Rotational thermodynamic parameters for asymmetric-top molecules: classical vs. quantum approaches and new analytical partition function

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ABSTRACT
We investigated classical and quantum rotational partition functions, rotational energies and rotational entropies for asymmetric-top molecules in a canonical system within a wide range of temperatures under the rigid rotor approximation. We then derived the temperature, $T_{\text{limit}}$, below which classical approach is not valid, and the complex quantum approach is strongly recommended. This temperature certainly increases with the inertia moment of the molecule and follows a power function when rotational partition functions are considered. As for linear-, spherical- and symmetric-top molecules, quantum approach is not needed at all for energetic rotational parameters, whatever the temperature for asymmetric-top molecules. Therefore, there is no real frontier between the classical and quantum approaches when energetic rotational parameters are concerned, though the frontier is naturally a bounded decreasing sequence converging to zero when rotational partition functions are rather concerned. Particularly, classical approach fails describing rotational partition functions for light molecules or molecules at low temperatures. Moreover, all the closed-form expressions proposed in the whole literature fail drastically approaching quantum and exact results for light molecules or molecules at low temperatures. In regard to the importance of partition functions in the evaluation of rate constants for chemical reactions and accurate intensities lines in spectroscopy, we proposed new accurate and simple analytic expression of the rotational partition functions of asymmetric-top molecules, valid at all temperatures.

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1. Introduction

Partition function or a sum of states, is useful in spectroscopy and favours accurate equilibrium and rate constants of chemical reactions [1–3]. The total partition function is the product of electronic, translational, vibrational and rotational components. We will focus here on the rotational partition function. In the computational chemist community, the classical partition function is used to derive relative populations of isomers [4–13], solvation free energies of species [14–16] as a function of the temperature, although it fails at low temperatures. So what is the ‘low’ T? In our initiating work [17], we investigated the temperature below which the classical approach is no longer valid for linear-top, spherical-top and symmetric-top molecules. We called this temperature the temperature limit ($T_{\text{limit}}$), the frontier of the classical approach. The main results were,

1. $T_{\text{limit}}$ increases with the inertia moment of the molecule, and when considering the rotational partition function, it follows an exact combination of three decreasing exponential functions for linear- and spherical-top molecules.

2. Contrary to what is well known, no matter what the temperature is, there is no need for a quantum approach for energetic rotational parameters at all. Therefore, when considering the energetic rotational parameters, there is no real boundary between classical and quantum approaches, though the frontier is naturally a bounded decreasing sequence that converges to zero when rotational partition functions are rather concerned.

3. Classical approach fails describing rotational partition functions for light molecules or molecules at low temperatures. Therefore, new simple and precise closed-form was proposed for linear- and spherical-top molecules.

Up to now, no work has pointed out any answer in this direction for asymmetric-top molecules. So, knowledge of $T_{\text{limit}}$ for asymmetric-top molecules would be very informative. Therefore, the present work is an extension of our previous investigation into special cases.

The rotational partition function can be obtained by directly summing thousands of rotational energy levels [18]. Thus, this sum converges slowly, and it is often replaced by a continuum summation that is objectively valid only at high temperatures. This approximation is known as a classical approach, and has been proposed in 1979 by Hynne and Anderson [19] as a good illustration of the canonical formalism in statistical mechanics. Five years later, Desloge [20] proposed a nicer description of this classical approach. This approach leads to a closed-form of a partition function and it is then easily implemented in several codes of quantum chemistry (Gaussian, Quantum Expresso, Turbomole, etc.).

Several closed-forms of the rotational partition function for linear, spherical and symmetric-top have been proposed by several authors [21–31]. For asymmetric-top, the approach is more complex. Indeed, asymmetric-top molecule has three different inertia moment. Therefore, energy levels do not have explicit expression. However, some authors investigated quantum rotational partition function for asymmetric-top molecule. Gordon [32] extended, to asymmetric-top molecules, the asymptotic equation developed by Viney [21] for symmetric-top molecules. He suggested replacing the rotational constant $B$ by $(BC)^{\frac{1}{2}}$. This new asymptotic function is accurate for medium and high temperatures but fail at very low temperatures. For very high temperatures and small rotational constants, it leads to the known classical rotational partition function for asymmetric-top molecules. More generally, Stripp and Kirkwood [33] proposed an asymptotic function by extending the function found in their previous work. They calculated the first two terms of the asymptotic expansion of the partition function in power of Plank’s constant. The reliability of this function is confirmed through the Viney [21] function obtained when two of the inertia moments are equal. This is valid at medium and high temperatures. Elsewhere, Kaplan [34] derived closed-form of the rotational partition function of asymmetric-top molecules by introducing the elliptical coordinates. However, Watson [35] showed that, in Kaplan’s asymptotic function, the second terms exert sign problem through Equations (18) and (19). Watson developed two new methods for obtaining asymptotic asymmetric-top rotational partition function. The first method uses the direct summation, and the second one is an extension of Kaplan’s calculation. He calculated the first three terms of the asymptotic expansion of the partition function. The first two terms of the direct method are consistent with Kaplan’s results without the sign problem [34]. More recently, Sharma et al. [36] compared the exact quantum partition function with the classical one for the case of the methanimine CH$_2$NH. They found that, for $T < 120$ K, the classical partition function deviates from the exact quantum values with error less than 1%. For $T > 120$ K, the deviation of the classical values increases in function of the temperature and reach 25% at 400 K. This is surprising, since we expect that at high temperatures the classical values converges to the exact quantum values [17]. This motivates, three years later, Wells and Raston [37] to investigate this limit for the case of the methanimine also. They found that, even for
temperatures going from 50 to 400 K, the deviation of the classical values is still of 1%. Wells and Raston [37] built their work by correcting the Stripp and Kirkwood [33] analytical partition function, adding the quantum and the centrifugal distortion corrections. They apply the new formula to the HDO, CH$_2$NH, CH$_2$CHOH and CHOCH$_2$OH molecules that have been identified in the hot core of Sgr B2. This Stripp and Kirwood corrected form gives good results than the classical values for temperatures limited to 17 K, 4.7 K, 1.4 K and 0.4 K, for HDO, CH$_2$NH, CH$_2$CHOH and CHOCH$_2$OH molecules, respectively. However, this closed-form function fails at very low temperatures to reproduce the exact quantum rotational partition function values.

