

Concerning the asymmetric top rotational partition function in astronomical spectroscopy

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ABSTRACT

The partition function plays an important role in determining column densities from emission lines in molecular clouds, since under typical conditions the two are linearly related. Here, we focus on successively applying quantum and centrifugal distortion correction terms to the classical rotational partition function for asymmetric top molecules, in an effort to uncover the relative importance of each term. We do this for example asymmetric top molecules that contain from one to four heavy atoms (water, methanimine, vinyl alcohol, and glycolaldehyde), at temperatures relevant to interstellar molecular clouds. Particular attention is paid to methanimine, for which it was recently attested that the value of the classical partition function significantly differs from the numerically summed (exact) value at several hundred Kelvin [Sharma *et al.*, *Astron. Nachrichten*, **338**, 125 (2017)]. We show that the classical values are in fact within 1% of the exact values from ~50 K to well above 400 K; the addition of three simple correction terms reduces the error to $\lesssim 0.001\%$ (down to 10 K).

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1. Introduction

The molecular partition function, $Q_{\text{tot}} = \sum_i g_i e^{-E_i/k_B T}$, is a dimensionless quantity that represents the number of thermally populated states, each with energy, E_i , and degeneracy, g_i . It provides a normalization constant to the Boltzmann factor, resulting in an equation (the Boltzmann distribution) that represents the probability of an upper state, u , being populated, viz., $p_u = \frac{g_u e^{-E_u/k_B T}}{Q_{\text{tot}}}$. If one assumes that p_u corresponds the ratio of column densities, $\frac{N_u}{N_{\text{tot}}}$, that Q_{tot} is equal to the rotational partition function, Q_R , and that we are in local thermodynamic equilibrium (LTE) with an excitation temperature, T_{ex} , that equals the rotational temperature, then $\frac{N_{\text{tot}}}{N_u} = \frac{Q_R}{g_u e^{-E_u/k_B T_{\text{ex}}}}$. This equation is widely used in astronomy in determining total column density from observations [1]. Accurate determination of Q_R values is therefore necessary for determining accurate N_{tot} values, since they are linearly dependent on each other. In this note we focus on an algebraic Q_R for asymmetric top molecules, and assess the relative importance of the various terms which account for high and low temperature deviations from the exact (numerically summed) Q_R values.

The range of temperatures considered here is chosen to extend beyond the broad range of rotational excitation temperatures

(~10–250 K) typically observed in giant molecular clouds (GMC's), which contain most of the molecular gas in our Milky Way galaxy [2]. While most of them consist of low density gas at low temperature, e.g., the dark cloud core, TMC-1, in Taurus [$n(\text{H}_2) = 10^4 \text{ cm}^{-3}$ and $T = 10 \text{ K}$], there are numerous warmer clouds that are characterized by higher densities and temperatures, e.g., the hot core region in Orion-KL [$n(\text{H}_2) = 10^7 \text{ cm}^{-3}$ and $T = 200 \text{ K}$] [3]. It is important to point out that most molecular clouds have a broad range of physical attributes, and for example, one of the most chemically rich and extensively studied is Sagittarius (Sgr) B2, which shows rotational temperatures extending beyond 10–200 K [4]. To date, more than 200 different molecules have been detected towards both the cold and warmer regions of GMC's [5], most of which are classified as asymmetric tops, which is what we focus on in the following.

Because there is no general analytic solution of the rigid asymmetric rotor Schrödinger equation, it follows that there is also no exact expression for the rotational partition function for asymmetric tops. This is not the case for symmetric tops for which the rotational partition function is $Q_R = \sum_{J=0}^{\infty} \sum_{K=-J}^{+J} g_K g_l (2J+1) e^{-hc[BJ(J+1)+(A-B)K^2]/k_B T}$ [6], where g_K is the K degeneracy, and g_l is the nuclear spin degeneracy (see Ref. [1] for details). Upon invoking Gordon's approximation for asymmetric rotors [7], which involves replacing B with \sqrt{BC} (a reasonable approximation when $B-C$ is small), then expanding the resulting

