

Unbound (resonance and scattering) states in high temperature thermodynamics.

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Abstract: The influence of unbound states (resonance and scattering) on partition function and heat capacity is investigated at high temperatures with the classical approach. The proposed approach avoids using the second virial coefficient. Inclusion of scattering states gives the negative contribution to the partition function; an straightforward way of eliminating this contribution is proposed.

Keywords: molecular partition function, unbound states, repulsive interaction.

1. Introduction

The partition functions at high temperatures are long known to be difficult to calculate even for a simple molecules. Fig. 1 shows the scale of the problem for some of molecules up to for temperatures 50000K.

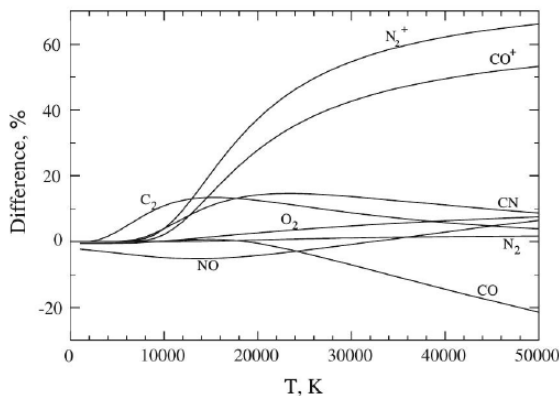


Fig. 1. Comparison of two calculations of the partition functions [1].

Most of the problem is the lack of accurate potential energy curves for all excited states needed.

Typical approach for this problem is the summation of rovibrational energy levels which may include only truly bound states or bound and metastable (resonance states).

Recently, there is a growing recognition for free (scattering) states. The inclusion of those states allows to treat the gas as an ideal one. The problem with this approach is that for a very shallow potentials the partition function can become negative [2,3].

Most convenient way to include both resonance and scattering states is the classical approach. This approach is typically connected to consideration of second virial coefficient [2,4].

2. Method.

The calculations avoiding the use of second virial coefficient, based on ideas of T. Hill [5], were proposed in [6,7]. The expression for rovibrational partition function (with resonance and scattering contributions) is:

$$Q_{rovib} = \frac{1}{2\sqrt{\pi}} \left(\frac{2\mu}{\beta} \right)^{3/2} \int_0^\infty [\exp(-\beta V) - 1] r^2 dr,$$

where β is the inverse temperature, μ is the reduced mass of diatomic molecule, and V is the potential energy of the molecule.

The positive part of potential energy curve (Fig.2) is the source of negative contribution to partition function which can be easily eliminating by changing lower integration limit, this procedure approximately removes scattering contribution.

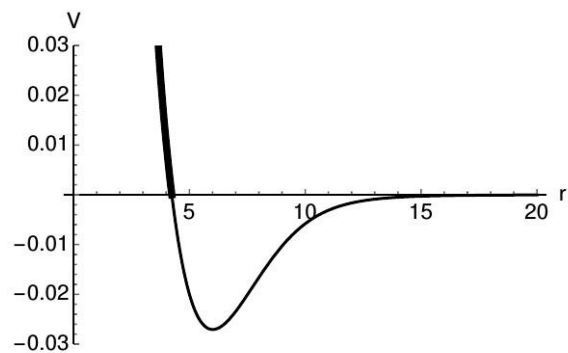


Fig. 2. The part of potential energy curve (here of Na₂ molecule) which is the source of negative contribution to partition function.

The more appropriate ways of removing scattering contribution were proposed for diatomic molecules [8,9] but they are much more difficult in practical use.

3. Results.

The partition functions of Na₂ molecule are presented in Table 1 – with all interactions included (Q), with negative part excluded (Q_{NE}); additionally the negative contribution alone (Q_N) and its approximation with hard spheres potential (Q_{NHS}) are shown [8].

Table 1. The rovibrational partition functions with with all interactions included (Q), with negative part excluded (Q_{NE}); additionally the negative contribution alone (Q_N) and its approximation with hard spheres potential (Q_{NHS}) are shown.

T/K	Q	Q _{NE}	Q _N	Q _{NHS}
1000	$6.315 \cdot 10^7$	$6.316 \cdot 10^7$	$-0.0005 \cdot 10^7$	$-0.0005 \cdot 10^7$
2000	$3.978 \cdot 10^6$	$3.992 \cdot 10^6$	$-0.014 \cdot 10^6$	$-0.016 \cdot 10^6$
3000	$2.177 \cdot 10^6$	$2.202 \cdot 10^6$	$-0.025 \cdot 10^6$	$-0.029 \cdot 10^6$
4000	$1.778 \cdot 10^6$	$1.815 \cdot 10^6$	$-0.037 \cdot 10^6$	$-0.044 \cdot 10^6$
5000	$1.642 \cdot 10^6$	$1.692 \cdot 10^6$	$-0.049 \cdot 10^6$	$-0.061 \cdot 10^6$
6000	$1.593 \cdot 10^6$	$1.655 \cdot 10^6$	$-0.063 \cdot 10^6$	$-0.081 \cdot 10^6$
7000	$1.579 \cdot 10^6$	$1.656 \cdot 10^6$	$-0.077 \cdot 10^6$	$-0.102 \cdot 10^6$
8000	$1.584 \cdot 10^6$	$1.675 \cdot 10^6$	$-0.091 \cdot 10^6$	$-0.124 \cdot 10^6$
9000	$1.598 \cdot 10^6$	$1.695 \cdot 10^6$	$-0.106 \cdot 10^6$	$-0.148 \cdot 10^6$
10000	$1.617 \cdot 10^6$	$1.738 \cdot 10^6$	$-0.121 \cdot 10^6$	$-0.174 \cdot 10^6$

Negative contribution is growing with temperature and at the lower temperatures hard spheres approximation is valid.

Comparison with the results for MgH [3] at the same relation of temperature and potential well depth shows that the present approach is the minimal way of excluding negative contribution to partition function.

Heat capacity at constant pressure of Na₂ molecule was calculated taking into account all the electronic states dissociating to the 3s+3s and 3s+3p limits (some of them in an approximate way) [10]. Table 2 compares the results with NIST database results and the ones of Biolsi [4]. In this case the need to include many electronic states make it impossible to assess the actual influence of unbound states. The results of Biolsi take into account also all unbound states but the excited states make the comparison impossible.

Finally results of influence of unbound states will be presented for H₂⁺ molecular ion [11] and compared with other known results without scattering states.

Table 2. Heat capacity of the present study (C_p U K), the NIST data (NIST) and the results of Biolsi (Biolsi).

T (K)	C _p U K	NIST	Biolsi
2000K	33.63	32.78	35.16
2500K	31.60	31.70	31.78
3000K	34.13	34.42	29.52
3500K	40.94	40.75	28.09
4000K	49.61	47.51	27.19
4500K	56.83	52.18	26.57
5000K	60.39	54.01	26.14
5500K	60.12	53.09	-
6000K	57.19	49.94	25.54

3. References

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