

High Rotational Levels and the Partition Function for Hydrogen

Harold W. Woolley

Citation: *The Journal of Chemical Physics* **9**, 470 (1941); doi: 10.1063/1.1750937

View online: <http://dx.doi.org/10.1063/1.1750937>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/9/6?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Rotational partition functions for linear molecules](#)

J. Chem. Phys. **88**, 356 (1988); 10.1063/1.454608

[Classical partition function of a rigid rotator](#)

Am. J. Phys. **52**, 261 (1984); 10.1119/1.13938

[Concise derivation of the rotational partition function](#)

Am. J. Phys. **47**, 649 (1979); 10.1119/1.11951

[Rotational partition function of the symmetric top](#)

J. Chem. Phys. **68**, 1511 (1978); 10.1063/1.435974

[The Rotational Partition Function of the Water Molecule](#)

J. Chem. Phys. **7**, 614 (1939); 10.1063/1.1750499



High Rotational Levels and the Partition Function for Hydrogen

HAROLD W. WOOLLEY

National Bureau of Standards, Washington, D. C.

(Received April 14, 1941)

The ordinary formula for the rotational energy of a simple rotating vibrator, when applied to a diatomic molecule, consists of the first few terms of a series that becomes poorly convergent for levels of high rotational energy. Inversion of the series results in a better approximation. An illustration is given using the results of calculations for the normal state of hydrogen. The inverted series is especially suited to derivation of approximation formulas for the partition function. Such an approximation formula should not be carried to powers of T so high that lack of coefficients for the ordinary formula introduces significant error.

IN the course of some calculations of thermodynamic properties of hydrogen¹ from spectroscopic data, a difficulty was encountered arising from the form of the expression for the rotational energy of a diatomic molecule. In ordinary spectroscopic work with heavy diatomic molecules the formula

$$E_v = B_v K(K+1) + D_v K^2(K+1)^2 \quad (1)$$

is fully adequate since the second term is very small. For hydrogen and for large energies this is no longer the case. A third term is in use in spectroscopic work on hydrogen and, to extend the application to higher energies, a fourth can be evaluated using relations from the theory of the simple rotating vibrator. The resulting formula for the rotational energy,

$$E_v = B_v K(K+1) + D_v K^2(K+1)^2 + F_v K^3(K+1)^3 + H_v K^4(K+1)^4, \quad (2)$$

while adequate for a somewhat greater range, is still not satisfactory since it is the beginning of a series that is too slowly convergent or even divergent for large but possible values of rotational quantum number, K . The formula is, in fact, not very suitable for calculating thermodynamic properties of hydrogen above 2000 degrees K. Some other treatment is therefore necessary.

Using a modification of the Klein-Rydberg method,² the molecular potential energy for the ground state of hydrogen was determined as a

function of internuclear distance and with this the quantum integral was evaluated numerically for several combinations of large rotational quantum number and total energy. The results indicated that, at least for the particular spectroscopic constants employed, the formula became adequate for the purpose when continued indefinitely as a geometric series with the ratio given by the last two terms of formula (2) and with the added part summed with the usual formula. Figure 1 shows, for $v=0$, the estimates which would be made for E_v as a function of K , using: for curve 1, the first term of formula (2); for curve 2, the first two terms; for curve 3, the first three terms; for curve 4, the first four terms; for curve 5, the sum including the continuation as a geometric series; and for curve 6, the

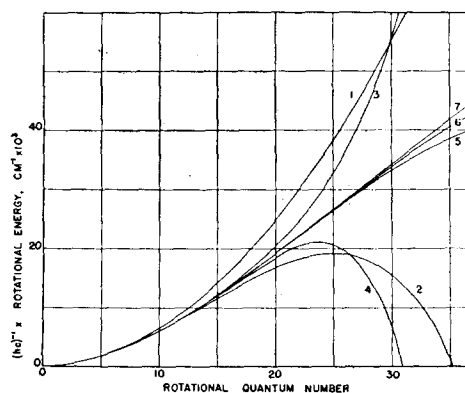


FIG. 1. Various estimates for the rotational energy of the hydrogen molecule as a function of rotational quantum number for the lowest vibrational state. Curves 1, 2, 3 and 4: Formula (2) evaluated to 1, 2, 3 and 4 terms, respectively. Curve 5: 4 terms of formula (2) with a geometric series continuation. Curve 6: Result of detailed numerical investigation. Curve 7: Formula (3) evaluated to 4 terms.