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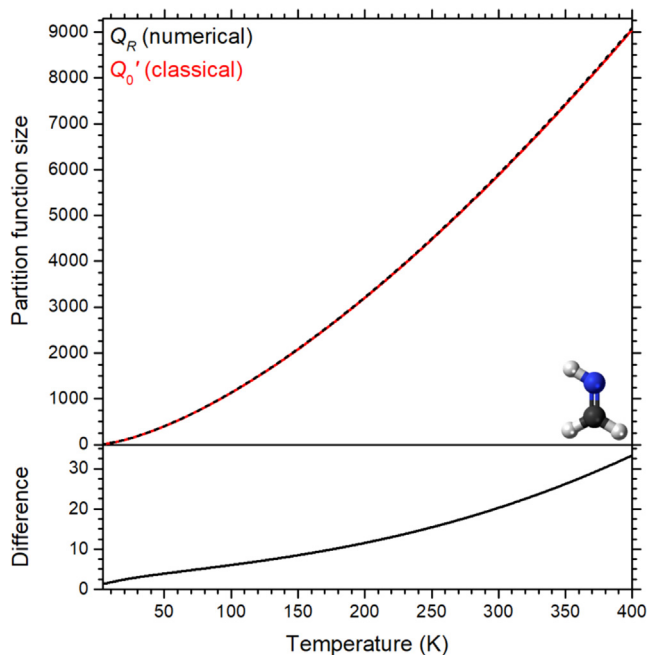


Fig. 1. Temperature dependence of the partition function determined by the classical formula in the high temperature limit, and the “exact” value determined by direct numerical summation (top). Note, these values need to be divided by a factor of three in order to properly compare with those shown in Fig. 1 of Ref. [13] (this accounts for the nuclear spin of ^{14}N that was intentionally not considered there). Also shown is the difference (numerical-classical) between the two methods (bottom).

expression according to [8], one gets [9–11]

$$Q_R = g_l e^{hc\sqrt{BC}/4k_B T} \sqrt{\frac{\pi}{2\beta\gamma}} \left(1 + \frac{1}{12} \sigma + \frac{7}{480} \sigma^2 + \frac{31}{8064} \sigma^3 + \frac{127}{92160} \sigma^4 + \dots \right),$$

where $\sigma = \frac{hc\sqrt{BC}}{k_B T} \left(1 - \frac{\sqrt{BC}}{A} \right)$, and α , β , and γ , are the dimensionless “temperature reduced rotational constants”, i.e., $hcA/k_B T$, $hcB/k_B T$, and $hcC/k_B T$, respectively. In the high temperature limit, this naturally reduces to the classical value, i.e., $Q_0' = g_l \sqrt{\frac{\pi}{2\beta\gamma}}$, which has often been used in astronomy to help determine molecular densities, e.g., see Ref. [4] (although it is becoming more common to use direct summation [12]).

In a recent investigation by Sharma *et al.* [13], a comparison was made between the partition function values for methanimine (CH_2NH) obtained using the classical expression for Q_0' , and that obtained by taking the direct numerical summation over a number of rotational states. Here, we focus on reinvestigating this comparison, and attempt to converge on the exact values by adding correction terms to the classical expression. We then apply them to lighter and heavier molecules, to assess their importance as a function of molecular size (and system temperature). The molecules considered are HDO, CH_2NH , CH_2CHOH , and CHOCH_2OH , all of which have been identified toward the northern hot molecular core of Sgr B2 [i.e., Sgr B2(N)] [14–17].

2. Results and discussion

2.1. Classical and numerical partition function

Fig. 1 (top) shows a comparison of the partition function size for methanimine that was calculated as a function of temperature for the two methods, using the constants from Ref. [18]. The numerical summation was performed with PGOPHER [19], which considers the Q values to be converged when the 8 highest J values have contributed less than 10^{-4} to the overall sum. The values we obtain by