It is remarkable that all the closed-form expressions suggested for the rotation partition function cannot be adapted at all temperatures, or to all molecules of the considered type. Specifically, all the closed-forms proposed in the entire literature so far fail at ‘low temperature’. Therefore, the expression of a closed-forms that are effective for any molecule at all temperatures is timely. This has been performed recently for linear-top and spherical-top molecules [17]. However, most molecules are asymmetric. We then need to extend our previous work to asymmetrical-top molecules.

We start this project by firstly look for $T_{\text{limit}}$ of a given asymmetric-top molecular system. Elsewhere, although we are aware that molecules cannot rotate without vibrating, in this work, we neglect the vibrations of the molecule during its rotation. We then assume the rigid rotor throughout this work. We also assume that molecules are not interacting each other, although real gases do. Furthermore, we will then propose a simple analytical partition function to replace excellently the more complex quantum partition function.

2. Theory and computational method

We are interested here in rotational thermodynamic parameters of a molecule. We then consider a system of $N$ identical, free and non-interacting such molecules at a fixed volume $V$ and temperature $T$. Such a system is then a canonical ensemble, and we then have $N$ independent and non-interacting rotators. The first step is to determine the rotational partition function, which serves as key parameters to deduce the rotational energy and the rotational entropy. If $Z$ is assumed to be the partition function, the energy and the entropy are deduced from Equations (1) and (2) (For the proof, see the SI in our previous paper) [17].

$$E = -\frac{\partial \log Z}{\partial \beta},$$

$$S = k_B \log Z + \frac{E}{T}.$$  

2.1. Rotational thermodynamic parameters in the classical approach

The classical rotational partition function of $N$ independent and non-interacting rotators at a fixed volume $V$ and temperature $T$ is given by Djefoulna et al. [17]. (For detailed developments, see the SI in our previous paper).

$$Z = \frac{z^N}{\sigma \ N!}, \quad \text{with}$$

$$z = 8\pi^2 \hbar^{-3}(I_a I_b I_c)^{\frac{1}{2}} (2\pi k_B T)^{\frac{3}{2}},$$

where $I_a$, $I_b$ and $I_c$, are the inertia moments of the molecular system. $\sigma$ is the order of the symmetry group of intrinsic rotations of the considered molecule. $\sigma$ is also called the symmetry factor. $z$ defined here is the rotational partition function for a single molecule. The resulting rotational internal energy and rotational entropy for a mole of non-interacting rotators are then given by Equations (5) and (6), respectively [17].

$$E_{\text{rot}} = \frac{3}{2}RT,$$

$$S(T) = \frac{5}{2}R + R \log \left[ \frac{(2\pi mk_BT)^{\frac{3}{2}} k_BT}{p h^3 g} \right] = S_d(T),$$

with $R$ the ideal gas constant. Note that Equation (6) is the Sackur–Tetrode equation [38, 39].

2.2. Rotational thermodynamic parameters in the quantum approach

When quantum approach is rather considered, the rotational partition function of a system of $N$ molecules is also given by Equation (3), but the single molecule rotational partition functions are given by Equation (20). We introduce the hermitian operators $\hat{J}$ representing the rotational kinetic moment for a given molecule. Thus, for a single and nonlinear-top molecule, the Hamiltonian can be defined as

$$\hat{H} = \left( \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z} \right),$$
Where $\hat{j}_x$, $\hat{j}_y$, and $\hat{j}_z$ are the components of $\hat{j}$ in the basis set $\hat{B} = (\hat{e}_x, \hat{e}_y, \hat{e}_z)$ associated to the motion of the molecule. If $\hat{j}_x$, $\hat{j}_y$, and $\hat{j}_z$ are the components of $\hat{j}$ in the fixed basis set $\hat{B} = (\hat{e}_x, \hat{e}_y, \hat{e}_z)$, we have

$$\hat{j}^2 = \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2 = \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2. \quad (8)$$

For asymmetric-top molecule $I_a \neq I_b \neq I_c$. Thus, operators $\hat{j}_x$, $\hat{j}_y$, and $\hat{j}_z$ do not allow simultaneously $|JKM\rangle$ as an eigenstate. Therefore, operators $\hat{j}_x$ and $\hat{j}_y$ are not diagonals in the basis sets $|JKM\rangle$. We then introduce ladder operators $\hat{j}_+$ and $\hat{j}_-$ to determine matrix elements of operators $\hat{j}_x$ and $\hat{j}_y$ define as,

$$\hat{j}_+ = \hat{j}_x + i\hat{j}_y \quad (9)$$
$$\hat{j}_- = \hat{j}_x - i\hat{j}_y \quad (10)$$

Thus, the non-zero matrix elements of $\hat{j}_x$ and $\hat{j}_y$ are,

$$\langle J, K, M | \hat{j}_x | J', K', M' \rangle = \frac{\hbar}{2} [J(J + 1) - K(K + 1)]^{\frac{1}{2}} \quad (11)$$

$$\langle J, K, M | \hat{j}_y | J, K \pm 1, M \rangle = \pm \frac{i\hbar}{2} [J(J + 1) - K(K + 1)]^{\frac{1}{2}}, \quad (12)$$

with $\hat{j}^2 = -1$.

