Analytical expression of tensorial rotational operators for semi-classical interpretation of molecular spectra. Relations between molecular Hamiltonian parameters in different formalisms

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Graphical Abstract

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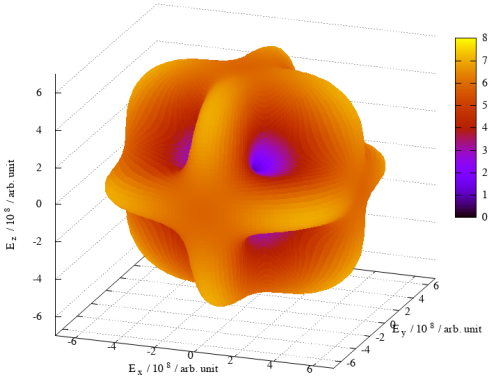

Highlights

Analytical expression of tensorial rotational operators for semi-classical interpretation of molecular spectra. Relations between molecular Hamiltonian parameters in different formalisms.

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- Full analytical expansion of the tensorial rotational Hamiltonian using symbolic programming.
- Application to the semi-classical approach to energy level structures.
- Exact comparison between tensorial and Watsonian Hamiltonians for various molecules.

Analytical expression of tensorial rotational operators for semi-classical interpretation of molecular spectra. Relations between molecular Hamiltonian parameters in different formalisms.

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Abstract

We present a formal development of the tensorial rotational Hamiltonian using symbolic calculations. Algebraic manipulations thanks to the open-source Maxima software allow us to get formal expressions of use for various molecular spectroscopy problems. We first present some simple applications to the so-called semi-classical approach that allows the study of level structures in the molecular rotational energy spectrum. Then, we perform some comparisons between the tensorial approach and Watson's Hamiltonian, giving exact effective molecular parameter correspondance formula between the two formalisms.

Keywords:
High-resolution molecular spectroscopy, Tensorial formalism, Watson's formalism, Molecular Hamiltonian, Rotational operators, Symbolic calculations

1. Introduction

The expression of the vibration-rotation Hamiltonian operator of polyatomic molecules is the essential starting point for high-resolution molecular spectroscopy studies. This expression is quite complex and has been the subject of many papers since the very beginning of quantum mechanics almost a century ago, with the first article on this subject by Born and Heisenberg [1]. A few years later, Born and Oppenheimer separated the electronic and vibration-rotation motions, leading to the famous Born-Oppenheimer approximation [2]. The detailed expansion mathematically relies on perturbation theory and especially benefited of its so-called contact transformation version as defined by Van Vleck [3]. Since then, the detailed form of the Hamiltonian has been adapted many times. In particular, a widely-used standard form has been defined by Watson in a seminal paper [4] and this was refined a few years later by Aliev and Watson [5, 6]. The final form to which authors

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nowadays refer to is the one given in the famous book of Papoušek and Aliev [7]. This molecular Hamiltonian is sometimes referred to as the Watsonian. More details about the Hamiltonian and its symmetry properties can be found in Ref. [8], which is another classical textbook on the subject.

This is, however, not the end of this story. For some molecules, a different form may be more adapted in practice. This is especially the case for species with a high-symmetry at equilibrium like spherical-top molecules with T_d or O_h symmetry, as for instance methane (CH_4) or sulfur hexafluoride (SF_6). This requires the intensive use of group theory and tensorial development methods and was investigated first in 1938-39 by Jahn [9, 10, 11]. Later on, Moret-Bailly set up a more general spherical-top version [12, 13] that was further refined by Champion [14, 15] and other authors in Russia and France [16, 17, 18, 19, 20]; this makes intensive use of tensorial formalism [15, 21, 22]. In 1998, Mourbat and Loëte gave analytical expressions of some tensorial effective Hamiltonian parameters for tetrahedral XY_4 molecules as a function of molecular constants (inertia, Coriolis and potential energy constants). A similar tensorial development approach has also been set up for the development of the dipole moment operator, which is essential for the calculation of absorption line intensities [23, 24, 25].

In fact, it appears that the tensorial approach is not necessarily restricted to spherical-top molecules. Sartakov *et al.* made use of this technique for the ethylene molecule with D_{2h} symmetry [26]. Our group in Dijon has set up a number of tensorial approaches for species with C_{4v} [27, 28, 29], C_{2v} [30, 31] and C_{3v} [32, 33, 34] symmetry. It should be also recalled that the famous molecular spectrum calculation and fit programs SPCAT/SPFIT by Pickett also rely on a tensorial development [35].

All these expansions are nowadays implemented in various programs that perform numerical calculations of Hamiltonian matrix elements. In this context, however, it is also very useful to be able to express these general developments in a formal algebraic way. This is for instance the basis of the so-called semi-classical approach that studies the topology of rotational energy surfaces for a qualitative understanding of spectral structures like clustering of energy levels [36, 37, 38, 39, 40, 41, 42, 43, 44]. This requires a literal expression of rotational operators as a function of elementary angular momentum components (J_x, J_y, J_z). Algebraic expressions are also of great importance to perform analytical contact transformations for perturbational treatments [19, 20] and, finally, for term-to-term comparisons of effective Hamiltonian parameters expressed using different formalisms [45, 46]

In this paper, we consider this problem for the purely rotational Hamiltonian. We present an algebraic expansion of the tensorial Hamiltonian using the Maxima [47] open-source symbolic calculation software. The method employed here makes use of non-commutative multiplication of operators ; commutation relations of angular momentum operators are used to reorder factors in each term in a standardized form in order to allow easy comparisons with other developments.

The paper is organized as follows. In section 2 we present the expression of tensorial rotational operators. Then, in Section 3, we detail the methods employed for formal calculations. Section 4 outlines how this could be used for semi-classical analyses and Section 5 gives comparisons between tensorial Hamiltonians and the Watsonian.

2. Definition of rotational tensorial operators

Rotational operators in the so-called "Dijon" tensorial formalism are symmetrized polynomials of the elementary rotational angular momentum operators, J_x, J_y and J_z. The construction described below was introduced by Moret-Bailly [48, 49] and further formalized by Zhilinskií [50], based on an original method from Buckmaster *et al.* [51]. Some more details can be found in a book chapter [15]. But all essential definitions are given here.

We start from the rank 1 spherical tensor in the $O(3)$ group:

$$J_{+1}^{(1)} = -\frac{1}{\sqrt{2}}\left(J_x - iJ_y\right), \tag{1}$$

$$J_0^{(1)} = J_z, \tag{2}$$

$$J_{-1}^{(1)} = \frac{1}{\sqrt{2}}\left(J_x + iJ_y\right). \tag{3}$$

We then define:

$$R_m^{1(1)} = 2J_m^{(1)}, \tag{4}$$

where $m = -1, 0$ or $+1$ and the factor 2 allows to match with Buckmaster's definition [51].

