Solution of the Schrödinger torsion equation in the basis set of Mathieu functions: verification by numerical experiment

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Abstract. The efficiency of the algorithm for the numerical solution of the Schrödinger torsion equation in the basis of Mathieu functions has been considered. The computational stability of the proposed algorithm is shown. The energies of torsion transitions determined in the basis sets of plane waves and Mathieu functions have been compared with the results of spectroscopy. A conclusion about the applicability of the algorithm using the basis set of Mathieu functions to the solution of the Schrödinger equation with a periodic potential has been derived.

1. Introduction
The creation of new materials with predetermined properties involves not only experimental research, which turns out to be very expensive and time-consuming, but also the development of mathematical models. Thus, the study of the internal rotation of molecules described by the Schrödinger torsion equation (1) is very important for predicting spectroscopic and thermodynamic properties [1].

\[
\left(-\frac{d}{d\varphi} F(\varphi) \frac{d}{d\varphi} + V(\varphi)\right) \Psi = E \Psi,
\]

where \( V(\varphi) \) is the potential, and \( F(\varphi) \) is the structural function of the internal rotation. Equation (1) can be written for multidimensional rotation with several torsion angles, and (1) is solved numerically for molecules with a complex internal structure, where the functions \( V(\varphi) \) are not described by single harmonics. In this case, the torsion potential \( V(\varphi) \) and the structure function \( F(\varphi) \) are approximated by a segment of the trigonometric basis

\[
V = V_0 + \sum_m v'_m \cos (m\varphi) + \sum_m v''_m \sin (m\varphi),
\]

\[
F = F_0 + \sum_m f'_m \cos (m\varphi) + \sum_m f''_m \sin (m\varphi),
\]

and the wave function \( \Psi \) is represented as a finite set of plane waves

\[
\Psi = \sum_n \psi_n e^{in\varphi}.
\]

The matrix of the Hamiltonian \( H_{mn} \) with complex-valued elements is obtained by solving (1) in matrix form. The diagonalization of complex matrices of large sizes at the time of publication of the works [2-6] was impossible due to the computational capabilities of computers. Therefore, the transformations considered in [7] were used (Wang transformations), which enable computing the elements of the Hamiltonian in the trigonometric basis.
The application of the basis set of Mathieu functions was proposed and justified in [8], as an alternative to (3)

\[ \Psi = \sum_{n} \psi_{n} U_{n}, \] (4.1)

\[ U_{n} = c_{e_{n}}(q, \varphi) + i \cdot s_{e_{n}}(q, \varphi), \quad U_{0} = c_{e_{0}}(q, \varphi), \quad U_{-n} = \bar{U}_{n} \] (4.2)

Moreover, the torsion potential is also approximated in the complex-valued basis in [8] (4.2), and it is proposed to use series with real coefficients in [9]

\[ V(\varphi) = V_{0} + v_{0}' \cdot c_{e_{0}}(q, \varphi) + \sum_{n=1}^{N_{1}} v_{n}' c_{e_{n}}(q, \varphi) + \sum_{n=1}^{N_{2}} v_{n}'' s_{e_{n}}(q, \varphi) \] (5.1)

\[ F(\varphi) = F_{0} + f_{0}' \cdot c_{e_{0}}(q, \varphi) + \sum_{n=1}^{K_{1}} f_{n}' c_{e_{n}}(q, \varphi) + \sum_{n=1}^{K_{2}} f_{n}'' s_{e_{n}}(q, \varphi) \] (5.2)

This method enables the significant increase in efficiency of the algorithm by reducing the number of retained terms in (4) and (5) compared to (2) and (3), which leads to a reduction in the size of \( H_{mn} \).

A technique for calculating the \( H_{mn} \) elements of the Hamiltonian matrix in the complex-valued basis (4) is described in [10], and it is shown in [11] that the computational error in this case is insignificant.

Numerical experiments to verify the application of the complex-valued basis of Mathieu functions (4) to solving the Schrödinger torsion equation are described in the present work. The experimental spectra (wave numbers) were compared with the energies of transitions between torsion levels obtained during solving (1) both in the basis of Mathieu functions (4) and in the basis set of plane waves (3) to accomplish this task.

Another indicator of the appropriateness of the model used is the computational stability of the proposed method - the absence of significant differences in the results when the parameter \( q \) changes. Obviously, the comparison should be carried out using examples of well-studied molecules with the vibrational spectra obtained experimentally and confirmed theoretically. Molecules of ethanol, 2,2,2-trifluoroethanol with their isotopic states and a molecule of methacrolein were selected to test the proposed method.

