# Vibrational Partition Function for the Multi-Temperature Theories of High-Temperature Flows of Gases and Plasmas

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# Vibrational Partition Function for the Multitemperature Theories of High-Temperature Flows of Gases and Plasmas

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**ABSTRACT:** The vibrational partition function is calculated using the classical method of integration over the whole phase space. The calculations were done for the ground electronic state of a carbon monoxide molecule. The main focus is on temperature in the range 5000−20 000 K, which is common in hypersonic flows of gases and plasmas. The method presented here, because of the exclusion of the noninteracting part of canonical partition function according to the ideas of T.L. Hill, is applicable at temperatures of tens of thousands of Kelvins, where the standard expression for the vibrational partition function fails. At lower temperatures (here 1000−6000 K), the correct quantum results can be obtained with the help of Wigner−Kirkwood expansion. The influence of vibrations on the rotational partition function by bond-length elongation is examined, and the results are compared with the exact ro-vibrational partition function.

High vibrational excitation
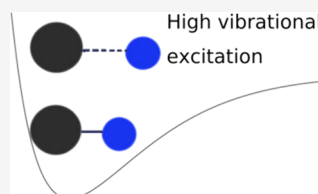
## 1. INTRODUCTION

In hypersonic reacting flows, the molecules undergo rapid exchange of energy quanta, the result of those processes are both extreme temperatures and thermodynamical nonequilibrium (various processes have different relaxation times), resulting, at least approximately, in different effective temperatures for vibrations and rotations. The most detailed description of the flows is provided by the state-to-state models (each vibrational state of a molecule on each electronic state is treated as a distinct entity).[1,2] In practice, such models are too complicated for simulation of three-dimensional flows. Because of that, multi-temperature models are being developed, and such models need vibrational partition functions.[3−5] In ref 2 a carbon monoxide molecule is studied in the range 5000−30 000 K, which uses both vibrational and rotational partition functions. In ref 6 the highest temperature considered is 50 000 K, which is also the highest temperature considered in the present study.

The vibrational partition functions are sometimes calculated in harmonic approximation but, because of high temperatures, such an approach is too simple. A more exact approach, assumed in this study, is to use an anharmonic oscillator with the Boltzmann distribution of vibrational energy. A further improvement would be to take into account non-Boltzmann distribution of vibrational energy, the most common approach in this case is to use the Treanor distribution (this distribution is also approximate and not correct at high energies).[7]

The aim of this study is to calculate the vibrational partition function in the classical approach (with quantum correction for lower temperatures) which takes into account also the unbound states (the result of scattering of atoms) which yield the negative contribution to the partition function.[8] In the case of vibrational partition functions (there are no rotations and no metastable states, as a result), the only unbound states are the scattering

states. In the following, such partition functions (containing both bound and unbound states) will be called all-state partition functions.

This study is done with a carbon monoxide molecule as an example. Preliminary studies of vibrational partition functions were performed by the author,[9] but neither unbound states nor quantum corrections were taken into account.

Analytical expressions for vibrational partition functions for some types of potential energy curves (PEC) were given by Jia et al.[10,11] A CO molecule was considered, but only thermody-namical functions were explicitly calculated, not the partition function itself.

This paper is organized as follows: Section 2 presents a method to obtain the all-state vibrational partition function and also the rotational partition function corrected for vibrations, Section 3 presents the results for the CO molecule and discusses them, and Section 4 concludes the study.

## 2. CLASSICAL VIBRATIONAL PARTITION FUNCTION WITH QUANTUM CORRECTIONS

The method used in this study is the modification of methods used in refs 12−14 by neglecting the rotation of a molecule so that the derivation becomes one-dimensional. Let $H = T + V = p^2/(2\mu) + V(r)$ be the classical Hamiltonian of a diatomic molecule with reduced mass $\mu$, momentum $p$, and potential

energy curve (PEC) $V(r)$. The canonical partition function can be split into vibrational and noninteracting parts, following the ideas from refs 15, 16

$$
\begin{aligned}
Q &= \frac{1}{2\pi} \iint e^{-\beta(T+V)} dp\, dr = \frac{1}{2\pi} \int e^{-\beta T} dp \int e^{-\beta V} dr \\
&= \frac{1}{2\pi} \int e^{-\beta T} dp \int (e^{-\beta V} - e^{-\beta V(\infty)}) dr \\
&\quad + \frac{1}{2\pi} \iint e^{-\beta T} e^{-\beta V(\infty)} dp\, dr = Q_{\text{vib}}^{\text{HD}} + Q_{\text{noninteract}}
\end{aligned}
$$

(1)

This procedure will be called Hill decomposition (HD), and $V(\infty)$ means the value at the $r \rightarrow \infty$ limit.