Then, a rotational operator of maximum degree Ω, rank K and component m in $O(3)$, with

$$K = \Omega, \Omega - 2, \Omega - 4, \ldots 0 \text{ or } 1 \tag{5}$$

and

$$-K \leq m \leq +K \tag{6}$$

(Ω, K and m being integers) is written as:

$$R_m^{\Omega(K)} = R_0^{\Omega - K(0)} \times R_m^{K(K)}, \tag{7}$$

where

$$R_0^{\Omega-K(0)} = \left(R_0^{2(0)}\right)^{\frac{\Omega-K}{2}} \tag{8}$$

and

$$R_0^{2(0)} = \left(R^{1(1)} \otimes R^{1(1)}\right)_0^{(0)} = -\frac{4}{\sqrt{3}}\left(J_x^2 + J_y^2 + J_z^2\right) = -\frac{4}{\sqrt{3}}\mathbf{J}^2. \tag{9}$$

Here, $\mathbf{J}$ represents the angular momentum vector with components (J_x, J_y, J_z). $R_m^{K(K)}$ is defined recursively as:

$$R_m^{K(K)} = \left(R^{K-1(K-1)} \otimes R^{1(1)}\right)_m^{(K)}. \tag{10}$$

In previous equations, the tensor product $\otimes$ of two operators is obtained through:

$$\left(R^{\Omega_1(K_1)} \otimes R^{\Omega_2(K_2)}\right)_m^{(K)} = \sqrt{2K+1} \sum_{m_1,m_2} (-1)^{K_1+K_2-m} \begin{pmatrix} K_1 & K_2 & K \\ m_1 & m_2 & -m \end{pmatrix} R_{m_1}^{\Omega_1(K_1)} R_{m_2}^{\Omega_2(K_2)}. \tag{11}$$

In this formula,

$$\begin{pmatrix} K_1 & K_2 & K \\ m_1 & m_2 & -m \end{pmatrix}$$

is a $3j-m$ symbol of Wigner [52, 53]. Non-zero symbols obey the two following rules:

$$|K_1 - K_2| \leq K \leq K_1 + K_2, \tag{12}$$

$$m_1 + m_2 - m = 0. \tag{13}$$

An essential point is that the J_x, J_y and J_z operators do not commute with each other, so that the order of terms is important. As usual, we have (in atomic units, so that $\hbar = 1$),

$$[J_\alpha, J_\beta] = i\epsilon_{\alpha\beta\gamma} J_\gamma, \tag{14}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita permutation symbol over coordinates (α, β, γ), those ones being any permutation of (x, y, z).

These rotational operators can then be symmetrized into the molecular point group of the molecule at equilibrium, which is a subgroup of $O(3)$. In the case of spherical-top molecules that have been considered at high-resolution up to now, this is either T_d (for molecules like CH_4, SiH_4, GeH_4, ...) or O_h (for molecules like SF_6, UF_6, ...). This symmetrization is realized thanks to:

$$R_\sigma^{\Omega(K,nC)} = \sum_m {}^{(K)}G_{nC\sigma}^m R_m^{\Omega(K)}. \tag{15}$$

In this expression, C is an irreducible representation of T_d or O_h, σ is one of its components and n is a multiplicity index. The coefficients of matrix ${}^{(K)}G_{nC\sigma}^m$ that performs this transformation are determined through the method explained in Refs. [54, 55]. As we show below (see Section 5), such a symmetrization can also be performed in other point groups or pushed further in T_d or O_h subgroups (like C_{2v}, C_{4v}, ...) for less-symmetrical molecular species. But let us first concentrate on spherical-top molecules.

3. Formal calculations

In order to express tensorial rotational operators as functions of J_x, J_y and J_z we use the Maxima formal calculation software [47]. Its Web site contains the full documentation. We outline here some specific elements used for the present calculations.

Wigner's symbols can be calculated by loading the built-in "Clebsch-Gordan" library through the command

```
load("clebsch_gordan");
```

Then, one can use functions like

```
wigner_3j(K1,K2,K,m1,m2,-m);
```

to calculate the necessary $3j-m$ symbols

$$\begin{pmatrix} K_1 & K_2 & K \\ m_1 & m_2 & -m \end{pmatrix}.$$

In Maxima, the asterisk (`*`) is used for normal multiplication, while the dot (`.`) is used for non-commutative multiplication, which is convenient (and mandatory) for operator calculations. For instance, we can use:

```
(Jx+%i*Jy).(Jx-%i*Jy);
```

where `%i` is the imaginary unit. In the same way,,the caret (`^`) is used for the standard exponent, while the double caret (`^^`) is used for the non-commutative exponent. For instance we can use:

```
(Jx+%i*Jy)^^2;
```

We have built a Maxima program applying the operator construction rules presented in the previous Section. The source is given as supplementary material to this paper, as explained in the Appendix. We now give some results as examples. The outputs presented in the following are formatted in LaTeX using the `tex()` command in Maxima, without any further change.

3.1. Expression of $R_m^{K(K)}$ operators

The program expands all operators in terms of J_x, J_y and J_z polynomials, firstly in their $O(3)$ form. For instance, the operator $R_0^{3(3)}$ is:

$$\begin{aligned} R_0^{3(3)} &= -\frac{2^{\frac{5}{2}}\, {J_z}\cdot {J_y}^2}{\sqrt{5}} - \frac{2^{\frac{5}{2}}\, {J_z}\cdot {J_x}^2}{\sqrt{5}} + \frac{2^{\frac{7}{2}}\, {J_z}^3}{\sqrt{5}} - \frac{8\sqrt{3}\, {J_y}^2\cdot {J_z}}{\sqrt{5}\sqrt{6}} \\ &\quad - \frac{2^{\frac{5}{2}}\, {J_y}\cdot {J_z}\cdot {J_y}}{\sqrt{5}} - \frac{8\sqrt{3}\, {J_x}^2\cdot {J_z}}{\sqrt{5}\sqrt{6}} - \frac{2^{\frac{5}{2}}\, {J_x}\cdot {J_z}\cdot {J_x}}{\sqrt{5}}. \end{aligned} \tag{16}$$

All $R_m^{K(K)}$ operators are obtained through the recursive rule (10).

