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Influence of scattering on the vibrational partition function at extreme temperatures

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Abstract. The vibrational partition function is calculated for three diatomic molecules of different character (CO, H_2^+, NH) and contributions of scattering interactions between atoms is analyzed. The classical method with the quantum Wigner-Kirkwood correction is used in version with only bound states. The partition function based on bound states of the present method is compared with the partition function based on the vibrational levels. It is also found that contribution of scattering states in the vibrational partition function is similar independently of molecule.

1 Introduction

The vibrational partition function can be calculated taking into account only bound or both bound and scattering states. Analysis of those contributions to that quantity is significantly easier than in case of the rovibrational partition function which contains also metastable states related to rotation of molecule [1, 2].

The scattering states exert non-negligible contributions only at very high temperatures (from the perspective of existence of the molecule), so that the sudy will be performed up to 30,000K for NH molecule and up to 50,000K for CO and H_2^+ molecules. Because of that the considerations of the scattering states will be relevant for systems like plasmas [3, 4] and hypersonic flows [5–10].

For such high temperatures the quality of potential energy curve (PEC) is of crucial importance. The present method do not use vibrational levels for bound contribution but in standard approach (used here for comparison) vibrational levels are calculated. Recently such studies were performed for K_2 molecule [11], Cs_2 molecule [12], H_2 and CO molecules [13, 14], and some cesium compounds [15], and several molecules in Ref. [16]; some number of more and less common molecules are considered in Refs. [17, 18] - the exact solvability of certain functional forms of PEC is was utilized.

Analytical calculations of vibrational energy levels is quite complicated and can be prone to errors [19, 20] and are done only for certain potentials.

Note finally that calculation of the scattering contribution to partition function in the quantum approach is not straightforward whereas the present method takes this contribution into account automatically.

The goal of the present research is to show at what temperature influence of the scattering states is non-negligible and quantify this contribution on vibrational partition function.

The rest of the article is organized as follows: the Methods section presents the method used for calculations, the Results section discusses the results, and finally Conclusions section summarize the study. The supplementary information (pdf file generated from Mathematica notebook) gives all the details of calculation for CO molecule. Note that the atomic units are used in this study.

2 Methods

Potential energy curves used in this study for CO [21], H_2^+ [22], and NH [23] are:

$$\begin{aligned} V_{CO}(r) = \; & 0.411383 - 0.411383 e^{-2.20355(r-2.13955)} \cdot \\ & \cdot \left(0.408807(r-2.13955)^3 + 0.962467(r-2.13955)^2 + 2.20355(r-2.13955) + 1\right), \end{aligned} \tag{1}$$

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$$V_{H_2^+}(r) = \frac{e^{-4.5r}\left(\frac{1}{r}+1\right) + e^{-1.05111r}\left(\frac{1}{r} - 0.917034r\right)}{e^{-r}\left(\frac{r^2}{3}+r+1\right)+1} + 0.1026, \tag{2}$$

$$\begin{aligned} V_{NH}(r) = \; & 0.12954 - 0.12954e^{-2.68774(r-1.96343)} \, . \\ & \cdot \left(0.733444(r-1.96343)^3 + 2.05526(r-1.96343)^2 + 2.68774(r-1.96343)+1\right). \end{aligned} \tag{3}$$

The classical method of integration over the phase space gives the following expression for the vibrational partition function [24]:

$$Q = \frac{1}{2\pi}\sqrt{\frac{2\pi\mu}{\beta}}\int_0^\infty [\exp(-\beta V(r))wk(r) - \exp(-\beta D_e)]dr, \tag{4}$$

where $\beta = (1/k_B T)$ is the inverse temperature, D_e is the depth of the potential well, and μ is the reduced mass of molecule.

The above expression takes into account all interaction between atoms (bound and scattering), the bound version of the vibrational partition function is given by [25, 26]:

$$Q_B = \frac{1}{2\pi}\sqrt{\frac{2\pi\mu}{\beta}}\int_\sigma^\infty erf\left(\sqrt{-\beta(V-D_e)}\right)\exp(-\beta V)wk(r)dr, \tag{5}$$

where σ is given by the $V(\sigma) = D_e$ condition and, erf is the error function.