The above expression for the vibrational partition function can be integrated over momenta (potential energy at infinity becomes the potential well depth $D_e$, provided $V(r_e) = 0$)

$$
\begin{aligned}
Q_{\text{vib}}^{\text{HD,WK}} &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p^2}{2\mu}\right) dp \\
&\quad \int_0^{\infty} [\exp(-\beta V)\text{wk2}(r) - \exp(-\beta D_e)] dr \\
&= \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_0^{\infty} [\exp(-\beta V)\text{wk2}(r) \\
&\quad - \exp(-\beta D_e)] dr
\end{aligned}
$$

(2)

where $\exp(-\beta V)$ was multiplied by

$$
\begin{aligned}
\text{wk2}(r) &= 1 - \frac{\beta^3}{24\mu}\left(\frac{dV}{dr}\right)^2 + \frac{\beta^4}{5760\mu^2}\left(\beta^2\left(\frac{dV}{dr}\right)^4 \right.\\
&\quad \left. - 8\beta\left(\frac{dV}{dr}\right)^2 \Delta V + 12(\Delta V)^2\right)
\end{aligned}
$$

(3)

which is a quantum Wigner–Kirkwood correction ($\Delta V = d^2V/dr^2$ in one-dimensional case).[17−19] If the quantum correction wk2 is omitted, the purely classical mechanics formula is recovered.

Note that the expression for the vibrational partition function of bound states is given in ref 20 (but not used with quantum correction)

$$
\begin{aligned}
Q_{\text{vib}}^{\text{B,WK}} &= \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_{\sigma}^{\infty} \text{erf}(\sqrt{-\beta(V - D_e)}) \exp(-\beta V) \\
&\quad \times \text{wk2}(r) dr
\end{aligned}
$$

(4)

where $\sigma$ is given by the $V(\sigma) = D_e$ condition (in dynamical terms, $\sigma$ can be called the inner turning point), and erf is the error function. Interatomic distances smaller than $\sigma$ pertain to the energies over the potential well (for $r > \sigma$: $V(r) < D_e$), which, in the absence of rotations, are the result of the scattering states only. Distances $r < \sigma$ give a negative contribution to the partition function (both vibrational and ro-vibrational).[13]

Finally, the standard expression for the classical partition function will be used (with the Wigner–Kirkwood correction)

$$
Q_{\text{vib}}^{\text{S,WK}} = \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_0^{\infty} \exp(-\beta V)\text{wk2}(r) dr
$$

(5)

The present method was applied to the ground electronic state of carbon monoxide. That molecule is of practical interest in

plasma science as a product of $CO_2$ decomposition and also in aerothermodynamics in Mars entry problems. The PEC used was according to Liu et al.,[21] transformed into atomic units and shifted so that the minimum of the curve has energy equals zero.

$$
\begin{aligned}
V_{\text{Liu}} &= -D_e(1 + a_1(r - r_e) + a_2(r - r_e)^2 + a_3(r - r_e)^3) \\
&\quad \exp(-a_1(r - r_e)) + D_e
\end{aligned}
$$

(6)

where $D_e = 0.4113827$ a.u., $r_e = 2.13955$ a.u., $a_1 = 2.20355$ a.u., $a_2 = 0.962467$ a.u., and $a_3 = 0.408807$ a.u.

The frequency of this PEC is $\omega = 0.00982934$ a.u. = 2157.29 cm$^{-1}$, and reduced mass for $^{12}C^{16}O$ isotope is $\mu = 12\,498.1$ a.u. In eq 4, $\sigma = 1.58216$ for that PEC.