2. Torsion levels and transitions in the ethanol molecule and its isotopic states

The choice of an ethanol molecule for testing the computational method can be easily explained by its simple structure and the presence of vibrational spectra repeatedly reproduced experimentally examples of which are the works [2, 3]. The ethanol spectrum is also relevant for several problems in radio astronomy [12]. Along with the ethanol molecule \( \text{C}_{2}\text{H}_{5}\text{OH} \), the torsion spectra of its O-d isotope \( \text{C}_{2}\text{H}_{5}\text{OD} \) were considered in [2] which can also be used for comparison with calculations with the Mathieu functions basis set. The torsion potentials \( V(\varphi) \) were reconstructed from the spectroscopic data in [2] and the dependence \( F(\varphi) \) was determined on the geometry.

| Transition | Calc [2] | Exp [2] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|----------|---------|-------------------|----------------|----------------|----------------|
| \( 1 \rightarrow 0 \) | 203.6 | 203.6 | 193.6 | 193.6 | 193.6 | 193.6 |
| \( 1' \rightarrow 1' \) | 243.1 | 243.1 | 245.1 | 245.1 | 245.1 | 245.1 |
| \( 1' \rightarrow 1' \) | 195.8 | 195.8 | 197 | 197.1 | 197.1 | 197.1 |
| \( 0' \rightarrow 0' \) | 3.227 | 3.227 | 3.7 | 3.694 | 3.694 | 3.694 |
Table 1.2 Comparison of the torsion transitions energies in C₂H₃OD, cm⁻¹.

| Transition | Calc [2] | Exp [2] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|----------|---------|--------------------|---------------------|---------------------|---------------------|
| 1→0        | 169.3    | 169.3   | 159.1              | 159.1               | 159.1               | 159.1               |
| 1'→1*      | 174.9    | 175.1   | 180                | 179.968             | 179.9684            | 179.9683            |
| 1*→1'      | 162.8    | 162.6   | 165.2              | 165.190             | 165.1902            | 165.1902            |
| 0'→0*      | 0.655    | 0.570   | 1                  | 0.98758             | 0.987583            | 0.987559            |

The internal rotation in the ethanol and its isotopes was also considered earlier in [3]. The data on torsion potentials from [3] were used for similar comparisons and the results are summarized in Tables 1.3 and 1.4.

Table 1.3 Comparison of the torsion transitions energies in C₂H₅OH, cm⁻¹.

| Transition | Calc [3] | Exp [2] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|----------|---------|--------------------|---------------------|---------------------|---------------------|
| 0'→0       | 40.0     | 41.2±5.0 [3] | 40.2               | 38.5               | 38.5               | 38.5               |
| 1→0        | 201.0    | 201 [13] | 214.6             | 214.1              | 214.1              | 214.1              |
| 1'→0*      | 189.2    | 207 [14] | 203.3             | 203.0              | 203.0              | 203.0              |
| 1→0*       | 251.2    | 251.4   | 251.4             | 251.4              | 251.4              | 251.4              |
| 0→0*       | 3.2270   | 3.2269 [3] | 2.9               | 2.8                | 2.8                | 2.8                |

Table 1.4 Comparison of the torsion transitions energies in C₂H₅OH, cm⁻¹.

| Transition | Calc [3] | Exp [2] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|----------|---------|--------------------|---------------------|---------------------|---------------------|
| 0'→0       | 42.6     | 169 [13] | 42.7              | 40.1               | 40.1               | 40.1               |
| 1→0        | 169.2    | 170 [14] | 179.3             | 180.0              | 180.0              | 180.0              |
| 1'→0*      | 162.7    | 173.6   | 173.6             | 173.0              | 173.0              | 173.0              |
| 1→0*       | 182.6    | 181.9   | 181.9             | 181.9              | 181.9              | 181.9              |
| 0→0*       | 0.5759   | 0.5703 [3] | 0.4000          | 0.4034            | 0.4034            | 0.4034            |

The growth of computing power and the advances in information technologies enabled to solve the problem of internal rotation in multidimensional cases [15, 16]. Thus, the results of torsion transition calculations for the one-dimensional case (1D) - rotation of the hydroxyl group OH and for the two-dimensional case (2D) - rotation of the hydroxyl group OH and methyl group CH₃ for an ethanol molecule in the plane wave basis set were compared in [15]. The same potentials from [15] were used with the Mathieu function basis set calculating. Tables 1.5 and 1.6 show the comparison of the results of calculations for the one-dimensional and two-dimensional cases in the basis set of plane waves from [15] with the results of calculations by the Mathieu function basis set.