3.2. Expression of $R_m^{\Omega(K)}$ operators

Then, rule (7) leads to the expansion of any operator $R_m^{\Omega(K)}$ with $\Omega > K$. For example:

$$\begin{aligned} R_0^{5(3)} = \quad & \frac{2^{\frac{9}{2}}\, {J_z}^3\cdot {J_y}^2}{\sqrt{3}\sqrt{5}} + \frac{2^{\frac{9}{2}}\, {J_z}^3\cdot {J_x}^2}{\sqrt{3}\sqrt{5}} + \frac{32\, {J_z}^2\cdot {J_y}^2\cdot {J_z}}{\sqrt{5}\sqrt{6}} + \frac{2^{\frac{9}{2}}\, {J_z}^2\cdot {J_y}\cdot {J_z}\cdot {J_y}}{\sqrt{3}\sqrt{5}} \\ & + \frac{32\, {J_z}^2\cdot {J_x}^2\cdot {J_z}}{\sqrt{5}\sqrt{6}} + \frac{2^{\frac{9}{2}}\, {J_z}^2\cdot {J_x}\cdot {J_z}\cdot {J_x}}{\sqrt{3}\sqrt{5}} - \frac{2^{\frac{11}{2}}\, {J_z}^5}{\sqrt{3}\sqrt{5}} + \frac{32\, {J_y}^4\cdot {J_z}}{\sqrt{5}\sqrt{6}} \end{aligned}$$

$$
\begin{aligned}
&+\frac{2^{\frac{9}{2}}\,{J_y}^3\cdot J_z\cdot J_y}{\sqrt{3}\,\sqrt{5}}-\frac{2^{\frac{11}{2}}\,{J_y}^2\cdot {J_z}^3}{\sqrt{3}\,\sqrt{5}}+\frac{2^{\frac{9}{2}}\,{J_y}^2\cdot J_z\cdot {J_y}^2}{\sqrt{3}\,\sqrt{5}}+\frac{2^{\frac{9}{2}}\,{J_y}^2\cdot J_z\cdot {J_x}^2}{\sqrt{3}\,\sqrt{5}}\\
&+\frac{32\,{J_y}^2\cdot {J_x}^2\cdot J_z}{\sqrt{5}\,\sqrt{6}}+\frac{2^{\frac{9}{2}}\,{J_y}^2\cdot J_x\cdot J_z\cdot J_x}{\sqrt{3}\,\sqrt{5}}+\frac{32\,{J_x}^4\cdot J_z}{\sqrt{5}\,\sqrt{6}}+\frac{2^{\frac{9}{2}}\,{J_x}^3\cdot J_z\cdot J_x}{\sqrt{3}\,\sqrt{5}}\\
&-\frac{2^{\frac{11}{2}}\,{J_x}^2\cdot {J_z}^3}{\sqrt{3}\,\sqrt{5}}+\frac{2^{\frac{9}{2}}\,{J_x}^2\cdot J_z\cdot {J_y}^2}{\sqrt{3}\,\sqrt{5}}+\frac{2^{\frac{9}{2}}\,{J_x}^2\cdot J_z\cdot {J_x}^2}{\sqrt{3}\,\sqrt{5}}+\frac{32\,{J_x}^2\cdot {J_y}^2\cdot J_z}{\sqrt{5}\,\sqrt{6}}\\
&+\frac{2^{\frac{9}{2}}\,{J_x}^2\cdot J_y\cdot J_z\cdot J_y}{\sqrt{3}\,\sqrt{5}}.
\end{aligned}
\tag{17}
$$

3.3. Expression of ${}^{(K)}G^m_{nC\sigma}$ coefficients

The T_d symmetrization matrix ${}^{(K)}G^m_{nC\sigma}$ calculation has not yet been implemented in the Maxima program. At present, since we use it for a few low K values only, we enter the values by hand. At a later stage, a program implementing the algorithm defined in Ref. [55] should be implemented.

3.4. Expression of $R_\sigma^{K(K,nC)}$ operators

To illustrate the use of the ${}^{(K)}G^m_{nC\sigma}$ coefficients, here is the example of the $R^{4(4,A_1)}$ operator [55]:

$$
R^{4(4,A_1)}=\sqrt{\frac{5}{24}}\left(R_4^{4(4)}+R_{-4}^{4(4)}\right)+\sqrt{\frac{7}{12}}R_0^{4(4)}. \tag{18}
$$

This one is the first non-scalar purely rotational operator for a tetrahedral molecule, *i.e.* the first one that is not a simple combination of $\mathbf{J}^2$ powers (we recall that the Hamiltonian operators for a molecule of a given point group symmetry must transform according to the totally symmetric irreducible representation of this point group; this is A_1 in the case of T_d).

The expansion of this important operator $R^{4(4,A_1)}$ is:

$$
\begin{aligned}
R^{4(4,A_1)} \;=\; &-\frac{16\sqrt{7}\,\left(J_z\cdot J_y\right)^2}{\sqrt{14}\,\sqrt{15}}-\frac{16\sqrt{7}\,\left(J_z\cdot J_x\right)^2}{\sqrt{14}\,\sqrt{15}}-\frac{16\sqrt{7}\,{J_z}^2\cdot {J_y}^2}{\sqrt{3}\,\sqrt{5}\,\sqrt{14}}-\frac{16\sqrt{7}\,{J_z}^2\cdot {J_x}^2}{\sqrt{3}\,\sqrt{5}\,\sqrt{14}}\\
&-\frac{2^{\frac{7}{2}}\,J_z\cdot {J_y}^2\cdot J_z}{\sqrt{3}\,\sqrt{5}}-\frac{2^{\frac{7}{2}}\,J_z\cdot {J_x}^2\cdot J_z}{\sqrt{3}\,\sqrt{5}}+\frac{2^{\frac{9}{2}}\,{J_z}^4}{\sqrt{3}\,\sqrt{5}}-\frac{2^{\frac{7}{2}}\,\left(J_y\cdot J_z\right)^2}{\sqrt{3}\,\sqrt{5}}\\
&+\frac{4\sqrt{7}\,\left(J_y\cdot J_x\right)^2}{\sqrt{14}\,\sqrt{15}}-\frac{4\sqrt{5}\,\left(J_y\cdot J_x\right)^2}{\sqrt{6}}-\frac{16\,{J_y}^2\cdot {J_z}^2}{\sqrt{5}\,\sqrt{6}}-\frac{4\sqrt{7}\,{J_y}^2\cdot {J_x}^2}{\sqrt{14}\,\sqrt{15}}\\
&+\frac{2^{\frac{7}{2}}\sqrt{7}\,{J_y}^2\cdot {J_x}^2}{\sqrt{5}\,\sqrt{6}\,\sqrt{14}}-\frac{4\sqrt{5}\,{J_y}^2\cdot {J_x}^2}{\sqrt{6}}-\frac{16\sqrt{7}\,J_y\cdot {J_z}^2\cdot J_y}{\sqrt{14}\,\sqrt{15}}+\frac{4\sqrt{7}\,J_y\cdot {J_x}^2\cdot J_y}{\sqrt{14}\,\sqrt{15}}\\
&-\frac{4\sqrt{5}\,J_y\cdot {J_x}^2\cdot J_y}{\sqrt{6}}+\frac{4\sqrt{7}\,{J_y}^4}{\sqrt{14}\,\sqrt{15}}+\frac{2^{\frac{7}{2}}\sqrt{7}\,{J_y}^4}{\sqrt{5}\,\sqrt{6}\,\sqrt{14}}+\frac{4\sqrt{5}\,{J_y}^4}{\sqrt{6}}\\
&-\frac{2^{\frac{7}{2}}\,\left(J_x\cdot J_z\right)^2}{\sqrt{3}\,\sqrt{5}}+\frac{4\sqrt{7}\,\left(J_x\cdot J_y\right)^2}{\sqrt{14}\,\sqrt{15}}-\frac{4\sqrt{5}\,\left(J_x\cdot J_y\right)^2}{\sqrt{6}}-\frac{16\,{J_x}^2\cdot {J_z}^2}{\sqrt{5}\,\sqrt{6}}\\
&-\frac{4\sqrt{7}\,{J_x}^2\cdot {J_y}^2}{\sqrt{14}\,\sqrt{15}}+\frac{2^{\frac{7}{2}}\sqrt{7}\,{J_x}^2\cdot {J_y}^2}{\sqrt{5}\,\sqrt{6}\,\sqrt{14}}-\frac{4\sqrt{5}\,{J_x}^2\cdot {J_y}^2}{\sqrt{6}}-\frac{16\sqrt{7}\,J_x\cdot {J_z}^2\cdot J_x}{\sqrt{14}\,\sqrt{15}}
\end{aligned}
$$

$$+\frac{4\sqrt{7}\,J_x\cdot {J_y}^2\cdot J_x}{\sqrt{14}\sqrt{15}}-\frac{4\sqrt{5}\,J_x\cdot {J_y}^2\cdot J_x}{\sqrt{6}}+\frac{4\sqrt{7}\,{J_x}^4}{\sqrt{14}\sqrt{15}}+\frac{2^{\frac{7}{2}}\sqrt{7}\,{J_x}^4}{\sqrt{5}\sqrt{6}\sqrt{14}}$$
$$+\frac{4\sqrt{5}\,{J_x}^4}{\sqrt{6}}. \tag{19}$$

4. Semi-classical analysis

The full expansion of rotational operators is very convenient to perform semi-classical analyses as proposed by Harter and co-workers, see for instance [56] and references therein, as well as the references cited in the Introduction of the present paper. In short, it consists in considering the J_x, J_y and J_z operators as classical continuous variables. If we then express them in spherical coordinates, the Hamiltonian for a given J value of the rotational quantum number spans a rotational energy surface, whose topology gives some information about the molecular behavior.

Figure 1 shows a formal example of the rotational energy surface $E(J_x, J_y, J_z) = E(J, \theta, \phi)$ for a tetrahedral molecule at some high value of the rotational quantum number J (θ and ϕ being the usual spherical coordinates angles).

[Figure 1 about here.]

The energy on extremal points (maxima, minima, saddle points, lying on symmetry axes) of the rotational energy surface, plotted as a function of the J rotational quantum number, follow the quantum energies obtained through the diagonalization of the quantum Hamiltonian, as illustrated on Figure 2.

[Figure 2 about here.]

Graphics in this section were obtained using the `draw` package in Maxima. See the source code given as supplementary material to this paper, as explained in the Appendix.

The two examples above use fictive effective rotational Hamiltonian values, for illustration purpose only. Real examples of such semiclassical analyses can be found in previous papers for GeF_4 [57], P_4 [44], $Mo(CO)_6$ [58], or CF_4 [59]. It should be noticed that these papers present such semiclassical curves and surfaces for excited vibrational states. The expansion of vibrational operators is not yet implemented in the present approach which thus does not allow this directly at present; but it is our next development goal, as we explain it in the Conclusion of this paper below.

5. Rotational Hamiltonian comparisons

The above-described R operators can also be used to construct effective rotational Hamiltonians for lower-symmetry molecules like symmetric- or asymmetric-tops. It is then possible to compare the result with Watson's Hamiltonian (see for instance Ref. [7]) and to express the relations between the parameters in both formalisms.

We can use this for:

- The "distorted" T_d tensorial formalism that we use for asymmetric C_{2v}-top molecules [30, 31] like SO_2F_2 [60, 45].
- The symmetric C_{3v}-top tensorial formalism [32, 33, 34] we use for molecules like CH_3D, CH_3I [46], trioxane [61], ...

The problem here is that although the Hamiltonian expressed in our formalism and Watson's expression should be fully equivalent (same number of operators), their expressions in terms of J_x, J_y and J_z operators are different. Thus, a one-to-one comparison needs to write both on the same standard form, that is all factors in each term should be reordered like:

$$J_x^m J_y^n J_z^p,$$

(with m, n and p integers). This is performed using commutators as defined in Eq. (14).

5.1. Implementation of factor reordering in Maxima

The Maxima operator package described above is written in the Maxima language. Although the package was primarily created to solve the computational problems in this paper, it is adaptable to a variety of symbolic operator computations. Users can define their own operators and extend Maxima's general simplifier with rules for simplifying compositions of operators. The simplification rules, for example, replace pq by $qp - i\hbar$ or J_yJ_x by $J_xJ_y - i\hbar J_z$ are handled by writing procedural Maxima code, not by using pattern matching.

The operator package has utilities for applying operators to functions and for converting from a Maxima dot (`.`) form (for example, $q.p.\Psi$) to a functional form (for example, $q(p(\Psi))$). Users can attach a formula to an operator (for example, attach $-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$ to the momentum operator). A utility in the operator package dispatches the operator formulae and is based on this conversion technique.

The source code of this utility named "`angular`" and that performs reordering of factors in the form $J_x^m J_y^n J_z^p$ is given as supplementary material to this paper, as explained in the Appendix.