The matrix elements of $\hat{j}^2_x$ and $\hat{j}^2_y$ are then calculated as,

$$\langle J, K, M | \hat{j}^2_x | J, K, M \rangle = \frac{\hbar^2}{2} [J(J + 1) - K^2] \quad (14)$$

$$\langle J, K, M | \hat{j}^2_y | J, K \pm 2, M \rangle = -\frac{\hbar^2}{4} [J(J + 1) - K(K + 1)]^{\frac{3}{2}} \times [J(J + 1) - (K \pm 1)(K \pm 2)] \quad (15)$$

$$\langle J, K, M | \hat{j}^2_z | J, K, M \rangle = \frac{\hbar^2}{2} [J(J + 1) - K^2] \quad (16)$$

$$\langle J, K, M | \hat{j}^2_y | J, K \pm 2, M \rangle = \frac{\hbar^2}{4} [J(J + 1) - K(K \pm 1)]^{\frac{3}{2}} \times [J(J + 1) - (K \pm 1)(K \pm 2)] \quad (17)$$

The non-zero matrix elements of the Hamiltonian for asymmetric-top molecules are then given by

$$\langle J, K | \hat{H} | J', K \rangle = \frac{\hbar^2}{4} \left[ J(J + 1) \left( \frac{1}{I_x} + \frac{1}{I_y} \right) + K^2 \left( \frac{2}{I_z} - \frac{1}{I_x} - \frac{1}{I_y} \right) \right] \quad (18)$$

$$\langle J, K | \hat{H} | J, K \pm 2 \rangle = \frac{\hbar^2}{8} [J(J + 1) - K(K \pm 1)]^{\frac{1}{2}} \times [J(J + 1) - (K \pm 1)(K \pm 2)]^{\frac{1}{2}} \left( \frac{1}{I_y} - \frac{1}{I_z} \right) \quad (19)$$

The Hamiltonian is then diagonalised using the numerical method of Jacobi. Finally, the rotational partition function is calculated using Equation (20).

$$\tilde{z}_{asym} = \sum_{j=0}^{\infty} \sum_{K=-j}^{j} \frac{1}{\sigma} \langle J, K | \exp(-\beta H) | J, K \rangle \quad (20)$$

Where $\tilde{z}_{asym}$ designate the rotational partition function for asymmetric-top molecules. $J, K \in \mathbb{N}$, are rotational quantum numbers. $\hbar$ is Planck’s constant, $h = \hbar/2\pi$ and $\sigma$ is the symmetry factor of the molecule. $\beta = 1/k_B T$. $I_x$, $I_y$, and $I_z$ are the different inertia moments of the molecule. The rotational energy and the rotational entropy are derived from Equations (1)–(3).

3. Results and discussions

In this section, we discuss classical and quantum rotational thermodynamic parameters for several asymmetric-top molecules. We then proposed closed-form expressions for the quantum rotational partition functions of asymmetric-top molecules.

3.1. Classical approach

We confront our partition functions calculated in the classical approach and entropies for O$_3$ and NO$_2$ molecules with those of Gaussian 09 suite of codes. Since classical approach is generally valid at high temperatures, we compare our findings with Gaussian 09 ones from $T = 100$ K. No comparisons are needed for classical rotational energy. Indeed, it is a linear function of temperature. The MP2/6–31 + G(d, p) level of theory has been used for the optimisations of molecular geometry using Gaussian 09 suite of codes [40]. Acquired results are presented in Table 1. Our findings are in very good agreement with those computed using Gaussian suite of codes (relative errors are repeatedly less than 1 %). The small
contrast could be accredited to values of constants used. We used constants from CODATA 2014 [41]. Note that a relative error of 1% in the partition function would lead to a relative error of 3% in rate constants, in reference to mathematical expressions of rate constants [42–44]. All over this work, we then accept relative error of 1% on all the calculated thermodynamic parameters [17].

### 3.2. Quantum correction

All the series involved in the evaluation of quantum parameters are convergent. Thus, for practical purpose, we stopped the summations when the difference between two consecutive terms reaches the epsilon machine of our computer (ε = 2.22446049e − 16) [17]. To check the reliability of our program named Rothermo, on evaluating quantum rotational thermodynamic parameters of asymmetric-top molecules we compare our results with those obtained using spherical (Equation (21)) and symmetric-top (Equation (22)) rotational partition function. We applied to spherical-top CH₄, symmetric-top C₂H₆ and NH₃. The agreement is excellent, see Table 2. Therefore, our Fortran code on evaluating rotational thermodynamic parameters for asymmetric molecules is well adapted for linear-top and spherical-top molecules. This is the first confirmation of the reliability of this code.

\[
Z_{\text{sph}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} \sum_{K=-J}^{J} (2J + 1) e^{-\beta Bh(J+1)}.
\]  
\[
Z_{\text{sym}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} \sum_{K=-J}^{J} (2J + 1) e^{-\beta Bh[(J+1)+(A-B)K^2]}.
\]  

#### 3.2.1. Asymmetric-top molecule (H₂O and NO₂)

We computed rotational partition function, rotational internal energy and rotational entropy energy of H₂O and NO₂ for several values of the temperatures from 1 to 5000 K. We then compare quantum results with classical ones.

**3.2.1.1. H₂O molecule.** The relative error between both approaches decreases monotonically as the temperature increases (Figure 1). For the partition function the relative error is up to ∼ 98% at 1 K. This error decreases monotonically and significantly down to 1% at 439 K (See Table S1 in the supplementary material). This indicates that quantum approach is required when evaluating partition functions (rate constants, for example) of the H₂O molecule below 439 K. The relative error in the evaluation of the entropy energy is ∼ 365% at 1 K and decreases drastically, and cancel practically above 28 K. Note that below 8 K, the relative error in the entropy energy behaves erratically (See Table S1 in the supplementary material). This can be explained by the fact that at those temperatures, rotational phenomena are strongly quantum in such a way that any classical approach drastically fails: this is a severe crash of the classical approach. However, rotational internal energy and rotational entropy energy errors are lower than 0.02 kcal/mol at all temperatures (see Table S1). Therefore, classical approach for rotational energetic parameters (energy, enthalpy, free energy, etc.) of the H₂O molecule is valid at all T, and it is then highly recommended instead of the quantum approach which is more complex.