In the above expressions $exp(-\beta V)$ was multiplied by $wk(r)$, which is the three-term Wigner-Kirkwood quantum correction which reads [27]

$$\begin{aligned} wk(r) = \; & 1 - \frac{\beta^3}{24\mu}(V')^2 + \frac{\beta^4}{5760\mu^2}\left(\beta^2(V')^4 - 8\beta(V')^2V'' + 12(V'')^2\right) + \frac{1}{362880}\left(\frac{\beta}{2\mu}\right)^3[3\beta^6(V')^6 + \\ & + 12\beta^4(V')^2(V'')^2 - 216\beta^2(V''')^2 - 50\beta^5(V')^4V'' + 480\beta^3V'V''V'''], \end{aligned} \tag{6}$$

Negative contribution to partition function can be removed by starting the integration from σ to remove contribution form the PEC above dissociation limit [24, 28]:

$$Q_{NE} = \frac{1}{2\pi}\sqrt{\frac{2\pi\mu}{\beta}}\int_\sigma^\infty [\exp(-\beta V(r))wk(r) - \exp(-\beta D_e)]dr, \tag{7}$$

Method of corrections for vibrational partition function based on the energy levels was considered by Horchani and Jelassi [29].

The vibrational energy levels, which are used for comparison, were calculated with the general purpose Mathematica software using function NDEigensystem (details are given in supplementary information), the vibrational partition function is then calculated as:

$$Q_{SUM} = \sum_v \exp(-\beta E_v), \tag{8}$$

where E_v are the vibrational energy levels of molecule.

The calculation of rovibrational levels is significantly more difficult and approximations are needed [11, 12, 30–32]; also accuracy worsens with increasing rotational excitation.

The present approach to vibrational partition function was already used in Ref. [24] but in that study the scattering states were not investigated in depth and calculation of vibrational energy levels were not considered at all.

3 Results

Tables 1, 2, and 3 compare the vibrational partition functions of CO, H_2^+, and NH molecules, respectively. The Q_{SUM} are values based on calculated energy levels according to Eq. 8 and as such they are fully quantum quantities.

The following values are based on the classical approach with quantum corrections: Q_B is based on the bound states of interacting atoms according to Eq. 5, Q is based on bound and scattering states according to Eq. 4, and Q_{NE} is based on bound and partially on scattering states (by negative contribution exclusion) according to Eq. 7.

As expected $Q_{SUM} \approx Q_B$; for each molecule there is a broader or narrower temperature range of agreement. In particular, the CO molecule (with deep potential well) shows an excellent agreement at a very broad temperature range. With increasing temperature the quantum corrected classical method is superior (high temperature is the

Table 1. The vibrational partition function of CO molecule according to Eq. 8 (Q_{SUM}), Eq. 5 (Q_B), Eq. 4 (Q), and Eq. 7 (Q_{NE}).

T(K)	Q_{SUM}	Q_B	Q	Q_{NE}
800	**0.1**47892	**0.1**39654	0.139654	0.139654
1000	**0.22**3421	**0.22**147	0.22147	0.22147
5000	**1.61907**	**1.61907**	1.61907	1.61907
10,000	**3.35077**	**3.35077**	3.35068	3.35071
20,000	**7.11**188	**7.11**117	7.03617	7.06258
30,000	**11.33**65	**11.33**00	10.5794	10.8589
40,000	**15.7**437	**15.7**239	13.2853	14.2311
50,000	20.0168	19.9786	14.9567	16.9675

classical regime and numerically it is a simple integration) to energy levels based method (which numerically involves quantum energy levels from eigenproblem). In contrary, at low temperatures the Q_{SUM} is superior because the classical mechanics based methods cannot include properly quantum effects (also at low temperatures only lower energy levels matter). In conclusion, those methods should be seen as complementary.