5.2. Example for an asymmetric-top molecule

As a first example, let us consider the SO_2F_2 case from Ref. [45] that uses an $O(3) \supset T_d \supset C_{2v}$ symmetrization, this amounts to compare:

$$\begin{aligned} H^{C_{2v}}_{\text{tensorial}} \;=\; & -t_1\frac{\sqrt{3}}{4}R^{2(0,A_1)} + t_2R_1^{2(2,E)} + t_3R_z^{2(2,F_2)} + t_4\frac{3}{16}R^{4(0,A_1)} \\ & + t_5R_1^{4(2,E)} + t_6R_z^{4(2,F_2)} + t_7R^{4(4,A_1)} + t_8R_1^{4(4,E)} \\ & + t_9R_z^{4(4,F_2)} - t_{10}\frac{3\sqrt{3}}{64}R^{6(0,A_1)} + t_{11}R_1^{6(2,E)} + t_{12}R_z^{6(2,F_2)} \\ & + t_{13}R^{6(4,A_1)} + t_{14}R_1^{6(4,E)} + t_{15}R_z^{6(4,F_2)} + t_{16}R^{6(6,A_1)} \\ & + t_{17}R_1^{6(6,E)} + t_{18}R_z^{6(6,0F_2)} + t_{19}R_z^{6(6,1F_2)}, \end{aligned} \tag{20}$$

(where the factors multiplying t_1, t_4 and t_{10} are used to match with the standard terms in $\mathbf{J}^2$, $\mathbf{J}^3$, $\mathbf{J}^6$, ..., see Refs. [15, 62, 21]) with the non-reduced Watsonian (see Eq. (17.3.1) of Ref. [7]):

$$\begin{aligned} H_{\text{Watson}}^{C_{2v}} &= B_{200}\mathbf{J}^2 + B_{020}J_Z^2 + T_{400}(\mathbf{J}^2)^2 + T_{220}\mathbf{J}^2J_Z^2 + T_{040}J_Z^4 \\ &+\Phi_{600}(\mathbf{J}^2)^3 + \Phi_{420}(\mathbf{J}^2)^2J_Z^2 + \Phi_{240}\mathbf{J}^2J_Z^4 + \Phi_{060}J_Z^2 \\ &+\frac{1}{2}[B_{002} + T_{202}\mathbf{J}^2 + T_{022}J_Z^2 + \Phi_{402}(\mathbf{J}^2)^2 + \Phi_{222}\mathbf{J}^2J_Z^2 \\ &+\Phi_{042}J_Z^4, J_+^2 + J_-^2]_+ \\ &+\frac{1}{2}[T_{004} + \Phi_{204}\mathbf{J}^2 + \Phi_{024}J_Z^2, J_+^4 + J_-^4]_+ \\ &+\Phi_{006}(J_+^6 + J_-^6), \end{aligned} \tag{21}$$

where $[A, B]_+ = AB + BA$ denotes the anticommutator and the ladder operators are defined as:

$$J_\pm = J_X \pm iJ_Y. \tag{22}$$

In this case, as explained by Eq. (14) in Ref. [45], it is necessary to perform a rotation between the T_d frame (x, y, z) used for tetrahedral molecules and the C_{2v} asymmetric-top frame (X, Y, Z) used for the Watsonian.

Once everything is expanded and all terms reordered as explained above, it is easy to express the constants in one formalism as a function of those in the other one by simply identifying the coefficients of identical $J_x^m J_y^n J_z^p$ terms in both Hamiltonians and then solve the resulting linear equation system.

As an example, the comparison of (20) and (21) leads to:

$$t_1 = \frac{C}{3} + \frac{B}{3} + \frac{A}{3} + \frac{\Phi_{060}}{21} - \frac{T_{040}}{15}$$

$$t_2 = -\frac{C}{4\sqrt{6}} - \frac{B}{4\sqrt{6}} + \frac{A}{2\sqrt{6}} + \frac{\Phi_{060}}{2\sqrt{6}} - \frac{5\,T_{040}}{14\sqrt{6}}$$

$$t_3 = -\frac{C}{2^{\frac{5}{2}}} + \frac{B}{2^{\frac{5}{2}}} - \frac{3\,\Phi_{042}}{7\sqrt{2}} + \frac{5\,T_{022}}{7\sqrt{2}}$$

$$t_4 = T_{400} - \frac{\Phi_{240}}{15} + \frac{T_{220}}{3} - \frac{\Phi_{060}}{7} + \frac{T_{040}}{5}$$

$$t_5 = \frac{5\,\Phi_{240}}{7\,2^{\frac{7}{2}}} - \frac{T_{220}}{2^{\frac{7}{2}}} + \frac{5\,\Phi_{060}}{7\,2^{\frac{5}{2}}} - \frac{3\,T_{040}}{7\,2^{\frac{5}{2}}}$$

$$t_6 = -\frac{5\sqrt{3}\,\Phi_{222}}{7\,2^{\frac{5}{2}}} - \frac{\sqrt{3}\,T_{202}}{2^{\frac{5}{2}}} - \frac{13\,\Phi_{042}}{28\sqrt{6}} - \frac{\sqrt{3}\,T_{022}}{7\,2^{\frac{5}{2}}}$$

$$t_7 = -\frac{7\sqrt{5}\,\Phi_{060}}{88\sqrt{6}} + \frac{T_{040}}{8\sqrt{30}} - \frac{19\sqrt{5}\,\Phi_{024}}{11\sqrt{6}} - \frac{\sqrt{5}\,T_{004}}{4\sqrt{6}}$$

$$t_8 = \frac{5\sqrt{7}\,\Phi_{060}}{88\sqrt{6}} - \frac{T_{040}}{8\sqrt{42}} - \frac{19\sqrt{7}\,\Phi_{024}}{11\sqrt{6}} - \frac{\sqrt{7}\,T_{004}}{4\sqrt{6}}$$

$$t_9 = \frac{41\,\Phi_{042}}{44\,\sqrt{14}} + \frac{T_{022}}{4\,\sqrt{14}}$$

$$t_{10} = \Phi_{600} + \frac{\Phi_{420}}{3} + \frac{\Phi_{240}}{5} + \frac{\Phi_{060}}{7}$$

$$t_{11} = \frac{\sqrt{3}\,\Phi_{420}}{2^{\frac{11}{2}}} + \frac{3^{\frac{3}{2}}\,\Phi_{240}}{7\,2^{\frac{9}{2}}} + \frac{5\,\sqrt{3}\,\Phi_{060}}{7\,2^{\frac{11}{2}}}$$

$$t_{12} = \frac{3\,\Phi_{402}}{2^{\frac{9}{2}}} + \frac{3\,\Phi_{222}}{7\,2^{\frac{9}{2}}} + \frac{\Phi_{042}}{7\,2^{\frac{9}{2}}}$$