**3.2.1.2. NO₂ molecule.** In this case, the relative error between both approaches decreases monotonically as the temperature increases (See Table S2 in the supplementary material or Figure 2). The relative error is ∼ 56% at 1 K for the partition function and ∼ 89% at 1 K for the internal energy. This error decreases monotonically down to ∼ 1% at 20 K for the partition function and down to ∼ 1% at 14 K for the internal energy. However, the relative error in the evaluation of the entropy energy is 295%
Table 2. Quantum partition functions of CH4, C2H6 and NH3 molecules.

| Molecule | T(K) | Zq     | Zasy   | ΔZ/Z(%) |
|----------|------|--------|--------|---------|
| C2H6     | 2    | 0.5196 | 0.5196 | 0.00    |
|          | 5    | 1.8481 | 1.8481 | 0.00    |
|          | 10   | 5.0711 | 5.0711 | 0.00    |
|          | 20   | 14.1282| 14.1282| 0.00    |
|          | 50   | 55.3437| 55.3437| 0.00    |
|          | 100  | 156.0645| 156.0645| 0.00    |
|          | 300  | 809.3077| 809.3075| 0.00    |
|          | 500  | 1740.6536| 1740.6533| 0.00    |
|          | 1000 | 4921.8290| 4921.8281| 0.00    |
|          | 3000 | 13,918.9381| 13,918.9354| 0.00    |
|          | 5000 | 55,014.4619| 55,014.4515| 0.00    |
|          | 7000 | 91,130.0163| 91,129.9991| 0.00    |
|          | 9000 | 132,853.8056| 132,853.7805| 0.00    |
|          | 10,000| 179,513.2956| 179,513.2617| 0.00 |
| CH4      | 2    | 0.0837 | 0.0837 | 0.00    |
|          | 5    | 0.1184 | 0.1184 | 0.00    |
|          | 10   | 0.2663 | 0.2663 | 0.00    |
|          | 20   | 0.6841 | 0.6841 | 0.00    |
|          | 50   | 2.5530 | 2.5530 | 0.00    |
|          | 100  | 7.0838 | 7.0838 | 0.00    |
|          | 300  | 36.3408| 36.3408| 0.00    |
|          | 500  | 77.9932| 77.9932| 0.00    |
|          | 1000 | 220.1752| 220.1752| 0.00    |
|          | 3000 | 622.1526| 622.1525| 0.00    |
|          | 5000 | 2457.8592| 2457.8590| 0.00    |
|          | 7000 | 7793.6035| 7793.6029| 0.00    |
|          | 9000 | 1294.8629| 1294.8626| 0.00    |
|          | 10,000| 179,513.2956| 179,513.2617| 0.00 |
| NH3      | 2    | 0.3334 | 0.3334 | 0.00    |
|          | 5    | 0.3562 | 0.3562 | 0.00    |
|          | 10   | 0.5957 | 0.5957 | 0.00    |
|          | 20   | 1.4359 | 1.4359 | 0.00    |
|          | 50   | 5.2017 | 5.2017 | 0.00    |
|          | 100  | 14.2945| 14.2945| 0.00    |
|          | 300  | 72.8680| 72.8680| 0.00    |
|          | 500  | 156.1892| 156.1892| 0.00    |
|          | 1000 | 220.1752| 220.1752| 0.00    |
|          | 3000 | 622.1526| 622.1525| 0.00    |
|          | 5000 | 2457.8592| 2457.8590| 0.00    |
|          | 7000 | 7793.6035| 7793.6029| 0.00    |
|          | 9000 | 1294.8629| 1294.8626| 0.00    |
|          | 10,000| 179,513.2956| 179,513.2617| 0.00 |

Note: Zq is the results calculated using Equation (21) for spherical-top CH4 and Equation (22) for symmetric-top C2H6 and NH3. Zasy is the partition function calculated using the asymmetric partition function. ΔZ/Z(%) is the relative error (in 1%) between both sets of results, and defined as, ΔZ/Z = |Zq - Zasy| × 100. The relative errors between both approaches is null for all molecular system at all temperatures.

at 0.1 K and we observed the severe crash of the classical approach as reported for the previous case for temperature below 0.43 K. The relative error on the rotational entropy energy decrease monotonically down to 1% at 7 K. Quantum approach is then required for the calculation of rotational entropy energy for temperatures below this limit. Elsewhere, the rotational internal energy and entropy energy errors are lower than 0.002 kcal/mol at all temperatures (see Table S2). Therefore, classical approach is enough for rotational energetic parameters of the NO2 at all T.

Moreover, the error accumulated by the classical approach decreases as the inertia moments (or the reduced mass) of the molecule increases or the temperature increases. This fact is satisfactory since high temperatures or high inertia moment lead to negligible values of the de Broglie wavelength and therefore favor classical phenomena. Note that the reduced mass effect or

Figure 1. Relative error between the classical and quantum values of the rotational partition function, internal energy and entropy energy for the H2O molecule. For this molecule, quantum approach is strongly recommended for the rotational partition function below 439 K. However, classical approach can be used excellently for describing rotational energetic parameters (energy, enthalpy, free energy, etc.) of the water molecule at all T.

Figure 2. Relative error between the classical and quantum values of the rotational partition function, internal energy and entropy energy for the NO2 molecule. For this molecule, quantum approach is strongly recommended for the rotational partition function below 20 K. However, classical approach can be used excellently for describing rotational energetic parameters (energy, enthalpy, free energy, etc.) of the hydrogen molecule at all T.
the inertia moment effect could be more appreciated if heavier molecules are considered.