¹ A project of the National Research Council Committee on Thermodynamic Data for Chemical Industries, Dr. F. R. Bichowsky, Chairman.

² R. Rydberg, *Zeits. f. Physik* **73**, 376 (1931); O. Klein, *Zeits. f. Physik* **76**, 226 (1932).

interpolated results of the numerical evaluation of the quantum integral previously mentioned.

Several other usable methods of representing the relation between E_v and K have been suggested to the writer. One of the most interesting of these is the inversion of the series of formula (2). This leads to

$$K(K+1) = \frac{1}{B_v} E_v - \frac{D_v}{B_v^3} E_v^2 + \frac{(2D_v^2 - B_v F_v)}{B_v^5} E_v^3 + \frac{(5B_v D_v F_v - B_v^2 H_v - 5D_v^3)}{B_v^7} E_v^4 + \dots \quad (3)$$

In using this, the total rotational and vibrational energy is to be $G_v + E_v$ where G_v is the purely vibrational energy. In contrast to formula (2), in which the terms alternate in sign, formula (3) as far as evaluated is rapidly convergent, with all terms positive, for all values which E_v can properly assume. In Fig. 1, curve 7 shows the result given by the first four terms of formula (3) for $v=0$. Comparison of this with curve 4 shows that, without including any estimates of re-

mainders, formula (3) is definitely superior to formula (2) for large values of K and E_v .

Formula (3) is particularly adapted to use in deriving one type of approximation formula for the partition function.³ In the customary derivation, the summation

$$\sum_K \{ \exp(-c_2(G_v + E_v)/T) \} (2K+1)$$

is represented in accordance with the Euler-Maclaurin summation formula as the sum of the integral

$$\int_{K_{\min}}^{K_{\max}} \{ \exp(-c_2(G_v + E_v)/T) \} (2K+1) dK$$

and other terms, known in this application as the Mulholland correction,⁴ and obtained from the integrand and its derivatives. In treating the integral it is preferable not to break up part of

$$\exp(-c_2 E_v/T)$$

into a power series expansion in $K(K+1)$ but rather to use the transformations:

$$\begin{aligned} \int_{K_{\min}}^{K_{\max}} \left\{ \exp\left(-\frac{c_2(G_v + E_v)}{T}\right) \right\} (2K+1) dK &= \int_{K=K_{\min}}^{K=K_{\max}} \left\{ \exp\left(-\frac{c_2(G_v + E_v)}{T}\right) \right\} d[K(K+1)] \\ &= \left\{ \exp\left(-\frac{c_2 G_v}{T}\right) \right\} \int_{(E_v)_{\min}}^{(E_v)_{\max}} \left\{ \exp\left(-\frac{c_2 E_v}{T}\right) \right\} \frac{d[K(K+1)]}{dE_v} dE_v. \end{aligned}$$

Continued integration by parts gives for this

$$\begin{aligned} - \left\{ \exp\left(-\frac{c_2(G_v + E_v)}{T}\right) \right\} &\left[\frac{T}{c_2} \frac{d[K(K+1)]}{dE_v} + \left(\frac{T}{c_2}\right)^2 \frac{d^2[K(K+1)]}{dE_v^2} + \left(\frac{T}{c_2}\right)^3 \frac{d^3[K(K+1)]}{dE_v^3} \right. \\ &\quad \left. + \left(\frac{T}{c_2}\right)^4 \frac{d^4[K(K+1)]}{dE_v^4} + \dots \right] \Big|_{(E_v)_{\min}}^{(E_v)_{\max}}. \end{aligned}$$

If $(E_v)_{\max}$ is great enough so that

$$\exp(-c_2(G_v + E_v)/T)$$

makes the contribution of the upper limit negligible and if $(E_v)_{\min}=0$, this becomes, by formula (3),

$$\left\{ \exp\left(-\frac{c_2 G_v}{T}\right) \right\} \left[\frac{T}{c_2 B_v} + \frac{T^2}{c_2^2} \left(-\frac{2D_v}{B_v^3} \right) + \frac{T^3}{c_2^3} \frac{12D_v^2 - 6B_v F_v}{B_v^5} + \frac{T^4}{c_2^4} \frac{120B_v D_v F_v - 24B_v^2 H_v - 120D_v^3}{B_v^7} + \dots \right] \quad (4)$$