$$t_{13} = -\frac{\Phi_{240}}{32\,\sqrt{10}} + \frac{\sqrt{5}\,\Phi_{204}}{2^{\frac{9}{2}}} - \frac{3\,\sqrt{5}\,\Phi_{060}}{11\,2^{\frac{11}{2}}} + \frac{\sqrt{5}\,\Phi_{024}}{11\,2^{\frac{7}{2}}}$$

$$t_{14} = \frac{\Phi_{240}}{32\,\sqrt{14}} + \frac{\sqrt{7}\,\Phi_{204}}{2^{\frac{9}{2}}} + \frac{15\,\Phi_{060}}{352\,\sqrt{14}} + \frac{\sqrt{7}\,\Phi_{024}}{11\,2^{\frac{7}{2}}}$$

$$t_{15} = -\frac{\sqrt{3}\,\Phi_{222}}{16\,\sqrt{14}} - \frac{3^{\frac{3}{2}}\,\Phi_{042}}{88\,\sqrt{14}}$$

$$t_{16} = -\frac{\Phi_{060}}{32\,\sqrt{462}} - \frac{\sqrt{7}\,\Phi_{024}}{8\,\sqrt{66}}$$

$$t_{17} = \frac{\Phi_{060}}{32\,\sqrt{66}} - \frac{\Phi_{024}}{8\,\sqrt{66}}$$

$$t_{18} = \frac{\sqrt{79\,\sqrt{421}+1684}\,\left(\sqrt{421}\,\Phi_{042} + \left(79\,\sqrt{421}-1684\right)\,\Phi_{006}\right)}{20208\,\sqrt{5}\,\sqrt{11}}$$

$$t_{19} = -\frac{\sqrt{79\,\sqrt{421}+1684}\,\left(\left(79\,\sqrt{421}-1684\right)\,\Phi_{042} - 495\,\sqrt{421}\,\Phi_{006}\right)}{3334320}$$

These relations can easily be inverted.

5.3. Example for a symmetric-top molecule

Our recent work on the trioxane molecule [61] with C_{3v} point group symmetry led us to perform a comparison between our C_{3v} tensorial formalism with the usual Watsonian expansion of the rotational Hamiltonian up to octic terms [5, 7, 63]. Thus, in this case, we compare the "Dijon" C_{3v} tensorial formalism in the $O(3) \supset C_{\infty v} \supset C_{3v}$ group chain [32, 33, 34]:

$$\begin{aligned} H^{C_{3v}}_{\text{tensorial}} &= -t_1\frac{\sqrt{3}}{4}R^{2(0,\Sigma^+A_1)} + t_2R^{2(2,\Sigma^+A_1)} + t_3\frac{3}{16}R^{4(0,\Sigma^+A_1)} + t_4R^{4(2,\Sigma^+A_1)} \\ &+t_5R^{4(4,\Sigma^+A_1)} + t_6R^{4(4,\Phi A_1)} - t_7\frac{3\sqrt{3}}{64}R^{6(0,\Sigma^+A_1)} + t_8R^{6(2,\Sigma^+A_1)} \\ &+t_9R^{6(4,\Sigma^+A_1)} + t_{10}R^{6(4,\Phi A_1)} + t_{11}R^{6(6,\Sigma^+A_1)} + t_{12}R^{6(6,\Phi A_1)} \\ &+t_{13}R^{6(6,IA_1)} - t_{14}\frac{9}{256}R^{8(0,\Sigma^+A_1)} + t_{15}R^{8(2,\Sigma^+A_1)} + t_{16}R^{8(4,\Sigma^+A_1)} \\ &+t_{17}R^{8(6,\Sigma^+A_1)} + t_{18}R^{8(8,\Sigma^+A_1)}, \end{aligned} \tag{23}$$

with the Watsonian [5, 7, 63]:

$$
\begin{aligned}
H^{C_{3v}}_{\text{Watson}} \;=\; & \\
& B\mathbf{J}^2-(B-C)J_z^2-D(\mathbf{J}^2)^2-D_{JK}\mathbf{J}^2J_z^2-D_kJ_z^4 \\
& \varepsilon\left[J_z,J_+^3+J_-^3\right]_+ +\varepsilon_J\mathbf{J}^2\left[J_z,J_+^3+J_-^3\right]_+ +\varepsilon_K\left[J_z^3,J_+^3+J_-^3\right]_+ \\
& +H_J(\mathbf{J}^2)^3+H_{JK}(\mathbf{J}^2)^2J_z^2+H_{KJ}\mathbf{J}^2J_z^4+H_KJ_z^6+h_3'(J_+^6+J_-^6) \\
& +L_{JJJJ}(\mathbf{J}^2)^4+L_{JJJK}(\mathbf{J}^2)^3J_z^2+L_{JJKK}(\mathbf{J}^2)^2J_z^4 \\
& +L_{JKKK}\mathbf{J}^2J_z^6+L_{KKKK}J_z^8, \qquad (24)
\end{aligned}
$$

In both cases, only scalar octic terms (*i.e.* powers of $\mathbf{J}^2$ and J_z only) have been considered, just as in Ref. [63]. At this point, we should notice an error in Eq. (18.2.4a) in the book of Papoušek and Aliev concerning the operator associated to ε_k. The anticommutator should be written as above, including J_z^3, otherwise this term does not get the correct symmetrization; this error was not present in Aliev and Watson's original paper [5].

As before, the comparisons leads to identify terms and to solve linear equations of parameters in both formalisms to get:

$$t_1=-\frac{L_{KKKK}}{15}+\frac{H_K}{21}+\frac{D_K}{15}+\frac{2\,B}{3}+\frac{A}{3}$$

$$t_2=-\frac{25\,L_{KKKK}}{22\sqrt{6}}+\frac{H_K}{2\sqrt{6}}+\frac{5\,D_K}{14\sqrt{6}}-\frac{B}{2\sqrt{6}}+\frac{A}{2\sqrt{6}}$$

$$t_3=\frac{L_{KKKK}}{5}-\frac{H_{KJ}}{15}-\frac{H_K}{7}-\frac{D_K}{5}+\frac{L_{JKKK}}{21}-\frac{D_{JK}}{3}-D_J$$

$$t_4=-\frac{19\,L_{KKKK}}{11\,2^{\frac{5}{2}}}+\frac{5\,H_{KJ}}{7\,2^{\frac{7}{2}}}+\frac{5\,H_K}{7\,2^{\frac{5}{2}}}+\frac{3\,D_K}{7\,2^{\frac{5}{2}}}-\frac{L_{JKKK}}{2^{\frac{7}{2}}}+\frac{D_{JK}}{2^{\frac{7}{2}}}$$