The splitting of the ro-vibrational partition function means separation of vibrations and rotations, but at high temperatures, the vibrations cause an average bond length to differ from the equilibrium value. The use of appropriate bond length in the rotational partition function will be investigated.

$$
Q_{\text{rot}} = \frac{2\mu\langle r\rangle^2}{\beta}
$$

(7)

where

$$
\langle r\rangle = \frac{\frac{1}{2\pi}\sqrt{\frac{2\pi\mu}{\beta}} \int_0^{\infty} r[\exp(-\beta V) - \exp(-\beta D_e)] dr}{Q_{\text{vib}}^{\text{HD}}}
$$

(8)

For lower temperatures, $\langle r\rangle \approx r_e$, but with the increase of temperature, $\langle r\rangle > r_e$.

For completeness, the expressions for ro-vibrational partition functions are reported ($\gamma$—incomplete $\gamma$ function)[14]

$$
\begin{aligned}
Q_{\text{rovib}}^{\text{B,WK}} &= \frac{1}{\pi}\left(\frac{2\mu}{\beta}\right)^{3/2} \int_{\sigma}^{\infty} \gamma(3/2, -\beta(V - D_e))\exp(-\beta V) \\
&\quad \times \text{wk2}(r) r^2 dr
\end{aligned}
$$

(9)

$$
\begin{aligned}
Q_{\text{rovib}}^{\text{HD,WK}} &= \frac{1}{2\pi}\left(\frac{2\mu}{\beta}\right)^{3/2} \int_0^{\infty} [\exp(-\beta V)\text{wk2}(r) \\
&\quad - \exp(-\beta D_e)] r^2 dr
\end{aligned}
$$

(10)

## 3. RESULTS

All of the partition functions in this section will be presented with an additional $\exp(\beta\omega/2)$ factor to comply with the common tradition of presenting partition functions without zero point energy.

**3.1. Vibrational Partition Function.** A comparison of quantum and classical harmonic results allows the estimation of the reliability of the classical approach at various temperatures. At 5000 K, the classical approach differs from the quantum one by 1.6%. To avoid this error, all of the results will be calculated with the two-term Wigner–Kirkwood expansion, which proves valid for temperatures down to 1000 K (where the classical and quantum values differ by 45%). Apart form 1000 K, the results will be calculated in the range 5000–150 000 K, which is important both for hypersonic flows and the effects of anharmonicity, bond elongation, and unbound states that play a non-negligible role. The results for 20 000, 25 000, 30 000, 40 000, and 50 000 K will be presented to show the region in which the unbound states have a very significant role for the ground electronic state of the CO molecule. Note that for the

excited states and other molecules, the relevant temperature ranges of the above-mentioned effects will be different.

Table 1 compares the following approaches to the vibrational partition function: the quantum harmonic oscillator (QHO),

**Table 1. Vibrational Partition Function: the Quantum Harmonic Oscillator (QHO), Bound State–Based $Q_{vib}^{B,WK}$, Standard Expression $Q_{vib}^{S,WK}$ of eq 5, the $Q_{vib}^{HD,WK}$ Value Taking into Account All States (Both Bound and Unbound States on a Given PEC), and $Q_{vib}^{HD,WK}$ NE Which is an All-State Expression with the Negative Part Excluded**