Table 1.5 Comparison of the torsion transitions energies in C₂H₅OH (1D), cm⁻¹.

| Transition | Calc 1D [15] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|--------------|--------------------|---------------------|---------------------|---------------------|
| 0'→0       | 25.5         | 24.0               | 24.0                | 24.0                | 25.5                |
| 0→0        | 28.5         | 27.1               | 27.1                | 27.1                | 28.5                |
| 1→0        | 205.8        | 207.5              | 207.5               | 207.5               | 205.8               |
| 1'→0       | 232.9        | 231.3              | 231.3               | 231.3               | 232.9               |
| 1→0        | 279.2        | 278.5              | 278.5               | 278.5               | 279.2               |
| 2→0        | 351.4        | 351.1              | 351.1               | 351.1               | 351.4               |
| 2'→0       | 469.2        | 469.3              | 469.3               | 469.3               | 469.2               |
| 2→0        | 470.0        | 469.4              | 469.4               | 469.4               | 470.0               |
an experiment similar to the ones for ethanol (see the previous section). The results are shown in Table 2.

The calculations in the plane waves basis set and in the Mathieu functions basis set were compared with spectroscopic data are given in [2] including deuterated isotopics $^{2,2,2}$

The difference between the energies becomes very insignificant with an increase in the number of levels.

3. Torsion levels and transitions in the 2,2,2-trifluoroethanol molecule and its isotopic states

2,2,2-trifluoroethanol is another example with a thoroughly studied rotational spectrum for which spectroscopic data are given in [2] including deuterated isotopics and the torsion potentials $V(q)$. The calculations in the plane waves basis set and in the Mathieu functions basis set were compared with an experiment similar to the ones for ethanol (see the previous section). The results are shown in Tables 2.1-2.4.

| Transition | Exp [2] | Planar waves basis | Mathieu basis $q=1$ | Mathieu basis $q=3$ | Mathieu basis $q=5$ |
|------------|---------|---------------------|---------------------|---------------------|---------------------|
| 0$^+\rightarrow 0$ | 284.2 | 286.0 | 285.9925 | 285.9925 | 285.9925 |
| 1$\rightarrow 0$ | 281.0 | 276.4 | 276.4217 | 276.4217 | 276.4216 |
| 1$^+\rightarrow 0^+$ | 272.0 | 273.8 | 273.8051 | 273.8051 | 273.8051 |
| 0$^+\rightarrow 0^+$ | 0.95 | 0.8 | 0.82 | 0.82 | 0.82 |

| Transition | Exp [2] | Planar waves basis | Mathieu basis $q=1$ | Mathieu basis $q=3$ | Mathieu basis $q=5$ |
|------------|---------|---------------------|---------------------|---------------------|---------------------|
| 0$^+\rightarrow 0$ | 280.0 | 281.6 | 281.5494 | 281.5493 | 281.5493 |
| 1$\rightarrow 0$ | 278.1 | 278.7 | 278.6944 | 278.6944 | 278.6943 |
| 1$^+\rightarrow 0^+$ | 268.1 | 267.1 | 267.0938 | 267.0938 | 267.0938 |
| 0$^+\rightarrow 0^+$ | 1.00 | 1 | 1.03759 | 1.037591 | 1.037545 |

It’s evident from Tables 1.5 and 1.6 that the results of calculations in the basis set of Mathieu functions are quite close to the results from [15] obtained in the plane waves basis set. Moreover, the difference between the energies becomes very insignificant with an increase in the number of levels.
Table 2.4 Comparison of the torsion transitions energies CF₃CD₂OD, in cm⁻¹.

| Transition | Exp [2] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=5 \) | Mathieu basis \( q=3 \) |
|------------|---------|---------------------|-----------------|-----------------|-----------------|
| 1→0        | 192.8   | 189.3               | 189.284         | 189.284         | 189.284         |
| 1'→0⁺       | 194.3   | 193.6               | 193.6143        | 193.6143        | 193.6143        |
| 1⁺→0⁻       | 187.4   | 189.7               | 189.7144        | 189.7144        | 189.7144        |
| 0⁺→0⁻       | 0.19    | 0.2                 | 0.136314         | 0.136313        | 0.136266        |

4. Torsion levels and transitions for the methacrolein molecule

High-resolution vibrational spectra for the methacrolein molecule considering hindered rotation have been studied in [16]. Torsion transitions were obtained experimentally from UV spectra [17] and by IR Fourier spectroscopy [18]. The potential function of internal rotation \( V(\varphi) \) was restored from the frequencies of the UV spectrum [17]. The curve \( F(\varphi) \) in the form of a Fourier series expansion in [17] was obtained by standard methods from geometry. We used the same Fourier expansions of the torsion potential for the numerical solution of the Schrödinger torsion equation (1) in the basis set of plane waves and in the basis set of Mathieu functions for different parameter \( q \) similar to the examples above.