$$t_5=\frac{249\sqrt{7}\,L_{KKKK}}{572\sqrt{10}}-\frac{\sqrt{35}\,H_K}{11\,2^{\frac{5}{2}}}-\frac{D_K}{4\sqrt{70}}$$

$$t_6=-\frac{\varepsilon}{4}-\frac{19\,\varepsilon_K}{88}$$

$$t_7=-\frac{2\,L_{KKKK}}{9}+\frac{H_{KJ}}{5}+\frac{H_K}{7}-\frac{L_{JKKK}}{7}+\frac{H_{JK}}{3}-\frac{L_{JJKK}}{15}+H_J$$

$$t_8=-\frac{35\,L_{KKKK}}{176\sqrt{6}}+\frac{3^{\frac{3}{2}}\,H_{KJ}}{7\,2^{\frac{9}{2}}}+\frac{5\sqrt{3}\,H_K}{7\,2^{\frac{11}{2}}}-\frac{5\sqrt{3}\,L_{JKKK}}{7\,2^{\frac{9}{2}}}+\frac{\sqrt{3}\,H_{JK}}{2^{\frac{11}{2}}}-\frac{5\sqrt{3}\,L_{JJKK}}{7\,2^{\frac{11}{2}}}$$

$$t_9=\frac{15\sqrt{105}\,L_{KKKK}}{143\,2^{\frac{7}{2}}}-\frac{\sqrt{3}\,H_{KJ}}{16\sqrt{70}}-\frac{3\sqrt{15}\,H_K}{176\sqrt{14}}+\frac{\sqrt{105}\,L_{JKKK}}{11\,2^{\frac{9}{2}}}$$

$$t_{10}=\frac{3^{\frac{3}{2}}\,\varepsilon_K}{176}+\frac{\sqrt{3}\,\varepsilon_J}{16}$$

$$t_{11}=\frac{H_K}{16\sqrt{231}}-\frac{\sqrt{21}\,L_{KKKK}}{40\sqrt{11}}$$

$$t_{12} = -\frac{\varepsilon_K}{4\sqrt{110}}$$

$$t_{13} = \frac{h'_3}{2^{\frac{5}{2}}}$$

$$t_{14} = \frac{L_{KKKK}}{9} + \frac{L_{JKKK}}{7} + \frac{L_{JJKK}}{5} + \frac{L_{JJJK}}{3} + L_{JJJJ}$$

$$t_{15} = -\frac{5\,L_{KKKK}}{11\,2^{\frac{11}{2}}} - \frac{15\,L_{JKKK}}{7\,2^{\frac{15}{2}}} - \frac{9\,L_{JJKK}}{7\,2^{\frac{13}{2}}} - \frac{3\,L_{JJJK}}{2^{\frac{15}{2}}}$$

$$t_{16} = \frac{9\sqrt{35}\,L_{KKKK}}{143\,2^{\frac{11}{2}}} + \frac{9\sqrt{5}\,L_{JKKK}}{704\sqrt{14}} + \frac{3\,L_{JJKK}}{64\sqrt{70}}$$

$$t_{17} = -\frac{\sqrt{7}\,L_{KKKK}}{240\sqrt{11}} - \frac{L_{JKKK}}{64\sqrt{77}}$$

$$t_{18} = \frac{L_{KKKK}}{48\sqrt{1430}}$$

This corrects and extends the formulas presented previously for the CH_3I molecule [46]. Again, it is easy to invert these relations in order to get Watson's parameters as a function of the tensorial ones. Such a conversion is used in Refs. [46, 61] to compare results of fits using both formalisms.

The program used in this Section is given as supplementary material to this paper, as explained in the Appendix.

6. Conclusion

In this paper, we have presented some algebraic manipulations on the effective rotational Hamiltonian for molecular spectroscopy. Such manipulations allow formal expressions up to any order of the development and are of particular interest for semi-classical approaches and for the comparison of different formalisms. In particular, we have shown how to express tensorial Hamiltonian parameters in terms of Watson's parameters for asymmetric- and symmetric-top molecules. The present work, however, only considered rotational operators in terms of elementary components of the angular momentum. A further step will be to consider the full rovibrational Hamiltonian by formally expressing vibrational operators (and their couplings with rotational operators) in terms of elementary creation (a^+) and annihilation (a) operators. The dipole moment operator will also be considered because of its importance for line intensity calculations. All this will be the subject of a future paper.

Appendix: Code examples for Maxima

This appendix decribes the Maxima [47] source code files that we provide as supplementary material to this paper. In particular, we explain here the operator numbering conventions we use in these codes. All Maxima code files are given in the form of a `.mac` text file (e.g. `OpRot.mac`) and has to be executed in Maxima thanks to the command `batch(".../OpRot");`, where `...` is the path to this file.

The first program is `OpRot.mac` and contains the code to generate operators for spherical-top molecules described in Section 2 using the method given in Section 3. It draws Figures 1 and 2.

Operators are put into an array (or matrix) named `R`. We define this array with maximal possible dimensions:

- First dimension: all possible Ω values up to $\Omega_{\max}$, that is $\Omega_{\max}+1$ (counting $\Omega=0$).
- Second dimension: all possible K values for $\Omega_{\max}$, that is $[\Omega_{\max}/2]+1$ ($[\,]$ being the integer part).
- Third dimension: all possible m values for $K_{\max}=\Omega_{\max}$, that is $2\Omega_{\max}+1$.

Array indexes in Maxima should always be strictly be positive integers. So we map $R_m^{\Omega(K)}$ operators to `R[i,j,k]` array elements such that `i=1` for $\Omega=0$, `j=1` for the minimum K value (0 or 1, depending whether Ω is even or odd) and `k=1` for $m=-K$. Then array indexes are incremented with increasing index values. For instance, $R_0^{2(0)}$ is stored in array element `R[3,1,1]` and $R_1^{4(2)}$ is stored in array element `R[5,2,4]`.

The second example code given here (file `HamRotC3v.mac`) corresponds to Section 5.3 where we compare the tensorial and Watsonian Hamiltonians for C_{3v} symmetric tops. The first program expands both Hamiltonian operators and performs the comparison; it outputs the parameter correspondance formulas. This code relies on a subroutine (file `angular.mac`), that performs the factor reordering in each term, as described in Section 5.1.