### 3.2.2. Inertia moment effect

Inertia moment effect is involved here by considering some heavier molecules as polyvinyl alcohol (CH₂CHOH, \( M = 44.05 \text{ g mol}^{-1} \)), glycolaldehyde (C₂H₄O₂, \( M = 60.05 \text{ g mol}^{-1} \)) and the sulfanide (SOOS, \( M = 96.13 \text{ g mol}^{-1} \)).

In our previous work [17], we investigated inertia moment effect for linear- and spheric-top molecules. We found that, \( T_{\text{limit}} \) decreases strictly as the inertia moment of the system increases. Could we expect the same trends, although asymmetric-top has three different inertia moments?

Therefore, we recomputed rotational thermodynamic parameters for several asymmetric-top molecules with various inertia moments \( I_c \). Usually, asymmetric molecules have three different inertia moments \( I_a, I_b \) and \( I_c \) in such a way that the highest inertia moment \( I_c \) is related to other as, \( I_c = I_a + I_b \). It is worth mentioning that we found a relationship between \( T_{\text{limit}} \) and the highest inertia moment of an asymmetric-top molecule. Results are reported in Figure 3. Interestingly, \( T_{\text{limit}} \) is a strictly decreasing function of \( I_c \). We then performed a fit on these data and proposed excellent correlated functions with extremely low root-mean-square errors (RMSE). As a result,

\[
T_{\text{limit}}(I_c) = a (I_c)^b 
\]

With \( I \) the highest inertia moment of an asymmetric-top molecule, \( a = 2870.52371 \text{ K} \) and \( b = -0.9912195 \). The correlation coefficient for this fit is \( R^2 = 0.9999 \) and the corresponding RMSE is 2.75 K. Therefore, the analytical proposed function reproduces perfectly the calculated \( T_{\text{limit}} \) as a function of the highest inertia moment of the asymmetric-top molecule. As linear-, spherical- and symmetric-top molecules are special cases of asymmetric-top molecules, Equation (23) is also valid for these special cases. Therefore, this analytical expression should be preferred to the previous analytical expressions [18] proposed for linear- and spherical-top molecules. In fact, for linear- and spherical-top molecules, Equation (23) can be used by taking respectively \( I_c = I \) and \( I_c = I/0.721 \), with \( I \) the non-zero inertia moment of the molecule. For symmetric-top molecules, this equation can be used taking \( I_c = I/0.942 \), with \( I \) the highest inertia moment of the molecule. (See Table 3 for application to few molecules). Therefore, we strongly recommend Equation (23) for the estimation of the maximum temperature below which the rotational partition function of a given molecule should be calculated using quantum approach instead of simple classical formulas.

Overall, we checked that classical approach does not provide exact partition functions below certain temperatures. Therefore, it would be interesting to provide an accurate closed-form expressions for the rotational partition function valid at all temperatures for asymmetric-top molecules. Note that the most robust and reliable closed-form for quantum partition function of asymmetric-top molecules was proposed by Stripp and Kirkwood. Stripp and Kirkwood [33] We then compare results from this approach with exact values and highlight its limits. This motivates the investigation of closed-forms valid at all temperatures for asymmetric-top molecules.

### 3.3. Analytical partition function for asymmetric-top molecules

We start this section by showing the limit of the closed-form for the partition function from the Euler–Maclaurin approximation. Gordon [32] proposed closed-form given by

\[
Z_{grd} = \frac{1}{\sigma} \exp(\sqrt{BCh}/4KT) \sqrt{\frac{\pi}{ABC}} \left( \frac{k_BT}{h} \right)^3 \left[ 1 + \frac{1}{12} \right]
\]
with $S$ where $h$ a ds i g np r o b l e m. W a t s o n [35]e x t e n d e dt h i sw o r ka n d
obtained also by Kaplan [34] b u th i ss e c o n dt e r m
as $A \mathrm{wood} [33] p o p o s e d a n a s y m p t o t i c f u n c t i o n o f t h e r o t a-
tional partition function of asymmetric-top molecules. They calculated the first two terms of the asymptotic
expansion of the partition function, given by

$$Z_{f_2} = \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC}} \left( \frac{k_B T}{\hbar} \right)^3 \left[ 1 + f_1 + f_2 + \cdots \right]$$

(25)

where $A$, $B$ and $C$ are the rotational constants defined as $A = \frac{\hbar}{8\pi^2 l_2}$, $B = \frac{\hbar}{8\pi^2 l_3}$ and $C = \frac{\hbar}{8\pi^2 l_4}$. Stripp and Kirkwood [33] proposed an asymptotic function of the rotational partition function of asymmetric-top molecules. They calculated the first two terms of the asymptotic expansion of the partition function, given by

$$\times \left( \frac{\sqrt{BCh}}{k_B T} \right)^2 + \cdots \right]$$

(24)

We compiled here the case of $\text{H}_2\text{O}$ molecule and results are summarised in Table 4. This table shows clearly that the Gordon closed-forms with and without the second term are not valid below 300 K. We also noted that, among this four closed-forms presented, the Stripp and Kirwood [33] closed-form gives the better and accurate results at average and high temperatures. Note that with the Stripp and Kirwood closed-form, the rotational partition function of $\text{H}_2\text{O}$ molecule is not valid below 30 K. Similar limits are obtained with Watson’s closed-form [35]. Indeed, this closed-form is not valid for temperature below 500 K. Test on other asymmetric-top molecules (See SI) show that the Stripp and Kirwood closed-form partition function fails at very low temperatures or for light particles. Therefore, the Euler–Maclaurin approximation for asymmetric-top molecules is not recommended at very low temperatures or for light particles. At these very low temperatures, quantum phenomena are yet strongly present in the evaluation of the partition function. We then propose a new closed-form expression which resolve the problem raised by the Euler–Maclaurin approximation.