| $T$ (K) | QHO | $Q_{vib}^{B,WK}$ | $Q_{vib}^{S,WK}$ | $Q_{vib}^{HD,WK}$ | $Q_{vib}^{HD,WK}$ NE |
|---|---|---|---|---|---|
| 1000 | 1.047 | 1.091 | 1.091 | 1.091 | 1.091 |
| 5000 | 2.162 | 2.208 | 2.208 | 2.208 | 2.208 |
| 6000 | 2.476 | 2.539 | 2.539 | 2.539 | 2.539 |
| 7000 | 2.792 | 2.876 | 2.876 | 2.876 | 2.876 |
| 8000 | 3.110 | 3.217 | 3.217 | 3.217 | 3.217 |
| 9000 | 3.428 | 3.563 | 3.563 | 3.563 | 3.563 |
| 10 000 | 3.748 | 3.913 | 3.913 | 3.913 | 3.913 |
| 11 000 | 4.067 | 4.268 | 4.268 | 4.268 | 4.268 |
| 12 000 | 4.388 | 4.627 | 4.632 | 4.626 | 4.626 |
| 13 000 | 4.708 | 4.991 | 5.005 | 4.989 | 4.989 |
| 14 000 | 5.029 | 5.360 | 5.385 | 5.355 | 5.357 |
| 15 000 | 5.350 | 5.734 | 5.781 | 5.725 | 5.728 |
| 20 000 | 6.957 | 7.685 | 8.153 | 7.604 | 7.632 |
| 25 000 | 8.565 | 9.763 | 11.67 | 9.447 | 9.562 |
| 30 000 | 10.17 | 11.93 | 16.86 | 11.14 | 11.44 |
| 40 000 | 13.39 | 16.35 | 33.05 | 13.81 | 14.79 |
| 50 000 | 16.61 | 20.61 | 56.30 | 15.43 | 17.50 |

bound state–based $Q_{vib}^{B,WK}$ of eq 4, the standard expression $Q_{vib}^{S,WK}$ of eq 5 based on simple integration of exponential factors without any discrimination of bound and unbound states, the $Q_{vib}^{HD,WK}$ value, taking into account all states (both bound and unbound states on a given PEC) by means of Hill decomposition (eq 2), and finally, $Q_{vib}^{HD,WK}$ NE which is an all-state expression with the negative part excluded according to ref 13 (in this reference, this was done for the ro-vibrational partition function).

Upper limit of integration over the interatomic distance is 30 a.u.

Table 1 allows us to draw the following conclusions: at 1000 K, the good performance of the quantum correction can be verified by comparison with the quantum harmonic oscillator. The higher temperatures (5000 K and higher) show the increasing importance of the anharmonicity in $Q_{vib}^{B,WK}$, which deviates from QHO values.

The next two columns (the standard expression $Q_{vib}^{S,WK}$ and all-state Hill decomposition–based $Q_{vib}^{HD,WK}$) show that unbound states exert an influence on this electronic state at high temperatures (starting around 13 000 K). These two expressions differ because standard expression also takes into account noninteracting atoms, and strictly speaking, its value is always infinity (if the upper limit of integration $r \to \infty$). This problem with the standard expression is seen as the highly increased value at the highest temperatures, so that at very high temperatures, this expression is useless.

The last column in Table 1 allows us to analyze the relative influence of bound and scattering states. In the expression eq 2, by setting the lower integration limit as $\sigma$, the negative contribution is removed. Note that the negative contribution arises from the negativity of $\exp(-\beta V) - \exp(-\beta D_e)$ when $V >$

$D_e$ (the quantum correction as insignificant at high temperatures was omitted). At temperatures from 14 000 K, it can be noted that the values without a negative part are closer to previous ones (with all states being included) than to the bound state–based ones. The scattering states result from the repulsive part of the potential but it proves that it is incorrect to identify their influence on the partition function mainly with the part of PEC over the dissociation limit (i.e., the part yielding a negative contribution to the partition function). It is actually the opposite—most of the contribution of the scattering states stems from the part of PEC below the dissociation limit.

Note that it is more difficult to transfer the reasoning above to the ro-vibrational partition function because in this case, apart from the bound and scattering states, there are also metastable states (which are the result of molecule rotations), but it can be expected that neglecting the negative part will exclude also no more than a half of contribution of the scattering states in the ro-vibrational partition function.

The research of ref 22 is one of the rare examples of the partition function calculation with the Wigner–Kirkwood expansion. In the case of the CO molecule, the vibrational partition functions at 5000 K reasonably agree (higher temperatures were not investigated), but at 1000 K, they do not, probably because that study uses only one term of the expansion.

For the convenient use of that results, the fit to a simple polynomial function is given: $Q_{vib}^{HD,WK} = 0.630707 + 0.000301163T + 2.99767 \times 10^{-9}\, T^2 - 2.89433 \times 10^{-14}\, T^3$, where $T \in [5000, 15\,000\,K]$.