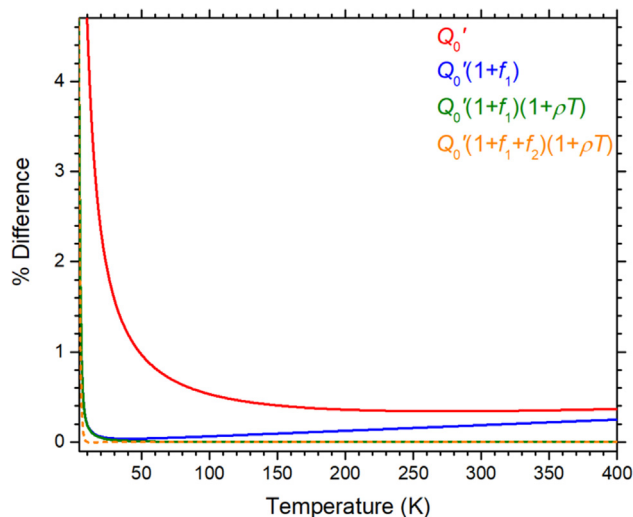


Fig. 2. Temperature dependence of the % difference [$100\% \times (\text{numeric-algebraic})/\text{numeric}$] in the partition function at various levels of approximation.

Table 1

Ground state rotational and quartic centrifugal distortion Cartesian coefficients for methanimine. Note that these values were transformed from previously reported S -reduced rotational and quartic centrifugal distortion constants (in the I' coordinate representation).

Parameter	Value	Units
B_x	34641.69139	MHz
B_y	29351.48875	MHz
B_z	196210.8883	MHz
T_{xx}	−79.9660	kHz
T_{yy}	−40.0736	kHz
T_{zz}	−7038.16	kHz
T_{xy}	−43.9558	kHz
T_{xz}	−365.317	kHz
T_{yz}	−345.369	kHz

the summation method are markedly different to those in Ref. [13] (after theirs are multiplied by 3 to account for ^{14}N spin), but agree with the values reported in Table 3 of Ref. [18]. While they are in reasonably good agreement with the classical values, there is room for improvement, and this is highlighted in Fig. 1 (bottom) where the difference between the two methods is plotted; this reveals a gradual increase in the difference with increasing temperature. In the following, we consider different corrections to the classical partition function to account for (most of) the differences.

2.2. Correction terms to the classical partition function

Expansion of the rigid rotor problem: Although still used somewhat, the analytic asymmetric top formula of Viney has been superseded by the work of several others [20–24], who have gradually determined the increasingly higher order quantum corrections to the rigid rotor partition function, $Q' = Q_0'(1 + f_1 + f_2 + f_3 + \dots)$ [25]. The first two (f_1, f_2) can be found in the work of Stripp and Kirkwood [20], who deduced them to be, $f_1 = \frac{1}{12} [4(\alpha + \beta + \gamma) - \frac{(\beta\gamma + \gamma\alpha + \alpha\beta)^2}{\alpha\beta\gamma}]$, and $f_2 = \frac{1}{480} [48(\alpha + \beta + \gamma)^2 + 32(\beta\gamma + \gamma\alpha + \alpha\beta) - 40 \frac{(\alpha + \beta + \gamma)(\beta\gamma + \gamma\alpha + \alpha\beta)^2}{\alpha\beta\gamma} + 7 \frac{(\beta\gamma + \gamma\alpha + \alpha\beta)^4}{(\alpha\beta\gamma)^2}]$. The third can be found in Ref. [24]; it is of little consequence, and shall not be repeated here.

Centrifugal distortion correction: Here we recall a relatively simple centrifugal distortion correction term to the partition function given by Wilson to the rigid rotor model [26]. The correction

term in $Q_R' = Q/(1 + \rho T)$ was provided in terms of Wilson-Howard centrifugal distortion constants (of the form $\tau_{\alpha\beta\gamma\delta}$). Transforming these to rotational and centrifugal Cartesian coefficients [27,28], the first order correction term becomes $\rho = \frac{-k_B}{4hc} \left(3 \left[\frac{T_{xx}}{B_x^2} + \frac{T_{yy}}{B_y^2} + \frac{T_{zz}}{B_z^2} \right] + 2 \left[\frac{T_{xy}}{B_x B_y} + \frac{T_{xz}}{B_x B_z} + \frac{T_{yz}}{B_y B_z} \right] \right)$. Other correction terms are available [21,29], however they do not significantly affect the partition function of molecules even in hot molecular cores, which are on the high temperature side of the range considered here for methanimine. They start to become important for light asymmetric rotors (e.g., water, formaldehyde, methanimine...) in the 500–1000 K range [29].

