Research paper

Partition functions of thermally dissociating diatomic molecules and related momentum problem

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A B S T R A C T

The anharmonicity and ro-vibrational coupling in ro-vibrational partition functions of diatomic molecules are analyzed for the high temperatures of the thermal dissociation regime.

The numerically exact partition functions and thermal energies are calculated. At the high temperatures the proper integration of momenta is important if the partition function of the molecule, understood as bounded system, is to be obtained. The problem of proper treatment of momentum is crucial for correctness of high temperature molecular simulations as the decomposition of simulated molecule have to be avoided; the analysis of O_2, H_2^+, and NH_3 molecules allows to show importance of βD_e value.

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1. Introduction

The classical internal partition functions of dissociating molecules were initially considered by Hill [1]. The main idea of that work is that when temperature is high enough or when the potential well is shallow enough the configurations of atoms pertaining to a molecule should be bounded in the sense that internal kinetic energy cannot exceed the potential energy of a system. This work considered clusters of atoms and its main follow up was in this field. The strictly molecular applications were van der Walls complexes [2–4] and molecules containing hydrogen [4,5] which, because of the light atoms, are typically correctly treated by classical mechanics in quite high temperatures. Also molecular simulations (Metropolis Monte Carlo or molecular dynamics) of single molecule are not performed in the thermal dissociation limit.

The procedure of calculating partition function involves integrating out momenta with the aforementioned bound system condition. Note that the proper integration of momenta was possible only for diatomic molecules. The resulting effective potentials of diatomic molecules are helpful in analysis of the problem of momenta integration.

In this Letter (Section 2 and 3) I calculate vibrational and ro-vibrational partition functions of diatomic molecules (O_2 and H_2^+) at the temperatures at which the molecules can be described classically. Anharmonicity and ro-vibrational coupling is analyzed up to 60,000 K. Note that purely vibrational partition function is not

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usually calculated but it can be useful in plasma chemistry in cases when vibrational and rotational temperatures are different [6]. Recently there are some theoretical developments in calculations of classical vibrational partition functions of weakly bounded diatomic molecules [7–9]. The temperatures of tens of thousands Kelvins are of interest for plasma thermodynamics [10].

Additionally (Section 3), the applicability of unrestricted integration of momenta is analyzed for molecular simulations which is the standard procedure [11]. The problem to be solved is avoiding decomposition of molecule at high temperatures, the sensitivity to different restrictions for interatomic distances is investigated.

The Morse and Wei-Hua potential energy curves (PEC) for O_2 and H_2^+ molecules used in this Letter are given by [12,13]

$$V_{O_2}^M(r) = 0.1916(1 - \exp(-1.4094r))^2, \tag{1}$$

and

$$V_{O_2}^{WH}(r) = 0.1916\left(\frac{1 - \exp(-1.4094r)}{1 - 0.0273\exp(-1.4094r)}\right)^2, \tag{2}$$

$$V_{H_2^+}^{WH}(r) = 0.1026\left(\frac{1 - \exp(-0.7330r)}{1 + 0.05\exp(-0.7330r)}\right)^2,$$

where r is the deviation from equilibrium geometry. The potential energy surface (PES) for ammonia is taken from Ref. [14].

Even if at high temperatures excited electronic states influence partition functions, only ground states were used here because the aim of this research is to analyze anharmonicity and ro-vibrational

coupling (it is done most naturally for a given PEC) not to calculate full partition function.

The atomic units are used if not specified otherwise.

2. Vibrations of O_2 and H_2^+

For calculations of classical vibrational partition function the hamiltonian $H = p^2/(2\mu) + V(r)$ is used. The reduced masses are $\mu_{O_2} = 14,580$ a.u. and $\mu_{H_2^+} = 918.6$ a.u. The resulting expression is

$$
\begin{aligned}
Q_v &= \frac{1}{h} \int \exp(-\beta H) dp dr \\
&= \frac{1}{h} \int_{-r_e}^{\infty} \exp(-\beta V) \left[\int_{-\infty}^{\infty} \exp(-\beta p^2/(2\mu)) dp \right] dr \\
&= \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_{-r_e}^{\infty} \exp(-\beta V) dr,
\end{aligned}
\tag{3}
$$

where r_e is the equilibrium bond length (note that $1/h = 1/(2\pi)$ in atomic units). The value of the above expression is always ∞ because $\int_{-r_e}^{\infty} \exp(-\beta V) = \infty$ for any real PEC with the $\lim_{r\to\infty} V \neq \infty$ property. Even though this expression is useful in practice because at the temperatures typically considered any reasonable choice of cut-off will result in the same value.

