

## SHORT COMMUNICATIONS

### QUANTUM EFFECTS IN DIPOLAR GASES

By A. POMPE\* and T. H. SPURLING\*

[Manuscript received 16 August 1972]

#### *Abstract*

The second-order translational and rotational quantum corrections to the second virial coefficient for the Stockmayer potential have been derived and numerical values computed with parameters appropriate for water vapour. The second-order corrections amount to about 10% of the first-order corrections at room temperature.

#### *Introduction*

It is becoming increasingly feasible by quantum mechanical methods to calculate the potential energy of interaction between quite complex molecules. Recent calculations on water dimers illustrate this point.<sup>1</sup> A necessary but not sufficient condition for the validity of any proposed potential energy function is that it should, by the use of the appropriate statistical mechanical formulae, be able to reproduce experimental second virial coefficients. It is therefore necessary to be sure that the statistical mechanical formulae used to calculate the second virial coefficients include all the important physical effects. It has been shown in two recent papers<sup>2,3</sup> that the first quantum corrections to the second virial coefficient for both dipolar and quadrupolar molecules can be quite significant at reduced temperatures as high as 1.0.

The only investigation of the second quantum correction for angle dependent potentials appears to be that of Wang Chang and Uhlenbeck.<sup>4</sup> This calculation indicates that, at least for the simple potential used, the second quantum correction can be as important as the first, once again at reduced temperatures around 1.0.

We have rederived the expression for the second quantum correction to the second virial coefficient for axially symmetric molecules and report calculations for Stockmayer parameters appropriate for water vapour.

#### *Theory and Calculations*

Kirkwood<sup>5</sup> developed the theory necessary for the calculation of the quantum corrections to the second virial coefficients for angle-dependent potentials. The main

\* Division of Applied Chemistry, CSIRO, P.O. Box 4331, Melbourne, Vic. 3001.

<sup>1</sup> Del Bene, J., and Pople, J. A., *J. chem. Phys.*, 1970, **52**, 4858.

<sup>2</sup> Singh, Y., and Datta, K. K., *J. chem. Phys.*, 1970, **53**, 1184.

<sup>3</sup> McCarty, M., Jr, and Babu, S. V. K., *J. phys. Chem.*, 1970, **74**, 1113.

<sup>4</sup> Wang Chang, C. S., Doctoral Dissertation, University of Michigan, 1944, as reported in Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids," p. 434 (John Wiley: New York 1954).

<sup>5</sup> Kirkwood, J. G., *J. chem. Phys.*, 1933, **1**, 597.

difference between his development and the development for angle-independent potentials lies in the fact that kinetic energy,  $\mathcal{T}$

$$\mathcal{T} = \frac{p_r^2}{2m} + \sum_{k=1}^2 \frac{1}{2I_k} [p_{\theta_k}^2 + (p_{\phi_k}^2 / \sin^2 \theta_k)] \dots \quad (1)$$

is a function of the coordinates and is therefore not an eigenvalue of the kinetic energy operator. The symbols in equation (1) are as given by Kirkwood.<sup>5</sup>

In Kirkwood's method the Slater sum is evaluated as a series expansion in Planck's constant ( $h$ ) and the second virial coefficient has the form

$$B = \frac{1}{4} N \int_0^\infty \int_0^{2\pi} \int_0^\pi \int_0^\pi |1 - \exp(-V/k_B T)(1 + \chi(V))| r^2 \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\phi dr \quad (2)$$

where  $V$  is the potential energy of interaction between pairs of axially symmetric molecules and  $\chi(V)$  is defined by equation (3):

$$\chi(V) = (h/2\pi)^2 g_2 + (h/2\pi)^4 g_4 + \dots \quad (3)$$

where  $h$  is Planck's constant. The explicit form of  $g_2$  is given in ref.<sup>5</sup> and we have reported the expression for  $g_4$  in a separate Appendix.\* Equation (2) for  $B$  can be written as

$$B = B_{\text{classical}} + B'_{\text{trans}} + B'_{\text{rot}} + B''_{\text{trans}} + B''_{\text{trans-rot}} + B''_{\text{rot}} \dots \quad (4)$$

where the terms with superscript ' are proportional to  $h^2/m$  and  $h^2/I$  respectively, and those with superscript '' are proportional to  $h^4/m^2$ ,  $h^4/mI$ , and  $h^4/I^2$  respectively. In finding a non-zero term proportional to  $h^4/mI$  we appear to differ from Wang Chang.<sup>4</sup> In these terms  $m$  is the mass of the axially symmetric molecule and  $I$  its moment of inertia.

The simplest intermolecular potential function for polar molecules which is at all realistic is the Stockmayer potential

$$V(r, \theta_1, \theta_2, \theta) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] - (\mu^2/r^3)(2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi) \quad (5)$$

where  $\varepsilon$  and  $\sigma$  are parameters describing the spherically symmetric part of the function and  $\mu$  is the dipole moment of the molecule. We have calculated values of all the fourfold integrals in equation (4) using the product Simpson's rule program used previously in the calculation of the classical second virial coefficient for water vapour.<sup>6</sup> The calculations were performed on a CD 6600 computer using parameters  $\varepsilon/k_B = 335$  K,  $\sigma = 2.62$  Å, and  $\mu = 1.83$  D. All the results are shown in Table 1. Our results for  $B'_{\text{trans}}$  and  $B'_{\text{rot}}$  agree to within 1 part in 1000 with those reported earlier.<sup>3</sup>

### Discussion

The results shown in Table 1 indicate that, for a strongly polar substance like water vapour, the second quantum corrections to the second virial coefficient are significant at temperatures as high as 313 K. However, they reduce very quickly with

\* Copies of this Appendix may be obtained on application to the Editor-in-Chief, Editorial and Publications Section, CSIRO, 372 Albert Street, East Melbourne, Vic. 3002.

<sup>6</sup> Johnson, C. H. J., and Spurling, T. H., *Aust. J. Chem.*, 1971, **24**, 1567.

increasing temperature and by 423 K are barely significant. It is above this temperature that the most accurate experimental virial coefficients are available,<sup>7</sup> and so the

TABLE 1  
SECOND VIRIAL COEFFICIENTS AND THE FIRST- AND SECOND-ORDER QUANTUM CORRECTIONS FOR WATER VAPOUR

All  $B$  values are in units  $\text{cm}^3 \text{mol}^{-1}$ .  $T^*$  is the reduced temperature

$T/\text{K}$	$T^*$	$B_{\text{classical}}$	$B'_{\text{trans}}$	$B'_{\text{rot}}$	$B''_{\text{trans}}$	$B_{\text{trans-rot}}$	$B''_{\text{rot}}$
313	0.936	-993.4	18.2	87.3	-0.6	-1.5	10.9
343	1.025	-637.3	11.3	58.4	-0.2	-0.5	4.8
373	1.149	-408.2	5.6	37.1	-0.1	-0.2	2.3
423	1.264	-285.8	3.1	23.7	-0.04	-0.05	0.9
473	1.414	-200.7	1.5	10.4	-0.02	-0.02	0.4
573	1.712	-105.2	0.6	4.8	-0.005	-0.0	0.1
673	2.011	-68.5	0.3	2.9	-0.002	+0.01	0.05

second quantum corrections can be safely ignored in fitting these values to proposed potential functions.

<sup>7</sup> Kell, G. S., McLaurin, G. E., and Whalley, E., *J. chem. Phys.*, 1968, **48**, 3805.