| Molecule         | $l_c$ | $T_{\text{limit}}$ | $T_{\text{limit}(l_c)} = a (l_c)^5$ |
|------------------|------|--------------------|----------------------------------|
| Linear-top ($l_c = 1$) |      |                    |                                  |
| $\text{H}_2$     | 0.97 | 2970               | 2957                             |
| HF               | 3.09 | 930                | 940                              |
| HCN             | 42.43| 67                 | 70                               |
| $\text{O}_2$    | 46.39| 61                 | 64                               |
| $\text{F}_2$    | 69.68| 41                 | 43                               |
| $\text{OS}$     | 91.65| 31                 | 33                               |
| Spherical-top ($l_c = 1/0.72$) | | | |
| $\text{CH}_4$   | 15.75| 190                | 187                              |
| $\text{SiH}_4$  | 28.94| 103                | 102                              |
| $\text{GeH}_4$  | 30.74| 98                 | 96                               |
| $\text{TiH}_4$  | 38.42| 77                 | 77                               |
| $\text{CF}_4$   | 447.76| 6                | 7                                |
| $\text{CCl}_4$  | 1472.32| 2            | 2                                |
| Symmetric-top ($l_c = 1/0.942$) | | | |
| $\text{NH}_3$   | 10.24| 286                | 286                              |
| $\text{FeH}_3$  | 16.34| 152                | 180                              |
| $\text{GeH}_6$  | 95.44| 31                 | 31                               |
| $\text{CH}_3\text{Cl}$ | 146.01| 21            | 21                               |
| $\text{CH}_3\text{Br}$ | 205.88| 15          | 15                               |
| $\text{BF}_3$   | 380.94| 9                | 8                                |
| Asymmetric-top ($l_c = l_a + l_b$) | | | |
| $\text{H}_2\text{O}$ | 6.58 | 439               | 444                              |
| $\text{NH}_2$   | 7.39 | 400                | 396                              |
| $\text{CH}_2$   | 8.53 | 340                | 343                              |
| $\text{SH}_2$   | 12.64| 230                | 232                              |
| $\text{CH}_3$N  | 53.68| 60                 | 55                               |
| $\text{CH}_2\text{NH}$ | 61.93| 47            | 48                               |

We then propose a new closed-form expression which resolve the problem raised by the Euler–Maclaurin approximation.

To this aim, we first diagonalised the Hamiltonian of the rotating molecular system using Equations (18) and (19). Thereafter, the partition function is calculated using Equation (20). Once we got these numerical values, we found the best related fit function. We then propose the function $Z_f$ defined in Equation (29), as the best

$$Z_f = \frac{1}{40320} \left[ 1472S_3^3 + 4224S_1S_2 - 1920S_3 - 2832 \frac{S_2^2}{S_3} \right]$$

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Table 4. Rotational partition function of H$_2$O.

| T(K) | $Z_q$  | $Z_{gdt}$ | $Z_{gdt'}$ | $Z_{as}$ | $Z_{as'}$ | $\Delta Z_1/Z$ (%) | $\Delta Z_2/Z$ (%) | $\Delta Z_3/Z$ (%) | $\Delta Z_4/Z$ (%) |
|------|--------|-----------|-----------|--------|---------|----------------|----------------|----------------|----------------|
| 1    | 0.5000 | 0.9502    | 2.6542    | 0.2020 | 95.2998 | 90.0389       | 430.8483       | 59.5917       | 18,959.9608   |
| 10   | 0.5669 | 0.4559    | 0.4693    | 0.4532 | 3.2629  | 19.5685       | 17.2109        | 20.0600       | 475.5936      |
| 20   | 1.0193 | 1.0132    | 1.0209    | 1.0039 | 1.7857  | 0.6042        | 0.1508         | 1.5172        | 75.1811       |
| 30   | 1.7039 | 1.7170    | 1.7228    | 1.7022 | 1.9358  | 0.7684        | 1.1128         | 0.0997        | 13.6102       |
| 40   | 2.5196 | 2.5388    | 2.5437    | 2.5195 | 2.4967  | 0.7607        | 0.9556         | 0.0044        | 0.9104        |
| 50   | 3.4398 | 3.4630    | 3.4673    | 3.4399 | 3.2629  | 0.6734        | 0.7985         | 0.0016        | 5.1418        |
| 60   | 4.4526 | 4.4791    | 4.4830    | 4.4526 | 4.1687  | 0.5963        | 0.6833         | 0.0014        | 6.3747        |
| 70   | 5.5498 | 5.5794    | 5.5830    | 5.5499 | 5.1846  | 0.5331        | 0.5971         | 0.0010        | 6.5816        |
| 80   | 6.7255 | 6.7579    | 6.7611    | 6.7255 | 6.2943  | 0.4812        | 0.5303         | 0.0006        | 6.4117        |
| 90   | 7.9746 | 8.0095    | 8.0126    | 7.9746 | 7.4876  | 0.4382        | 0.4769         | 0.0003        | 6.1068        |
| 100  | 9.2930 | 9.3303    | 9.3333    | 9.2930 | 8.7573  | 0.4019        | 0.4333         | 0.0002        | 5.7643        |
| 200  | 25.7002| 25.7564   | 25.7584   | 25.7001| 24.8416 | 0.2185        | 0.2264         | 0.0004        | 3.3409        |
| 300  | 46.8654| 46.9335   | 46.9372   | 46.8652| 45.7908 | 0.1497        | 0.1532         | 0.0005        | 2.2929        |
| 500  | 100.2444| 100.3363  | 100.3375  | 100.2439| 98.8418 | 0.0916        | 0.0929         | 0.0005        | 1.3992        |
| 1000 | 282.2857| 282.4165  | 282.4174  | 282.2842| 280.2923 | 0.0476        | 0.0480         | 0.0008        | 0.7062        |