At the high temperatures if only bound states of molecule (i.e. non-dissociated molecule) are to be considered the condition that the internal energy should be lower than PEC depth $H < D_e$ (equivalent to $p^2/(2\mu) < -V'(r)$, where $V'(r) = V - D_e$) condition is applied [5]

$$
\begin{aligned}
Q_v^B &= \frac{\exp(-\beta D_e)}{h} \int_{H<D_e} \exp(-\beta(H - D_e)) dp dr \\
&= \frac{\exp(-\beta D_e)}{h} \int_{-r_e}^{\infty} \\
&\quad \times \exp(-\beta V') \left[\int_{-\sqrt{-2\mu V'(r)}}^{\sqrt{-2\mu V'(r)}} \exp(-\beta p^2/(2\mu)) dp \right] dr \\
&= \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_{-r_e}^{\infty} \exp(-\beta V) \mathrm{erf}(\sqrt{-\beta V'(r)}) dr.
\end{aligned}
\tag{4}
$$

In this case the resulting integral is finite because the error function (erf) at high intermolecular distances tends appropriately to zero. Additionally in both Eqs. (3) and (4) to obtain only bound states the condition $V'(r) = 0$ should be applied which results in certain σ instead of $-r_e$.

The results of the above equations are compared with harmonic approximation

$$
\begin{aligned}
Q_{v,harm} &= \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \int_{-\infty}^{\infty} \exp(-\beta k r^2/2) dr = \frac{1}{2\pi} \sqrt{\frac{2\pi\mu}{\beta}} \sqrt{\frac{2\pi}{k\beta}} \\
&= \frac{1}{\beta} \sqrt{\frac{\mu}{k}} = \frac{1}{\beta\omega}
\end{aligned}
\tag{5}
$$

and approximated closed form expression of Morse vibrational partition function [15]

$$
Q_{v,Morse,approx} = \frac{1}{2\sinh(\omega\beta/2)} \exp\left[\frac{\omega^2 \beta}{4 D_e} \left(\frac{1}{4} + \frac{1}{2\sinh^2(\omega\beta/2)} \right) \right]
\tag{6}
$$

In case of O_2 molecule the lowest temperature considered is 5000 K at which system can be considered classical because $\omega\beta < 0.5 \ll 1$. With this condition the difference between quantum harmonic and classical harmonic vibrational partition functions is less than 1%. If classical calculations are done at lower temperatures one have to accept a more significant error. In Eqs. (3) and (4) integrations were performed from $\sigma = -0.4918$ for Morse PEC and $\sigma = -0.4727$ for Wei-Hua PEC up to 10 a.u.

For O_2 molecule the results are given in Table 1. For both Morse and Wei-Hua PECs deviations from harmonic values are significant. Note also that at the highest temperatures the exact Wei-Hua values of Eq. (4) (and also the exact Morse ones) are getting closer to harmonic values and finally are lower than harmonic value (at lower temperatures the anharmonic values are higher then harmonic ones); this observation is in agreement with Ref. [15] where analysis of vibrational Morse function shown that there is a certain temperature at which exact Morse and harmonic values cross. Ref. [15] reports also existence of the crossover temperature at which approximated values of Eq. (6) and exact Morse values cross and increasingly diverge – this effect is also seen in table with increasing divergence from 10,000 K. The Morse and approximated Morse values will not be calculated from now on.

Table 1
Classical vibrational partition functions of O_2 in harmonic approximation of Eq. (5) and Morse and Wei-Hua values of Eqs. (3), (4), and (6); % values are deviations from harmonic value.

T (K)	$Q_{v,harm}$	$Q_{v,Morse,approx}$	$Q_{v,Morse}$ (4)	$Q_{v,Morse}$ (3)	$Q_{v,WH}$ (4)	$Q_{v,WH}$ (3)
5000	2.191	2.265	2.297	2.297	2.237	2.237
		3.4%	4.8%	4.8%	2.1%	2.1%
6000	2.630	2.748	2.788	2.790	2.716	2.718
		4.5%	6.0%	6.1%	3.3%	3.4%
7000	3.068	3.237	3.293	3.303	3.210	3.219
		5.5%	7.3%	7.7%	4.6%	4.9%
8000	3.506	3.734	3.814	3.846	3.719	3.750
		6.5%	8.8%	9.7%	6.1%	7.0%
9000	3.945	4.239	4.352	4.431	4.244	4.323
		7.5%	10%	12%	7.6%	9.6%
10,000	4.383	4.751	4.906	–	4.786	–
		8.4%	12%		9.2%	
15,000	6.574	7.436	7.837	–	7.659	–
		13%	19%		17%	
20,000	8.766	10.34	10.77	–	10.54	–
		18%	23%		20%	
30,000	13.15	16.84	15.63	–	15.31	–
		28%	19%		16%	
60,000	26.30	43.18	20.97	–	20.56	–
		64%	−20%		−22%	