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Figures

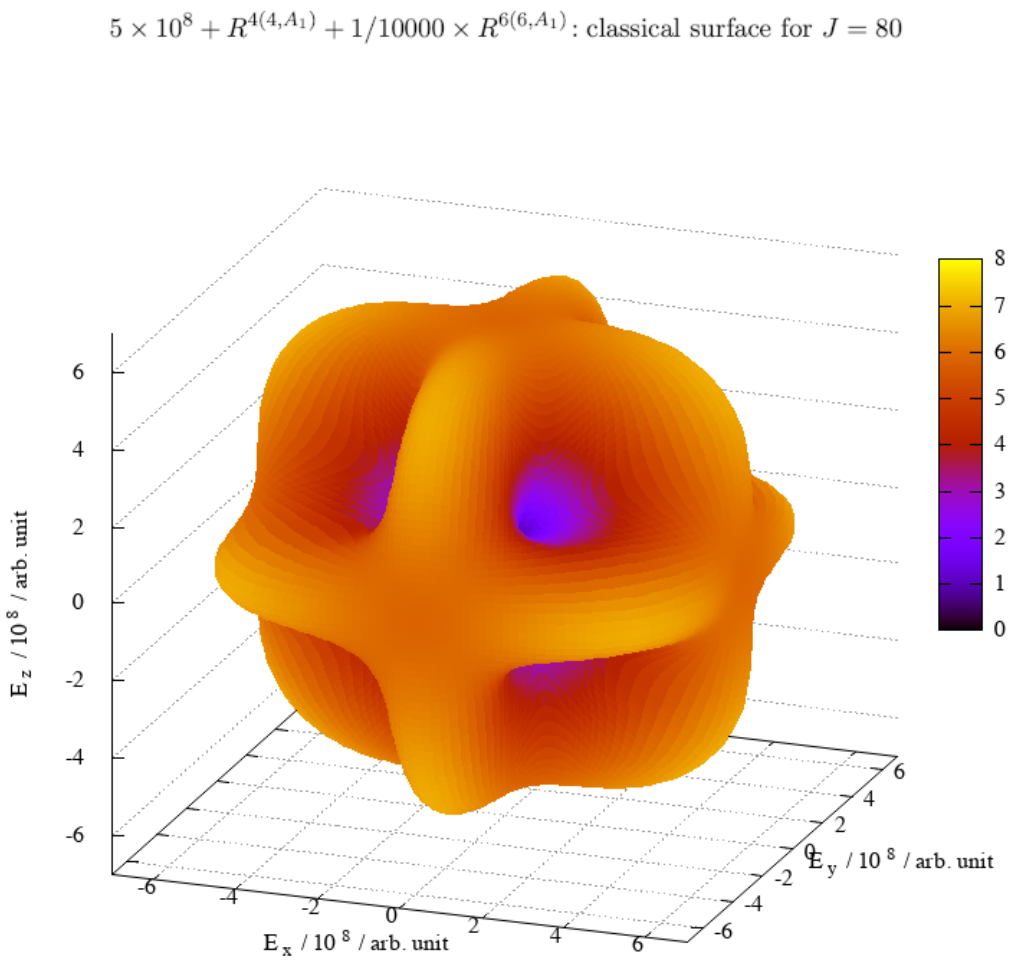

Figure 1: Rotational energy surface for a tetrahedral molecule at $J = 80$. The parameter constants (shown on top) are arbitrary and for illustration purpose only, as a simple example. The value of the rotational energy $E(J, \theta, \phi)$ is plotted for each direction (θ, ϕ) and also coded by the color scale shown on the right, for a better visualization. The three axis labels correspond to the energy value along each of the corresponding x, y or z direction, defined as: $E_x = E(J, \pi/2, 0)$, $E_y = E(J, \pi/2, \pi/2)$, $E_z = E(J, 0, 0)$. The energy unit is arbitrary.

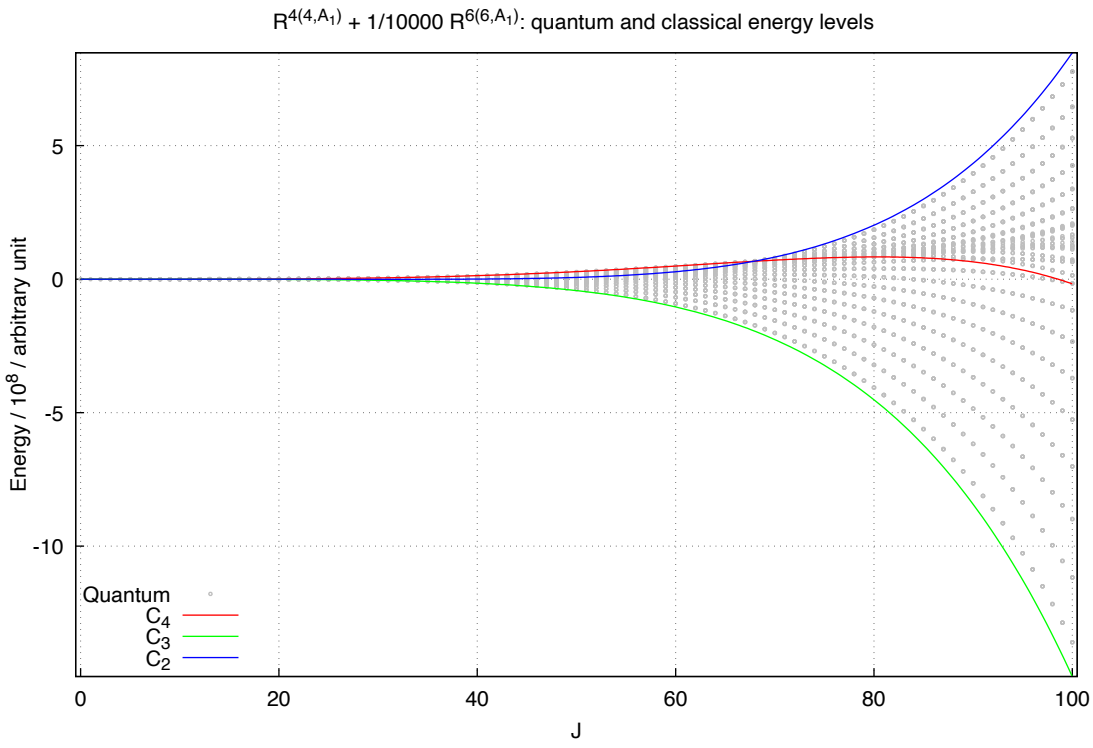

Figure 2: Classical rotational energy curves on symmetry axes compared to quantum eigenvalues for a tetrahedral molecule. As in Figure 1, the constants are arbitrary and for illustration purpose only. See references in the text for concrete real examples.