The scattering states in Q exert very significant effect only at extreme temperatures of tens of thousands Kelvins (compare to the bound states only quantity Q_B). Excluding the negative contribution [24, 28] removes some of the scattering states effect.

Figure 1 shows the percent of scattering calculated at a few βD_e values; D_e is included to take into account the different values of D_e (smaller depth of potential well means more scattering in relation to bound states). Percent of scattering is calculated as:

$$\frac{Q - Q_B}{Q_B} \cdot 100\%. \tag{9}$$

The results show that for high enough values of βD_e the contributions for different molecules turns out to be similar.

The above observation allows to fit exponential expression to contributions of scattering states (s):

$$s = \frac{Q - Q_B}{Q_B} = 1.74exp(-2.29(\beta D_e)^2) - 1.35exp(-0.686\beta D_e), \tag{10}$$

in the range $\beta D_e \in [1, 10]$. The points and function of scattering contribution in the vibrational partition function $s(\beta D_e)$ are given in Figure 2. For this figure and fit more points were used than in Figure 1.

The fit for the $\beta D_e \in [2, 10]$ translates to temperature range 13,000K-65,000K for CO, 3200K-16,000K for H2+, and 4000K-21,000K for NH.

That result allows to estimate for various molecules:

$$Q_B(\beta; D_e) = \frac{1}{s(\beta D_e) + 1} Q(\beta; D_e). \tag{11}$$

In case of the rovibrational partition function where rotations generate effective potential energy curves the hypothesis that scattering exerts similar influence seems reasonable. It can be suggested that rovibational partition function with scattering excluded $Q_{rovib,SE}$ can also be approximated as

$$Q_{rovib,SE}(\beta; D_e) = \frac{1}{s(\beta D_e) + 1} Q_{rovib}(\beta; D_e), \tag{12}$$

where Q_{rovib} is rovibrational function with bound, metastable, and scattering contribution included. Unfortunately, the differences of rovibrational partition functions at extreme temperatures from different sources are large and confirmation of this hypothesis seems impossible because it is masked by uncertainty of partition functions even at temperatures lower than needed to the presence scattering states.

4 Conclusions

The vibrational partition functions based on only bound an bound and scattring states are compared and agreement of the bound states based partition function with summation of the vibrational energy levels is studied. The simple method of calculation of energy levels (implemented in Mathematica package) is found to be sufficient only if temperature is not extremely high.

Table 2. The vibrational partition function of H_2^+ molecule according to Eq. 8 (Q_{SUM}), Eq. 5 (Q_B), Eq. 4 (Q), and Eq. 7 (Q_{NE}).

T(K)	Q_{SUM}	Q_B	Q	Q_{NE}
800	**0.1**33537	**0.1**1932	0.11932	0.11932
1000	**0.20**5489	**0.20**1951	0.201951	0.201951
5000	**1.63**445	**1.63**361	1.61949	1.62206
10,000	**3.6**4335	**3.6**3196	3.19964	3.28541
20,000	**7**.13239	**7**.08014	4.47309	5.0452
30,000	**9**.43544	**9**.34807	4.42996	5.57461
40,000	**10**.9717	**10**.8588	4.00131	5.66233
50,000	**1**2.0528	**1**1.9211	3.48217	5.58734

Table 3. The vibrational partition function of NH molecule according to Eq. 8 (Q_{SUM}), Eq. 5 (Q_B), Eq. 4 (Q), and Eq. 7 (Q_{NE}).

T(K)	Q_{SUM}	Q_B	Q	Q_{NE}
1400	**0.1**87617	**0.1**68317	0.183021	0.183021
2000	**0.33**5558	**0.33**1381	0.335083	0.335083
5000	**1.053**40	**1.053**17	1.05087	1.05170
10,000	**2.3**4475	**2.3**3385	2.15611	2.22343
20,000	**4**.87359	**4**.78016	3.0681	3.77905
30,000	**6**.76394	**6**.5755	2.74049	4.42200

