing the minimum at  $(240, 120)$  (right).

If we solve the problem for eigenvalues with such potential, then the solutions will be doubled. The introduction of the additional potential (4) with  $f(t) = 0.00012(\sin(t) + \sqrt{3}/2)^{10}$  removes one minimum. In this case, the eigenvectors at the needed minimum change insignificantly. In some cases, it is necessary to lift the edges of the potential well. This can be done with the additional potential, proportional to  $f(t) = (\cos(t) + 1/2)^{10}$ . For some molecules, it is reasonable to introduce additional angular potentials. For example, for  $^{12}\text{CH}_4$  we can introduce the additional potential, proportional to  $\sum_{ij} (\cos(q_{ij} + 1/3))^n$ , where  $n$  is greater than or equal to

the maximal power used in the angular part of PES. The introduction of additional potentials extends the applicability of the PES program for different molecules.

## Numerical examples of application of the torsion basis

Table 2 presents the examples of solution of the two-dimensional torsion problem. The first seven eigenvalues nearly coincide.

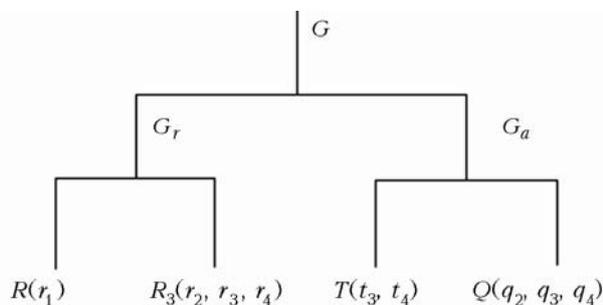
**Table 2. Comparison of solutions of the two-dimensional torsion problem for three bases**

Representation	$t_{n_3}(T_3)t_{n_4}(-t_4)$	Basis (2)	
		$M_{\max} = 35$	$M_{\max} = 40$
$A_1$	1312.785146	1312.785146	1312.785146
$E$	2621.432267	2621.432267	2621.432267
$A_1$	3918.344736	3918.344736	3918.344736
$E$	3927.744705	3927.744705	3927.744705
$E$	5212.684394	5212.684390	5212.684390
$A_1$	5231.746970	5231.746968	5231.746968
$A_2$	5231.823276	5231.823269	5231.823269
—	—	—	—
$A_2$	13009.316066	13009.230100	13009.230014
$A_1$	13009.316348	13009.230394	13009.230308
$A_1$	13999.279505	13998.042907	13998.041412
$E$	14010.745382	14009.818399	14009.816693

Eigenvalues in the range 13000–14000  $\text{cm}^{-1}$  differ markedly, since the basis  $T_{n_3}(t_3)T_{n_4}(-t_4)$  was restricted by the product of  $T_{n_3}(t_3)$  and  $T_{n_4}(-t_4)$  so that the total energy of one-dimensional eigenvalues was lower than 80000  $\text{cm}^{-1}$ . The number of basis functions for the basis  $T_{n_3}(t_3)T_{n_4}(-t_4)$  was 1020. The number of basis functions for the basis (2) with  $m_{\max}=35(40)$  was 666(861), 595(780), and 1260(1640), respectively, for the  $A_1$ ,  $A_2$ , and  $E$  blocks, while the number of nonsymmetric basis functions was 3781(4921).

### Calculation of vibrational matrix elements

The problem of determination of vibrational matrix elements is computationally expensive. A simple method of sequential computation of matrix elements is possible only for a very small basis. Initially, PES is determined in the basis of vibrational trees like in Ref. 9. Figure 3 shows the tree structure, whose each branch corresponds to the representation of the permutation group of three identical atoms. Leaves of the PES tree contain various symmetrized coordinates  $R(r_1)$ ,  $R_3(r_2, r_3, r_4)$ ,  $T(t_3, t_4)$ ,  $Q(q_2, q_3, q_4)$ .

**Fig. 3.** PES tree.

The tree of wave functions is defined analogously, but their leaves represent symmetrized

one-, two-, and three-dimensional wave functions. Using 9G symbols for the point group  $C_{3v}$ , it is possible to reduce the calculations of a reduced matrix element to the calculation of one-, two-, and three-dimensional reduced matrix elements. For the efficient operation of this algorithm, it is necessary to have a memory capacity sufficient for storage of one-, two-, and three-dimensional reduced matrix elements.

Another method applied, in particular, for  $\text{CH}_4$  consists in preliminary solution of the radial and angular problems, followed by solution of the complete problem in the basis of radial and angular eigenfunctions. In this case, the problem is in the calculation and storage of angular matrix elements.

In some cases, it is possible to apply a somewhat improved method of sequential computation of matrix elements. For this purpose, wave functions and PES terms are sorted first with respect to the angular part and then with respect to the radial part. All radial matrix elements are precalculated and stored in the memory. Then every calculated angular matrix element is multiplied by a radial matrix element and the resultant matrix element is saved on the disk. Such a scheme does not require the storage of angular matrix elements in the memory, but does not use the advantages of high symmetry of the problem. The selection of some or other computational scheme depends, to a great extent, on the form of PES representation.

### Calculation of vibrational levels of the $^{12}\text{CH}_3^{35}\text{Cl}$ molecule

Table 3 presents the experimental vibrational energy levels of the  $^{12}\text{CH}_3^{35}\text{Cl}$  molecule along with those calculated from the six-order PES.<sup>10</sup>

**Table 3.** Vibrational energy levels of  $^{12}\text{CH}_3^{35}\text{Cl}$ 

Assignment	Experiment	Calculation I	Calculation II
$v_3$	732.84216	733.580255	733.0826
$v_6$	1018.07090	1017.585	1015.914
$v_2$	1354.88112	1359.794	1355.645
$v_5$	1452.17844	1452.926	1451.302
$2v_3$	1456.76266	1458.867	1457.767
$v_3 + v_6$	1745.37113	1745.833	1744.97
$2v_6(A_1)$	2029.37523	2031.441	2028.798
$2v_6(E)$	2038.32636	2039.59	2037.216
$v_2 + v_3$	2080.53577	2082.950	2084.948
$3v_3$	2171.88765	2175.591	2174.777
$v_3 + v_5$	2182.57173	2184.234	2183.205
$v_2 + v_6$	2367.72216	2376.223	2374.192
$v_5 + v_6(A_1)$	2464.90270	2468.811	2465.555
$v_5 + v_6(A_2)$	2467.66902	2469.278	2467.276
$v_5 + v_6(E)$	2461.64821	2464.098	2461.721
$2v_3 + v_6(E)$	2463.81796	2466.634	2464.734
$2v_3(A_1)$	2879.360	2882.618	2880.711
$v_1$	2967.777	2969.623	2968.632
$v_4$	3039.286	3044.760	3042.556

The calculations were performed with two sets of basis functions. In the first set, the number of basis functions was 11000, in the second one – 17523. The calculation of matrix elements for 17523 basis functions on the Athlon 3800 × 2 processor took 2 h with the use of the algorithm based on the reduced matrix elements. The improved method took more than 6 h. Thus, the algorithm based on the reduced matrix elements is significantly more efficient than the sequential computation of matrix elements.

## Conclusions

The algorithm described can be generalized to more complex molecules. In this case, only the tree structure and the dimension of the problem change. An advantage of the described technique for determination of vibrational levels consists in the possibility of localizing the basis functions near the minimum, which diminishes the sensitivity to errors in PES far from the minimum. The algorithms presented in the paper have been used to calculate energy levels of molecules CH<sub>3</sub>Cl and CH<sub>4</sub>.

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