³ W. F. GIAUQUE and R. OVERSTREET, J. Am. Chem. Soc. **54**, 1731 (1932); L. S. KASSEL, J. Chem. Phys. **1**, 576 (1933); H. L. JOHNSTON and C. O. DAVIS, J. Am. Chem. Soc. **56**, 271 (1934).

⁴ H. P. MULHOLLAND, Proc. Camb. Phil. Soc. **24**, 280 (1928).

It must be pointed out that evaluation of formula (4) cannot be extended to higher powers of T without first evaluating additional coefficients of formula (2).⁵ For example, the coefficient of T^4 in formula (4) is thrown off by several hundred percent by setting $H_v=0$. In addition to the numerical error which would be introduced, this could lead to the inference that the series is somewhat less convergent and hence less adapted for calculation than is in fact the case.

With g representing the average statistical weight due to nuclear spin degeneracy and with the zero of the energy scale chosen so that $G_0=0$, the internal partition function is the sum over v of

$$Q_v = g \sum_K \left\{ \exp \left(-\frac{c_2(G_v + E_v)}{T} \right) \right\} (2K+1) = g \left\{ \exp \left(-\frac{c_2 G_v}{T} \right) \right\} \left[\frac{T}{c_2 B_v} + \frac{T^2}{c_2^2} \left(-\frac{2D_v}{B_v^3} \right) + \frac{T^3}{c_2^3} \right. \\ \left. \times \frac{12D_v^2 - 6B_v F_v}{B_v^5} + \frac{T^4}{c_2^4} \frac{120B_v D_v F_v - 24B_v^2 H_v - 120D_v^3}{B_v^7} + \cdots + \frac{1}{3} + \frac{1}{15} \frac{c_2 B_v}{T} + \frac{4}{315} \frac{c_2^2 B_v^2}{T^2} + \cdots \right].$$

A few terms of the Mulholland correction have been included in the formula. They are to be used with caution since the true correction is not properly developable in powers of T^{-1} and the apparent convergence is too optimistic an indication of the closeness of the approximation, especially with T small. As is well known, this correction does not distinguish between sums over even and over odd values of K .

It is desired to acknowledge the encouragement by Dr. F. G. Brickwedde of the calculation of thermodynamic properties of hydrogen at high temperatures from spectroscopic data. Several suggestions made by Professor David M. Dennison have been very helpful in leading to this paper.

⁵ For the simple rotating vibrator, see J. L. Dunham, *Phys. Rev.* **41**, 721 (1932); I. Sandeman, *Proc. Roy. Soc. Edinburgh* **60**, 210 (1940).

On Some Properties of Bose-Einstein Gases

LOUIS GOLDSTEIN
New York, New York

(Received March 13, 1941)

The condition which has to be fulfilled in order that the Bose-Einstein condensation be accompanied by a discontinuity of the heat capacity at the condensation temperature is discussed. The nature of the transition depends on the distribution of the energy levels of the individual particles forming the gas. The condensation is studied for several types of individual energy spectra. It is shown that all those Bose-Einstein (B.E.) assemblies which admit a non-ambiguous definition of the statistical distribution function present, beside interesting analogies, a qualitatively different behavior from that observed in liquid helium. It appears that as long as the transition in momentum space of non-ideal B.E. systems is not understood, the possibility of connection between B.E. condensation and the transition observed in liquid helium remains an open problem.

IN a previous paper¹ we have discussed the condensation of B.E. ideal gases in presence of conservative force fields which acted directly on the motion of the center of gravity of the gas atoms. It has been assumed there that the classical Hamilton function could be used for the

description of the motion of the individual gas atoms. This was equivalent to the assumption that practically no serious error was introduced by leaving aside the quantization of the motion of the individual atoms in those fields. The modification brought about by the field in the properties of the gas around the condensation

¹ L. Goldstein, *J. Chem. Phys.* **9**, 273 (1941).