Note: $Z_q$, $Z_{gdt}$, $Z_{gdt'}$, $Z_{as}$, and $Z_{as'}$ are, respectively, the quantum partition functions from direct summation, from the proposed formula of Gordon [32] without the second term and with the second term, Stripp and Kirkwood [33] formula and Watson [35] analytical function, respectively. $\Delta Z_1/Z$ (%) is the relative error between $Z_q$ and $Z_{gdt}$ sets of results, and defined as, $\Delta Z_1/Z = |Z_q - Z_{gdt}|/Z_{gdt} \times 100$. $\Delta Z_2/Z$ (%) is the relative error between $Z_q$ and $Z_{gdt'}$ sets of results, and defined as, $\Delta Z_2/Z = |Z_q - Z_{gdt'}|/Z_{gdt'} \times 100$. $\Delta Z_3/Z$ (%) is the relative error between $Z_{as}$ and $Z_{as'}$ sets of results, and defined as, $\Delta Z_3/Z = |Z_{as} - Z_{as'}|/Z_{as} \times 100$. $\Delta Z_4/Z$ (%) is the relative error between $Z_{as}$ and $Z_{as'}$ sets of results, and defined as, $\Delta Z_4/Z = |Z_{as} - Z_{as'}|/Z_{as} \times 100$.

It is worth mentioning that the Stripp and Kirkwood [33] closed-form converges to the classical partition function at high temperatures. Therefore, in regard of the complexity of this closed-form function and its limitations, we recommend it for the evaluation of the rotational partition function for asymmetric-top molecules only at average temperature. Of course, the question would be, what is the average temperature? We applied our proposed closed-forms expressions to several asymmetric-top molecules, (see Tables S3–S34 in the SI for results). As we noted that our proposed closed-form expressions are valid at low temperatures, results are presented up to the maximum temperature ($T_{\text{max}}$) below which our proposed closed-forms expressions are valid and are extremely accurate. The illustration of the supremacy of our proposed analytical rotational partition function for asymmetric-top molecules is summarised in Figures 4 and 5. $T_{\text{max}}$ is the temperature from which the error between exact calculation $Z_q$ and the analytical function of Stripp and Kirkwood $Z_{as}$ is around 1%. The reason of the choice of the analytical function of Stripp and Kirkwood as reference is that it is the most accurate among previous proposed ones. It is important to report that the relative error on the Stripp and Kirkwood [33] partition function decreases as the temperature increases. Therefore, beyond $T_{\text{max}}$, this error is lower than 1%. Thus, for the calculation of rotational partition function of asymmetric-top molecules, we recommend the closed form proposed by Stripp and Kirkwood [33] for $T_{\text{max}} \leq T \leq T_{\text{limit}}$. Note that diagonalisation of matrices consumes much computational time. Aiming to save computational time, we strongly recommend the use of

$$Z_f(T) = \frac{1}{\sigma} \left( d + \frac{a}{1 + \left( \frac{T}{c} \right)^b} \right),$$

(29)

where, $T$ is the temperature and $a$, $b$, $c$ and $d$ are real coefficients associated to each molecular system. This analytical function is reliable with the physical insight of rotation partition function at very low temperatures. In fact, at those temperatures, the proposed function tends to $1/\sigma$ which is in agreement with the quantum requirements as indicated by the exact quantum rotational partition function in Equation (20).

Furthermore, a precise estimation of the column density of molecular interstellar species is required in order to investigate the possible chemical reactions taking place in the interstellar medium [45]. Accurate partition function favors accurate intensities lines in spectroscopy, accurate equilibrium and rate constants of possible chemical reactions in interstellar medium. Therefore, we summarised in Table 5 coefficients $a$, $b$, $c$ and $d$ for 22 asymmetric-top molecules of astrophysical interest for the calculation of accurate rotational partition function. For all these various sets of four coefficients, the correlation coefficient of Pearson between the fitted data and the calculated ones is close to 1 and the related root mean square error is very low (see Table 5). Therefore, our proposed analytical rotational partition function at low temperatures and defined by Equation (29) is an excellent approximation of the complex quantum partition function at very low temperatures.
Table 5. Coefficients $a$, $b$, $c$ and $d$ for 22 astrophysical detected molecules.

| Molecule | $a$       | $b$       | $c$       | $d$       | RMSE     | $R^2$    |
|----------|-----------|-----------|-----------|-----------|----------|----------|
| H$_3^+$  | -2.287016 | 3.787502  | 50.534650 | 3.275825  | 0.0040   | 0.9998   |
| H$_2$O   | -3.211483 | 3.323399  | 24.789430 | 4.198700  | 0.0034   | 0.9999   |
| H$_2$D$^+$| -2.250092 | 3.818145  | 50.164611 | 3.240232  | 0.0040   | 0.9999   |
| CH$_2$   | -3.171985 | 3.820199  | 18.799750 | 4.160593  | 0.0072   | 0.9995   |
| C$_2$O   | -2.079284 | 3.930283  | 1.395840  | 3.072293  | 0.0037   | 0.9996   |
| C$_2$Si  | -12.671547| 2.006659  | 2.461922  | 13.637990 | 0.0126   | 0.9999   |
| N$_2$O   | -10.712867| 2.284690  | 11.683980 | 3.302861  | 0.0034   | 0.9998   |
| CH$_4$+  | -2.546267 | 3.710654  | 11.754460 | 3.538975  | 0.0023   | 0.9998   |
| HNO      | -6307693.07| 1.477151  | 122406.30 | 6307694.00| 0.0426   | 0.9999   |
| CH$_2$NH | -44.861877| 1.821469  | 18.433250 | 45.802100 | 0.0237   | 0.9987   |
| CCl$_2$  | -9071149.08| 1.442225  | 18227.55  | 9071150.00| 0.0271   | 0.9997   |
| CH$_2$N  | -452.074684| 1.619223  | 11627.300 | 457.9400  | 0.0037   | 0.9999   |
| CF$_2$   | -6401.292  | 2.634107  | 33.539760 | 7.389569  | 0.0037   | 0.9999   |
| O$_3$    | -2.300971  | 3.825469  | 1.702427  | 3.923303  | 0.0047   | 0.9998   |
| CH$_2$O  | -3213.92   | 1.284400  | 399.174170| 3214.827520| 0.0224   | 0.9999   |
| C$_2$H$_4$O$_2$| -5.828895 | 2.722767  | 0.645396  | 6.814486  | 0.0062   | 0.9999   |
| CH$_2$CHOH| -21.044500| 1.925940  | 3.421860  | 22.016970 | 0.0185   | 0.9998   |