**3.2. Influence on Rotations and the Resulting Ro-vibrational Partition Function.** In multitemperature models, the vibrational temperature differs from the rotational temperature. If the vibrational temperature is high, the average bond length will increase (1000 K − 2.149 a.u.; 10 000 K − 2.197 a.u.; 20 000 K − 2.285 a.u.). This increase suggests a straightforward way to correct the rotational partition function using the actual average bond length at a given temperature instead of the equilibrium one in eq 7.

The ro-vibrational partition function based on the separated rotational and vibrational partition function ($Q_{vib}^{B,WK}\, Q_{rot}$) is compared with the exact value $Q_{rovib}^{B,WK}$ (according to[14]) and the values given in the HITRAN database[23] in Table 2.

**Table 2. Bound State–Based Ro-vibrational Partition Functions: the Separated Rotational and Vibrational Partition Function ($Q_{vib}^{B,WK}\, Q_{rot}$), the Exact Ro-vibrational Partition Function $Q_{rovib}^{B,WK}$, and the Values from the HITRAN Database (HITRAN)**

| $T$ (K) | $Q_{vib}^{B,WK}\, Q_{rot}$ | $Q_{rovib}^{B,WK}$ | HITRAN |
|---|---|---|---|
| 5000 | $4.001 \times 10^3$ | $3.648 \times 10^3$ | $4.001 \times 10^3$ |
| 6000 | $5.521 \times 10^3$ | $5.064 \times 10^3$ | $5.644 \times 10^3$ |
| 7000 | $7.295 \times 10^3$ | $6.731 \times 10^3$ | $7.501 \times 10^3$ |
| 8000 | $9.326 \times 10^3$ | $8.661 \times 10^3$ | $9.645 \times 10^3$ |
| 9000 | $1.162 \times 10^4$ | $1.086 \times 10^4$ | $1.208 \times 10^4$ |
| 10 000 | $1.418 \times 10^4$ | $1.335 \times 10^4$ | |
| 11 000 | $1.701 \times 10^4$ | $1.612 \times 10^4$ | |
| 12 000 | $2.012 \times 10^4$ | $1.921 \times 10^4$ | |
| 13 000 | $3.351 \times 10^4$ | $2.261 \times 10^4$ | |
| 14 000 | $2.719 \times 10^4$ | $2.634 \times 10^4$ | |
| 15 000 | $3.117 \times 10^4$ | $3.040 \times 10^4$ | |
| 20 000 | $5.569 \times 10^4$ | $5.585 \times 10^4$ | |

The effective influence of ro-vibrational coupling makes the $Q_{rovib}$ smaller than the separated rotation one.[9] This effect is also seen in Table 2 so that simple correction (increase) of $Q_{rot}$ would not work. The ro-vibrational energy has various contributions with different signs (Dunham expansion), and effectively, the exact $Q_{rovib}$ is lower than its counterpart without ro-vibrational coupling effects.

Interestingly, the effect of ro-vibrational coupling is different in the all-state (bound and unbound)-based partition function. Table 3 shows that the exact $Q_{rovib}^{HD,WK}$ is higher than the separated

**Table 3. All-State (Bound and Unbound)-Based Ro-vibrational Partition Functions: the Separated Rotational and Vibrational Partition Function ($Q_{vib}^{HD,WK} Q_{rot}$), the Separated Rotational and Vibrational Partition Function with Bond-Length Correction ($Q_{vib}^{HD,WK} Q_{rot}^{C}$), the Exact Ro-vibrational Partition Function $Q_{rovib}^{HD,WK}$, and the Values from the HITRAN Database (HITRAN)**