2.3. Application of correction terms to various interstellar molecules

Methanimine: As noted above, the numerically determined partition function of methanimine is reasonably well reproduced by the classical partition function equation, however, there is room for improvement. Fig. 2 shows the % difference between the exact (numeric) and algebraically determined partition function values when we include the additional terms introduced above (f_1, f_2, ρ). As can be seen, the inclusion of f_1 results in a large improvement in the algebraic method, especially at low temperatures where centrifugal distortion effects are not expected to be pronounced. Inclusion of the centrifugal distortion term (ρ) using the constants listed in Table 1 [18], brings the partition function into very good agreement, especially at higher temperatures, while inclusion of f_2 results in a small improvement at low temperature. The normalized RMS deviation over the temperature range from 10 to 400 K is 8.1×10^{-3} for the classical partition function, 1.5×10^{-3} when we include f_1 , 1.9×10^{-4} when we also include ρ , and 5.1×10^{-5} when we include all three correction terms (f_1, f_2, ρ). Additional terms will be necessary to further account for quantum effects at low temperature, as evidenced in Fig. 2 by the steep increase in the partition function below ~8 K.

From 1 to 4 heavy atoms (water, methanimine, vinyl alcohol, and glycolaldehyde): Here, we explore how accurate the algebraic method is in determining the partition function for select example molecules [with 1–4 heavy atoms (C, N, O)]. Table 2 shows a comparison of the % error in the “classical” and “corrected” partition functions over a broad range of temperatures (1–1000 K). It is evident that the accuracy of the corrected partition function improves with molecular size, showing an improvement of several orders of magnitude in going from water (HDO) to glycolaldehyde (CHOCH₂OH). In fact, the error for glycolaldehyde is less than 0.1% for all temperatures, and does not suffer the rapid increase in going to even the lowest temperature tested (1 K), unlike the

lighter molecules investigated. It should be noted that this rapid increase results from approximations made in deriving the various terms in the analytic function, and it has been recommended that direct summation is used when the algebraic method fails at low temperature [21]. Incidentally, it seems that the rapid increase begins to occur at temperatures below $B_z/2k_B$, which corresponds to 17 K, 4.7 K, 1.4 K, and 0.4 K, for HDO, CH₂NH, CH₂CHOH, and CHOCH₂OH.

We now estimate the error in some previously determined interstellar molecular densities that relied on the classical formulation of the partition function. Glycolaldehyde has been observed towards Sgr B2(N) with a rotational temperature of only 8 K [30]. In that investigation the classical rotational partition function was used, and Table 2 shows that while it is orders of magnitude worse than the corrected values, it only carries an error of ~1% at that temperature. Vinyl Alcohol has also been observed towards Sgr B2(N) with a rotational temperature of 11.6 K [16]. Once again the classical rotational partition function was used, and Table 2 shows that it carries an error of slightly more than 1% at that temperature. These values seem pretty typical of small complex organic molecules, with the error for propylene oxide at 6 K being 1.3% [31]. While methanimine has been observed towards Sgr B2 (N) [15], its spectrum is not in LTE which makes for a much more involved determination of its interstellar densities [32]; note that we included it in this work to illustrate the shortcomings of the previous investigation (*vide supra*). Finally, HDO lines have also been observed in both absorption and emission from Sgr B2(N), and non-LTE modelling is also required to accurately determine abundances, as previously discussed [33].