Note: RMSE and $R^2$ are respectively the root mean square error and the correlation coefficient of Pearson associated to the fit function obtained from Equation (29) as compared to exact calculations from Equation (20).

Figure 4. Quantum rotational partition functions for H$_2$O, as a function of the temperature. $Z_q$ is the partition function calculated using the exact formula as indicated by Equation (20). $Z_{KS}$ is the partition function calculated using the analytic expression proposed by Stripp and Kirkwood [33] as indicated by Equation (25). $Z_f$ is the partition function calculated using our analytic expression proposed for $T \leq 21$ K (Equation (29)). $Z_c$ is the classical partition function calculated using Equation (4). We cannot note that our analytic expression proposed and applied to H$_2$O molecule gives results extremely close to exact values, while results from the proposed formula of Stripp and Kirkwood [33] and the classical one are very far for $T \leq 21$ K. Therefore, the Stripp and Kirkwood [33] analytical formula is not recommended at all for $T \leq 21$ K.

Figure 5. Quantum rotational partition functions for CH$_2$, as a function of the temperature. $Z_q$ is the partition function calculated using the exact formula as indicated by Equation (20). $Z_{KS}$ is the partition function calculated using the analytic expression proposed by Stripp and Kirkwood [33] as indicated by Equation (25). $Z_f$ is the partition function calculated using our analytic expression proposed for $T \leq 21$ K (Equation (29)). $Z_c$ is the classical partition function calculated using Equation (4). We cannot note that our analytic expression proposed and applied to C$_2$O molecule gives results extremely close to exact values, while results from the proposed formula of Stripp and Kirkwood [33] and the classical one are very far for $T \leq 17$ K. Therefore, the Stripp and Kirkwood [33] analytical formula is not recommended at all for $T \leq 17$ K.

analytical formulas for determination of quantum rotational partition functions of asymmetric-top molecules. Therefore, taking into account the limitation of Stripp and Kirkwood [33] formula, the most accurate one, we recommend the following analytical formula for the quantum rotational partition function of asymmetric-top
molecules (see (30)).

\[ Z_q(T) = \begin{cases} 
Z_f(T) & \text{defined by Equation (29) if } T \leq T_{\text{max}}, \\
Z_{ks}(T) & \text{defined by Equation (25) if } T_{\text{max}} < T \leq T_{\text{limit}}, \\
Z_c(T) & \text{defined by Equation (3) if } T > T_{\text{limit}}.
\end{cases} \]

Note that with this analytical formula, there could be a problem. In fact, \( T_{\text{max}} \) is not known explicitly as \( T_{\text{limit}} \) is. Thus, we do not have it always, unless it is calculated. Fortunately, obtained results using the analytical formulas (25) and (29) show that for a specific temperature, the most accurate analytical formula provides the highest rotational partition function (see Tables S3–S34 in the SI). Therefore, as a rule of thumb, we recommend a user to calculate both analytical quantum rotational partition functions for a specific temperature below \( T_{\text{limit}} \), and to consider the highest result. Therefore, Equation (30) could be replaced easily by Equation (31)

\[ Z_q(T) = \begin{cases} 
\text{Max } (Z_f(T), Z_{ks}(T)) & \text{if } T \leq T_{\text{limit}}, \\
Z_c(T) & \text{if } T > T_{\text{limit}}.
\end{cases} \]

with \( Z_f \) and \( Z_{ks} \) defined, respectively, by Equations (29) and (25). Max stands for the maximum.

5. Conclusion

We derived in this work, the temperature \( T_{\text{limit}} \) below which the classical approach is no longer valid evaluating rotational thermodynamic parameters for asymmetric-top molecules. We also proposed closed-form expressions for the quantum rotational partition functions of asymmetric-top molecules under the rigid rotor approximation.

This work is the extension of our previous work on linear- and spherical-top molecules. It brings general insights into asymmetric-top molecules. It comes out that although quantum theory is recommended at all temperatures, classical approach is often enough for some systems above some specific temperatures. \( T_{\text{limit}} \) is then 439 K for H\(_2\)O and 20 K for NO\(_2\) molecules for the partition function. Moreover, the temperature, \( T_{\text{limit}} \), below which the classical approach is no more valid in investigating rotational partition functions, certainly increases with the inertia moment and follows an exact combination of the power function \( I_i \in \mathbb{R}^n \rightarrow a_i I_i^b \) for asymmetric-top molecules. As for linear-, spherical- and symmetric-top molecules [17], quantum approach is not needed at all for energetic rotational parameters, whatever the temperature for asymmetric-top molecules. Therefore, there is no real frontier between the classical and quantum approaches when energetic rotational parameters are concerned, though the frontier is naturally a bounded decreasing sequence converging to zero when rotational partition functions are rather concerned.

A new analytical partition function is proposed and strongly recommended to replace the complex quantum partition function. This will reduce significantly computational efforts without altering the accuracy. We then recommend the implementation of the proposed partition function in quantum chemistry computational codes.

Disclosure statement

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Supplementary Material

See the supplementary material for complete data indicated in tables S1–S23.

Data Availability

The data that supports the findings of this study are available within the article [and its supplementary material].

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