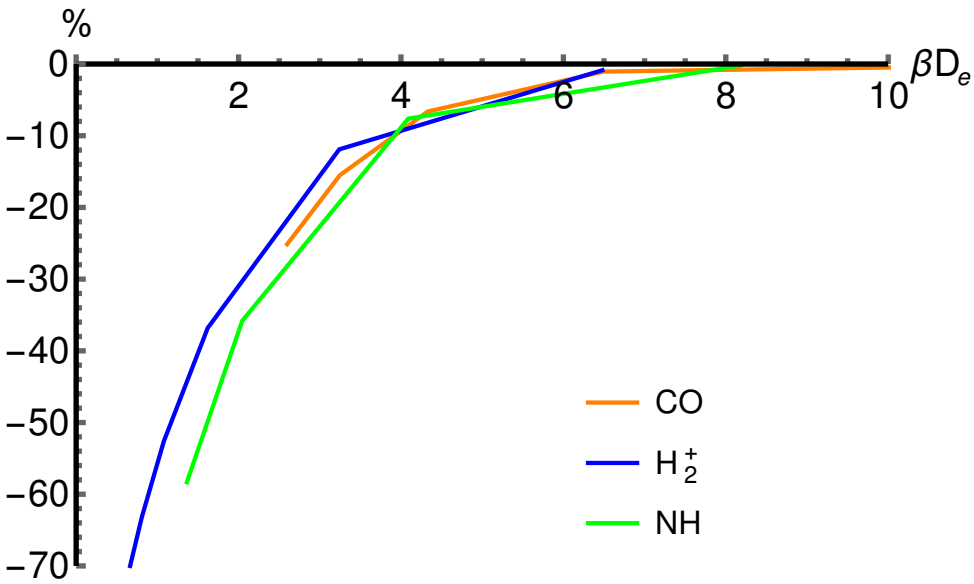

Fig. 1. Percent of scattering with respect to bound states in the vibrational partition functions.

The influence of the scattering states on the vibrational partition function is quantified for three molecules in a wide temperature range. The scattering states exert significant influence only at extreme temperatures.

Interestingly, it if found that scattering contribution is quite insensitive to the potential energy and can be estimated by a common factor for each molecule (that factor is dependent on βD_e).

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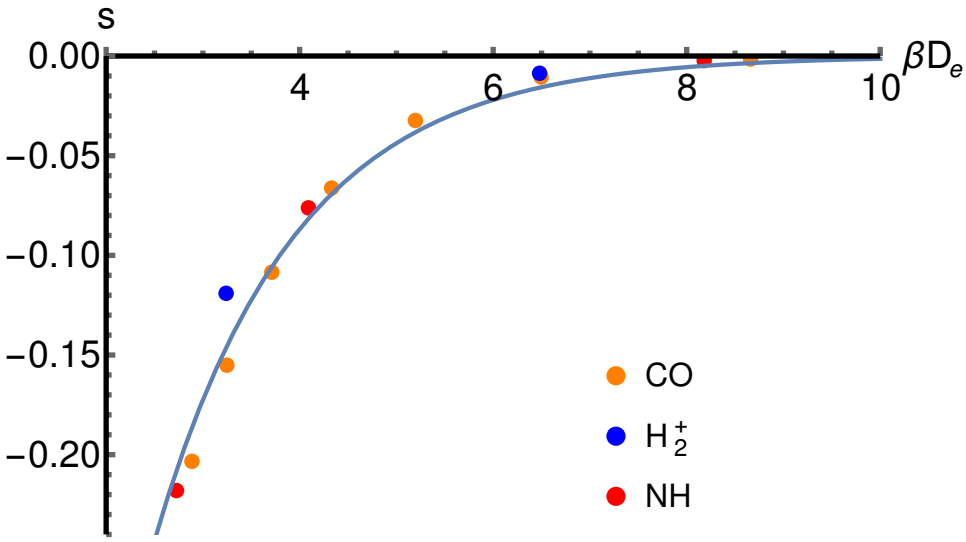

Fig. 2. Contribution of scattering states (s) in the vibrational partition functions with fit to the points (blue line).

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