3. Conclusions

Here, we considered correcting the classical rotational partition function of asymmetric top molecules by including quantum and centrifugal distortion terms. The relatively simple equation that was used which should be satisfactory for most asymmetric tops at temperatures relevant to interstellar molecular clouds is

$Q_R' = \sqrt{\frac{\pi}{ABC} \left(\frac{k_B T}{h} \right)^3} (1 + f_1 + f_2)(1 + \rho T)$, where f_1 and f_2 are the first and second order quantum corrections [20], and ρ is the first order centrifugal [26] correction to the classical partition function. This corrected partition function provides an improvement of roughly two orders of magnitude compared to the classical function alone, and is found to provide accurate values down to $T \approx B_z/2k_B$, where B_z is the largest rotational constant (typically denoted A). Finally, we note that it is sometimes useful to analytically calculate the

Table 2

Comparison of the % difference in the “classical” [$100 \times (\text{numeric} - \text{classical}) / \text{numeric}$] and “corrected” [$100 \times (\text{numeric} - \text{corrected}) / \text{numeric}$] partition functions for the example molecules (with 1–4 heavy atoms; indicated parenthetically). The numeric values used (in this table) were determined from previously reported rotational and centrifugal distortion (quartic and sextic) constants (HDO [35], CH₂NH [18], CH₂CHOH [36], and CHOCH₂OH [37]). The corrected values were determined using both quantum correction terms (f_1 and f_2) as well as the first order centrifugal distortion term (ρ).

T (K)	HDO (1)		CH ₂ NH (2)		CH ₂ CHOH (3)		CHOCH ₂ OH (4)	
	classical	corrected	classical	corrected	classical	corrected	classical	corrected
1	9.7×10^1	6.3×10^1	6.7×10^1	4.5×10^1	1.9×10^1	6.2×10^0	7.8×10^0	1.9×10^{-6}
2.725	8.7×10^1	5.8×10^1	2.6×10^1	1.1×10^1	5.2×10^0	6.6×10^{-3}	2.9×10^0	-3.6×10^{-4}
5	7.0×10^1	4.0×10^1	1.0×10^1	1.0×10^0	2.9×10^0	-2.1×10^{-3}	1.6×10^0	-1.1×10^{-4}
9.375	4.0×10^1	1.4×10^1	5.0×10^0	1.2×10^{-3}	1.5×10^0	-3.5×10^{-4}	8.5×10^{-1}	-6.7×10^{-5}
18.75	1.7×10^1	9.4×10^{-1}	2.5×10^0	-1.6×10^{-3}	7.8×10^{-1}	-6.1×10^{-5}	4.4×10^{-1}	-5.5×10^{-5}
37.5	8.2×10^0	-1.6×10^{-2}	1.3×10^0	-3.2×10^{-4}	4.1×10^{-1}	-2.4×10^{-5}	2.4×10^{-1}	-3.5×10^{-5}
75	4.2×10^0	-9.8×10^{-3}	6.7×10^{-1}	-1.5×10^{-4}	2.4×10^{-1}	-2.8×10^{-5}	1.6×10^{-1}	4.3×10^{-5}
150	2.4×10^0	-1.0×10^{-2}	4.1×10^{-1}	-1.4×10^{-4}	1.9×10^{-1}	-6.4×10^{-5}	1.7×10^{-1}	3.5×10^{-4}
225	1.9×10^0	-1.4×10^{-2}	3.5×10^{-1}	-1.6×10^{-4}	2.0×10^{-1}	-1.3×10^{-4}	2.1×10^{-1}	8.8×10^{-4}
300	1.7×10^0	-2.0×10^{-2}	3.4×10^{-1}	-1.9×10^{-4}	2.3×10^{-1}	-2.2×10^{-4}	2.6×10^{-1}	1.6×10^{-3}
500	1.7×10^0	-4.6×10^{-2}	4.0×10^{-1}	-3.5×10^{-4}	3.3×10^{-1}	-6.2×10^{-4}	4.0×10^{-1}	4.6×10^{-3}
1000	2.4×10^0	-1.9×10^{-1}	6.7×10^{-1}	-1.3×10^{-3}	6.2×10^{-1}	-2.8×10^{-3}	7.9×10^{-1}	1.9×10^{-2}

asymmetric top rotational partition function due to a lack of availability of line lists (e.g., see Ref. [34]), in which case it is desirable to include the correction terms mentioned above, particularly at high temperature when centrifugal distortion becomes important.

CRediT authorship contribution statement

Tyler Wells: Investigation. **Paul L. Raston:** Methodology, Conceptualization, Writing - review & editing.

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