INTERPOLATION FUNCTIONS FOR MOLECULAR
PARTITION FUNCTIONS

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ABSTRACT. A short discussion of approximation schemes to interpolate the partition function is presented.

Key words: Partition Functions, Molecules.

Computation of partition functions by means of formulae given by Tatum (1966, for diatomic molecules), Herzberg (1945) and Schadee (1964, for polyatomic species) is a rather clumsy process, because of the great number of parameters and the complex functional dependence on the temperature. If one considers the derivation of the internal energy, specific heat, and free-energy, through the thermodynamic relations

$$E = kT^2 \frac{d}{dT} (\ln Q), \qquad (1)$$

$$C = \frac{dE}{dT}, \qquad (2)$$

$$S = k \frac{d}{dT} (T \ln Q), \qquad (3)$$

$$F = -kT (\ln Q), \qquad (4)$$

the awkwardness of the standard expressions for Q is move evident.

Therefore, it is usefull to consider suitable approximation schemes to interpolate the partition function with a minimum set of fitting parameters and with a simple enough functional structure.

However, the presence of terms of the form exp $(-a/T)$ arises severe fitting problems, because of the marked singularity at the origin.

This singularity explains the dramatic failure of naïve fitting schemes to interpolate Q. For example, the straighforward fitting of a fourth degree polynomial to Q, in the interval from 1000 to 5000K, is absolutely un-

capable to represent the partition function near the lower temperature   limit
for polyatomic molecules. Even in the case of diatomic species, where   the
fitting is acceptable (see Fig. 1 for H$_2$ molecule), the derived energy and spe
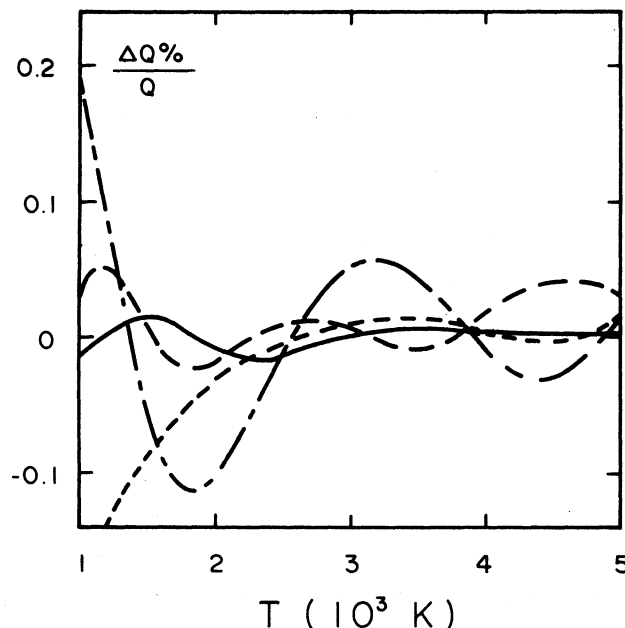cific heat present errors of several percent.

Fig. 1 - Relative errors of the partition functions
given by Irwin (1981) (__ __), Bohn and Wolf (1984)
(— - — -), fourth degree polynomial fitting
(----), and Rossi et al. (1985) (_____) as
functions of the temperature, for H$_2$ molecule.

Bohn and Wolf (1984) have made use of a rational function to interpolate
the partition function for H$_2$ and CO. The number of free parameters is seven and
errors are kept within reasonable bounds. The final accuracy is not as good as
one could have expected from the number of free parameters. This is probably
due to the departure of these authors' solution from a strict least squares
procedure (see Fig. 1).

Substancial improvement of the fitting accuracy is achieved by
considering lnQ instead of Q itself. Bolton (1970) and Irwin (1981) have fitted
lnQ with polynomials in lnT. With fifth degree polynomials, the last author
claims 0.1% accuracy for many atomic and molecular species over intervals near
to 1000 - 5000k (see Fig.1).

A simpler alternative is the fitting of lnQ with polynomials in T,
since the derived quantities keeps the polynomials form. However the differentiation
of an approximate expression enhances short period error components. As a
consequence, the approximation procedure should concern the quantity which

involves the highest derivative. We proceed then backwards and obtain the other quantities by integration.

Let us write for the specific heat C (Rossi et al, 1985):

$$\frac{C}{k} = \sum_{n=0}^{4} a_n T^n \tag{5}$$

For the internal energy and $\ln Q$ we get

$$\frac{E}{k} = \sum_{n=0}^{4} \frac{a_n}{n+1} T^{n+1} + a_5 \tag{6}$$

and

$$k \ln Q = a_0 \ln T + \sum_{n=1}^{4} \frac{a_n}{n(n+1)} T^n - \frac{a_5}{T} + a_6 \tag{7}$$

We see that the energy is still a polynomial, while $\ln Q$ involves $\ln T$ and T^{-1}. Numerical experiments have shown that inclusion of these terms improve very much the results.

Rossi et al (1985) have employed such a scheme to 53 molecular species with very good results. In the interval 1000 to 5000k errors in Q are generally smaller than 0.02%. The same bound applies to errors in the entropy and free-energy, while for the energy and specific heats the derivations are smaller than 0.1 and 1%, respectively (see Fig. 1).

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