| $T$ (K) | $Q_{vib}^{HD,WK} Q_{rot}$ | $Q_{vib}^{HD,WK} Q_{rot}^{C}$ | $Q_{rovib}^{HD,WK}$ | HITRAN |
|---|---|---|---|---|
| 5000 | $4.001 \times 10^3$ | $4.104 \times 10^3$ | $4.116 \times 10^3$ | $4.001 \times 10^3$ |
| 6000 | $5.521 \times 10^3$ | $5.692 \times 10^3$ | $5.714 \times 10^3$ | $5.644 \times 10^3$ |
| 7000 | $7.295 \times 10^3$ | $7.561 \times 10^3$ | $7.596 \times 10^3$ | $7.501 \times 10^3$ |
| 8000 | $9.326 \times 10^3$ | $9.721 \times 10^3$ | $9.773 \times 10^3$ | $9.645 \times 10^3$ |
| 9000 | $1.162 \times 10^4$ | $1.218 \times 10^4$ | $1.226 \times 10^4$ | $1.208 \times 10^4$ |
| 10 000 | $1.418 \times 10^4$ | $1.495 \times 10^4$ | $1.506 \times 10^4$ | |
| 11 000 | $1.701 \times 10^4$ | $1.805 \times 10^4$ | $1.820 \times 10^4$ | |
| 12 000 | $2.012 \times 10^4$ | $2.149 \times 10^4$ | $2.168 \times 10^4$ | |
| 13 000 | $2.350 \times 10^4$ | $2.528 \times 10^4$ | $2.554 \times 10^4$ | |
| 14 000 | $2.717 \times 10^4$ | $2.943 \times 10^4$ | $2.977 \times 10^4$ | |
| 15 000 | $3.112 \times 10^4$ | $3.397 \times 10^4$ | $3.441 \times 10^4$ | |
| 20 000 | $5.511 \times 10^4$ | $6.285 \times 10^4$ | $6.409 \times 10^4$ | |

one. Moreover, surprisingly the separated ro-vibrational partition function can be corrected very effectively using an average bond length of eq 8 in $Q_{rot}$. Such a result means that all of the effects other than bond elongation are very small for the all-state partition function (at least effectively; most probably, there is no simple explanation for that as various effects are not additives).

That simple behavior of all-state partition functions can be seen as an additional argument for using such partition functions (another argument used so far is to obtain ideal-gas thermodynamics). It has to be noted that for highly anharmonic molecules, correction for the bond length will work with good accuracy only at relatively low temperatures, for example, in the case of the $H_2^+$ molecule (calculated on Xie-Gong PEC[14]), at 1000 K, the corrected ro-vibrational partition function is 14.1 (the rigid-rotor HO value is 12.07, and the exact value is 13.9), but at 5000 K, the corrected value is 166 (the rigid-rotor HO value is 120, and the exact value is 176); but still, it provides a significant correction against the standard rigid rotor harmonic oscillator method. From Tables 1 and 3, it can be observed that because (except for 50 000 K) $Q_{vib}^{QHO} < Q_{vib}^{HD,WK}$, there are relations: $Q_{vib}^{QHO} Q_{rot} < Q_{vib}^{HD,WK} Q_{rot} < Q_{vib}^{HD,WK} Q_{rot}^{C} < Q_{rovib}^{HD,WK}$, that is, $Q_{vib}^{QHO} Q_{rot}$ (that is rigid-rotor HO) is the worst, and $Q_{vib}^{HD,WK} Q_{rot}^{C}$ is the best approximation to $Q_{rovib}^{HD,WK}$ (note that the previous inequalities are not always fulfilled in the case of the $H_2^+$ molecule but still bond-length correction works).

Finally, comparison with the HITRAN database is much better for the all-state partition function (Table 3) than with the bound-state version (Table 2). Indeed, the check at temper-

atures below 5000 K shows that the HITRAN database includes metastable states for the carbon monoxide molecule.

## 4. CONCLUSIONS

The method of calculation of the all-state vibrational partition function was presented, and the high-temperature effect of scattering states on the partition function was quantitatively investigated. In particular, it was found that the scattering states effect results from the part of PEC over the dissociation limit only to a small degree.

The increase of bond length at high temperatures was studied and used to correct the rotational partition function. If the separated rotations and vibrations are assumed, only the all-state based partition function can be corrected by bond elongation to obtain the correct ro-vibrational partition function.

In general, the method presented here is aimed at multi-temperature models, in which vibrational and rotational partition functions are calculated at different temperatures. In this case, correction of the rotational function can also be advised especially if the vibrational temperature is high and the bond elongation effect will be considerable.

Finally, note the numerical advantage of a single one-dimensional integration instead of solving of multiple differential equations to obtain energies for the partition function as is traditionally done.

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**Notes**

The author declares no competing financial interest.

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