On the application of statistical mechanics to diatomic molecules

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Abstract

We argue that the results proposed recently for the \( \tilde{a}^{3}\Sigma_{u}^{+} \) electronic state of \( ^{7}\text{Li}_{2} \) do not exhibit any physical utility because the canonical vibrational partition function for an excited electronic state makes no sense according to the principles of statistical mechanics. Such an approach may, in principle, be applied to the ground state of a diatomic molecule. We show that the simpler model based on the harmonic oscillator and rigid rotor enables one to derive a theoretical expression for the equilibrium constant of a simple chemical reaction that agrees remarkably well with experimental data. It is not clear whether the complicated formulas mentioned above are suitable for any comparison with experimental data.

1 Introduction

In a recent paper Jia et al [1] derived analytical expressions for the vibrational mean energy, vibrational specific heat, vibrational free energy and vibrational entropy for diatomic molecules. To this end they resorted to the analytic vibrational energy eigenvalues obtained from the Schrödinger equation with the so-called improved Manning-Rosen potential-energy function. In order to obtain

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analytical expressions for those thermodynamic functions the authors resorted to the Poisson summation formula \[2\]. As a particular example Jia et al \[1\] chose the state $a^3\Sigma_u^+$ of $^7\text{Li}_2$.

The purpose of this paper is the analysis of the validity of such results. In section 2 we briefly address the problem of deriving the canonical partition function for a diatomic molecule. In section 3 we summarize the textbook calculation of the equilibrium constant for a simple chemical reaction and compare theoretical results with available experimental data. Finally, in section 4 we summarize the main results and draw conclusions.

## 2 The canonical partition function for a diatomic molecule

By means of the well known Born-Oppenheimer approximation one commonly solves the Schrödinger equation for a diatomic molecule in two steps \[3\]. In the first one, one solves an eigenvalue equation for the electrons for different nuclear configurations and obtains the electronic potential-energy curves $U_k(r)$, $k = 0, 1, \ldots$. In the second step, one solves a Schrödinger equation for the nuclei in every potential-energy curve; for example

$$H_k \psi_{k,J,\nu} = E_{k,J,\nu} \psi_{k,J,\nu}, \quad H_k = -\frac{\hbar^2}{2\mu} \nabla^2 + U_k(r), \quad (1)$$

where $\mu$ is the nuclear reduced mass and $J = 0, 1, \ldots$ and $\nu = 0, 1, \ldots$ are the rotational and vibrational quantum numbers, respectively. In order to simplify the discussion we suppose that all the electronic potential-energy curves required for the calculation support bound states. Besides, we do not consider the nuclear statistics in order to facilitate the comparison with the results of Jia et al \[1\].

According to the well known principles of statistical mechanics, the canonical partition function is given by \[4\]

$$Q = \sum_k g_{e,k} \sum_{J_k} \sum_{\nu_k} (2J_k + 1) \exp \left(-\beta E_{k,J,\nu}\right), \quad (2)$$
where $g_{e,k}$ is the degeneracy of the $k$-th electronic state, $\beta = 1/(k_B T)$, $k_B$ is the Boltzmann constant and $T$ the absolute temperature. All the thermodynamic functions can be obtained from $\ln Q$ [4].

At sufficiently low temperatures $\exp (-\beta E_{k,J,\nu}) \ll \exp (-\beta E_{0,J,\nu})$, $k = 1, 2, \ldots$ and only the ground electronic state contributes:

$$Q \approx Q_0 = g_{e,0} \sum_J \sum_\nu (2J + 1) \exp (-\beta E_{0,J,\nu}).$$

At higher temperatures, we should add excited electronic states but the ground state is always present. Therefore, the calculation of thermodynamic functions with the canonical vibrational partition function based only on an excited electronic state makes no sense [4]. In the case of $^7\text{Li}_2$ the $a^3\Sigma^+_u$ electronic state is an excited one and, consequently, the results derived by Jia et al [1] do not have any physical utility. In principle, it would have been reasonable to carry out the calculation with the experimental data for the ground electronic state $X^1\Sigma^+_g$ [5].

Since the approach proposed by Jian et al [1] may be of potential utility when properly applied to the ground electronic state of a diatomic molecule, in what follows we briefly summarize the equations that will arise in such a situation. For concreteness we assume that we have the energy eigenvalues $0 < E_0 < E_1 < \cdots < E_M$ and define the sums

$$S_m(\beta) = \sum_{n=0}^M E_n^m \exp (-\beta E_n), \quad m = 0, 1, \ldots.$$  

All these sums are positive, monotonically increasing functions of $T$

$$\frac{\partial}{\partial T} S_m = k_B \beta^2 S_{m+1},$$

that satisfy $\lim_{T \to 0} S_m = 0$ and $\lim_{T \to \infty} S_m = S_m(0)$. Obviously, the canonical partition function and the mean energy can be expressed in terms of these sums as $S_0 = Q$ and $U = S_1/S_0$, respectively. It is clear that one should add the continuum spectrum to the partition function but for simplicity we assume that this contribution is negligible.
A straightforward calculation shows that the specific heat is given by

\[ C = \frac{\partial U}{\partial T} = k_B \beta^2 \left( \frac{S_2}{S_0} - \frac{S_1^2}{S_0^2} \right) = k_B \beta^2 \sum_{n=0}^{M} \frac{(E_n - U)^2}{S_0} \exp(-\beta E_n) > 0. \] (6)