Table 3.1 Comparison of spectroscopic data with calculations of the torsion transitions energies from zero to several lower levels in different bases for methacrolein, in cm⁻¹.

| Transition | UV spectrum [17] | FTIR spectrum [18] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|------------------|---------------------|---------------------|-----------------|-----------------|-----------------|
| 1→0        | 169.6            | 169.82              | 169.8               | 169.8139        | 169.8135        | 169.8137        |
| 2→0        | 338.0            | 338.08              | 338.6               | 338.6154        | 338.6154        | 338.6151        |
| 3→0        | 505.0            | 505.25              | 506.2               | 506.2757        | 506.2749        | 506.2752        |
| 4→0        | 670.6            | 671.03              | 672.6               | 672.6708        | 672.6702        | 672.6705        |
| 5→0        | 835.0            | 835.59              | 837.7               | 837.6836        | 837.6824        | 837.6822        |

Table 3.2 Comparison of spectroscopic data with calculations of the torsion transitions energies between several lower levels in different bases for methacrolein, in cm⁻¹.

| Transition | FTIR spectrum [18] | Planar waves basis | Mathieu basis \( q=1 \) | Mathieu basis \( q=3 \) | Mathieu basis \( q=5 \) |
|------------|---------------------|---------------------|-----------------|-----------------|-----------------|
| 1→0        | 169.82              | 169.8               | 169.8139        | 169.8135        | 169.8137        |
| 2→1        | 168.26              | 168.8               | 168.8015        | 168.8019        | 168.8015        |
| 3→2        | 167.17              | 167.6               | 167.6604        | 167.6595        | 167.6601        |
| 4→3        | 165.78              | 166.4               | 166.3951        | 166.3953        | 166.3953        |
| 5→4        | 164.56              | 165.1               | 165.0128        | 165.0122        | 165.0117        |

5. Conclusions and discussions

Comparison of the tables showed that the calculation results in the considered basis sets with the same input data are close enough that enables deriving a conclusion that the developed model is working. However, the variational limit (the convergence of the torsion level energies to a constant value that does not depend on the size of the basis set) in the basis set (4) is reached faster [19]. This value is a measure of the efficiency of the obtained solution (1) and allows recommending (4) and all previously obtained relations and algorithms [8-11] for use in multidimensional cases.

The following conclusions can be drawn from the results of the work:
1. Several solutions of the Schrödinger equation (1) with different periodic potentials in the basis sets of plane waves (3) and Mathieu functions (4) have been considered. Comparison of the corresponding transition energies showed that their relative difference is in the range of $10^{-2}$% while the relative difference in the energies of transitions between the lower levels at different $q$ is in the range of $10^{-3}$%. The coincidence of the calculation results for different parameter $q$ indicates the computational stability of the proposed algorithms.

2. The calculation results in the Mathieu functions basis set are in very good correlation with the experimental data. It is especially true for the transition energies between the lower torsion levels in methacrolein and trifluoroethanol and its isotopic states. The main discrepancies were observed by comparing the energies in Tables 1.1 and 1.2 with the experimental data from [2] for the fundamental transitions in ethanol and account to about 10 cm$^{-1}$. Similar discrepancies were also observed in Table 1.3 when comparing the theoretical energies with the spectroscopic data from [3] for the transitions $1^\rightarrow 0^*$, $1^0 \rightarrow 0^*$ and the fundamental.

3. It should be noted that the energies of torsion levels obtained in [2, 3] may slightly differ from updated results even with the same input data. The reason for this is quite trivial - the calculations were carried out on devices from different eras of development of computers and software. The use of 64-bit processors leading to a decrease in the computational error in floating point operations, multiple increases in the memory capacity, the development of efficient algorithms including the ones for parallel computations, the improvement of software - all this made it possible to carry out calculations directly in the plane waves basis set (3) even in the case of large matrices obtained for molecules with a complex internal structure. We will notate that these discrepancies do not reduce the value of the results even after a long time after obtaining them.

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