We appreciate that \( U \) increases monotonously from \( E_0 \) to \( S_1(0)/(M+1) \). When \( T \to 0 \) the specific heat tends to zero exponentially as \( k_B \beta^2 \Delta^2 e^{-\beta \Delta} \), where \( \Delta = E_1 - E_0 \). On the other hand, when \( T \to \infty \) the specific heat tends to zero as \( T^{-2} \). Therefore, \( C \) should exhibit a maximum somewhere between \( 0 < T < \infty \).

This simple mathematical analysis accounts for some of the numerical results obtained by Jia et al [1].

The following question arises: what expressions are simpler, those given in terms of the sums \( S_m \) or the analytical ones provided by Jia et al? In the former case we can directly resort to the experimental data given by the vibrational-rotational spectrum of the diatomic molecule. In the latter case, one should derive the parameters of the improved Manning-Rosen potential from experimental data, solve the Schrödinger equation, and finally obtain the thermodynamic functions either from the sums shown above or from the cumbersome expressions derived from the Poisson summation formula and the expansion for \( \beta \ll 1 \) [1]. Of course, adjectives like simple, straightforward, practical, etc. are a matter of taste.

Jia et al did not compare their theoretical results with any experimental data because their expressions do not exhibit any physical utility as argued above. In the next section we show an application of statistical mechanics to an actual chemical problem.

3 Equilibrium constant for a simple chemical reaction

For concreteness, we choose the chemical reaction

\[ 2\text{Na} \rightleftharpoons \text{Na}_2. \] (7)
The equilibrium constant is given by \[4\]

\[
K_P(T) = \frac{p_{Na_2}}{p_{Na}^2} = (k_B T)^{-1} \frac{q_{Na_2}/V}{(q_{Na}/V)^2},
\]

where

\[
\frac{q_{Na}(T, V)}{V} = \left( \frac{2\pi m_{Na} k_B T}{\hbar^2} \right)^{3/2} g_e (Na)
\]

\[
\frac{q_{Na_2}(T, V)}{V} = \left( \frac{2\pi m_{Na_2} k_B T}{\hbar^2} \right)^{3/2} \left( \frac{T}{2 \theta_r} \right)^{-1} \left( 1 - e^{-\theta_v/T} \right)^{-1} \times g_e (Na_2) e^{D_0/(k_B T)}
\]

In this expression \(m_A\) and \(g_e(A)\) are the mass and electronic degeneracy, respectively, of the species \(A\), \(V\) the volume, \(\theta_r\) and \(\theta_v\) the characteristic temperatures of rotation and vibration, respectively, and \(D_0\) the dissociation energy \(4\).

On the other hand, Ewing et al \(6\) fitted experimental data to the following empirical expression

\[
\log K_P = -4.3249 + \frac{4002.3}{T}.
\]

Figure \(1\) shows that the theoretical results given by the textbook formula \(8\) (blue line) agree with the empirical formula \(10\) (red circles) in the whole range of temperature values considered. According to Ewing et al \(6\) the empirical formula \(10\) was derived from experimental data in the temperature range \(1135 \leq \theta (\text{K}) \leq 1413\). However, figure \(1\) suggests that its range of validity is considerably larger.

The analysis just given clearly shows the utility of the well known textbook model based on the rigid rotor and harmonic oscillator. The remarkable agreement of the theoretical results thus obtained with available experimental data enabled us to argue that the range of validity of the empirical formula \(10\) is greater than expected. It is not clear to us if the complicated formulas derived by Jia et al \(1\) from a different model are suitable for a successful comparison with experimental data.
4 Conclusions

The results derived by Jia et al \[1\] for the $\sigma^3 \Sigma_u^+$ of $^7\text{Li}_2$ are of no physical utility because the vibrational energies of an excited electronic state do not appear alone in the calculation of the thermodynamic functions of diatomic molecules. We cannot calculate thermodynamic functions for particular electronic states, except for the ground one at sufficient low temperatures. The results of Jia et al may be useful for the study of the thermodynamic functions of diatomic molecules at sufficiently low temperatures if we apply the approach to the ground electronic state. Even in such a case the question arises as to the practicality of such expressions compared with well known alternative ones as argued above.

The standard model given by the rigid rotor and harmonic oscillator commonly suffices for many physical applications as shown by the results in section \[3\].

The agreement between such theoretical results and available experimental data is remarkable and enabled us to test the empirical formula \[(10)\] beyond the temperature range used to derive it. It is not clear to us whether the theoretical results proposed by Jia et al \[1\] are suitable for any comparison with experimental data.

References

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Figure 1: Experimental data (red circles) and theoretical results (blue line) for the equilibrium constant for the chemical reaction [7]

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