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Second virial coefficients of asymmetric top molecules

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A short self-contained derivation is given for the second virial coefficient \( B_2(T) \) of a gas consisting of identical interacting asymmetric rigid rotors. The resulting expression is correct through \( \hbar^2 \). First, the canonical partition function is derived by means of an \( \hbar \) expansion of \( \exp[-H/(k_B T)] \) due to Friedmann [Adv. Chem. Phys. 4, 225 (1962)]. The present work applies angular momentum operators and known facts from angular momentum theory. It is considerably more accessible than Friedmann’s exposition, which is not based on angular momentum operators, but instead on explicit derivatives with respect to Euler angles. The partition function obtained from the \( \hbar \) expansion is applied to the derivation of an expression for \( B_2(T) \) that is identical in appearance to the expression for symmetric rotors of T Pack [J. Chem. Phys. 78, 7217 (1983)]. The final equation in this work is valid for rigid rotors of any symmetry. © 2005 American Institute of Physics.

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I. INTRODUCTION

Second virial coefficients \( B_2(T) \), which describe the first nonideality correction to the Boyle–Gay–Lussac (ideal gas) law \( pV=RT \), depend sensitively on the pair potential of the molecules in the gas. Because virial coefficients can be measured, their \( ab initio \) computation and comparison with experimental values provide a valuable check on the accuracy of \( ab initio \) computational results. See for a recent example of such comparisons Ref. 1.

About 20 years ago T Pack 2 published a paper on the first quantum corrections to \( B_2(T) \). He gave a compact formula and restricted its validity specifically to symmetric tops. The reason for this restriction was that T Pack used a formula and restricted its validity specifically to symmetric tops. His expansion, which is not based on angular momentum operators, but instead on explicit derivatives with respect to Euler angles. The partition function obtained from the \( \hbar \) expansion is applied to the derivation of an expression for \( B_2(T) \) that is identical in appearance to the expression for symmetric rotors of T Pack [J. Chem. Phys. 78, 7217 (1983)]. The final equation in this work is valid for rigid rotors of any symmetry.

II. ONE-BODY THEORY

We establish notation and review a few necessary facts concerning a canonical ensemble (\( T-V-N \) constant) of systems of \( N \) identical noninteracting rigid rotors.

A rigid rotor has six degrees of freedom: the position \( r \) of its center of mass, and its orientation, given by the three Euler angles \( \omega = (\omega_1, \omega_2, \omega_3) \). Thus, a rotor has the coordinates \( x = (r, \omega) \). The quantum mechanical kinetic energy of a
rotor is a sum of a translational part $H_T = p \cdot v / (2M)$, with $M$ the mass of the rotor, and a rotational part $H_{rot}$ [Eq. (3)]. The one-body partition function factorizes

$$Q_1 = \text{Tr}(e^{-\beta H_T})\text{Tr}(e^{-\beta H_{rot}}) = Q_{rot}^T Q_{1 rot}. $$

The operator $p_u = -i\hbar \partial / \partial a$ ($a = x, y, z$) is Hermitian. By partial integration this can be proved, provided the resulting surface integrals vanish, which we assume to be the case. The angular momentum operators $J_x$, $J_y$, and $J_z$ are Hermitian since they act on periodic functions of the Euler angles. Note that while $[p_u, p_d] = 0$ ($a = x, y, z$), the body-fixed operators $J_u$ satisfy the well-known anomalous commutation relations.

Let us consider first the necessary translational equations. The one-body partition function computed in the $r$ representation is the integral over the diagonal element (Slater sum):

$$Q_1^T = \int \mathcal{D}r W_T(r) = \langle r | e^{-\beta H_T} | r \rangle. $$

We assume on the one hand that the operators $r$ and $p$ have a continuous spectrum, while on the other we assume that $V$ is finite. In the final result $V$ will drop out and we then take the limit of infinite $V$. As is well-known, the Slater sum is independent of $r$ and is related to de Broglie thermal length $\lambda$ by

$$W_T^r = \lambda^{-3} \left( \frac{2 \pi M k_B T}{\hbar^2} \right)^{3/2}, $$

so that $Q_1^T = V \lambda^{-3}$.

In the following section we will meet the expression $\langle r | p_a p_b \exp(-\beta H_T) | r \rangle$ bilinear in the momenta ($a, b = x, y, z$) and a similar expression linear in $p_a$. Temporarily widening our view somewhat, we introduce the homogeneous polynomial $P(p_1, p_2, p_3)$ and consider

$$\langle r | P(p_x, p_y, p_z) e^{-\beta H_T} | r \rangle. $$

If $P$ is of odd order, this expectation value vanishes. Indeed, the $p_a$’s commute mutually so that the total operator in Eq. (6) is Hermitian and the expectation value is real. Further, the operator is antisymmetric under time reversal if $P(p_1, p_2, p_3)$ is of odd order, so that its expectation value over a state that is even or odd under time-reversal symmetry is purely imaginary. In total the expectation value vanishes for odd-order $P$. Using the resolution of the identity in the $p$ representation and $\langle r | p \rangle = h^{-3/2} \exp(\mathbf{i} \mathbf{r} \cdot \mathbf{p})$, so that $\langle r | p \rangle | p \rangle = h^{-3}$, we find by simple integration,

$$\frac{1}{2M} \langle r | p_a p_b \exp(-\beta H_T) | r \rangle = \delta_{ab} \frac{k_B T}{2} \lambda^{-3} = \delta_{ab} \frac{k_B T}{2} \frac{Q_1^T}{V}, $$

where the Kronecker $\delta$ is due to reflection symmetry in $p$ space. Since the translational matrix element is independent of $a = x, y, z$, we find here the equipartition of energy over the three translation degrees of freedom. The statistical averages of the energies of the three translational modes add up to the total translational energy $\frac{3}{2} k_B T$.

We now turn to the required rotational equations. An asymmetric top wave function and its eigenvalue are obtained by diagonalizing $H_{rot}$ on the space spanned by the elements (symmetric top eigenfunctions) in row $M$ of the complex conjugate of a Wigner $D$ matrix. The result is independent of $M$. That is, the eigenfunctions belonging to the $(2J+1)$-degenerate energy $E_J$, are

$$\langle \omega | J M \tau \rangle = \sqrt{\frac{2J+1}{8 \pi^2}} \sum_{K=-J}^{J} c_K D_{MK}^J(\omega)^* \cdot M = -J, \ldots, J, $$

where $D_{MK}^J(\omega)^*$ is a symmetric top eigenfunction. Invocation of the great orthogonality relation for the Wigner $D$ matrices [which constitute an irreducible matrix representation of the full rotation group $SO(3)$] shows that the states are orthogonal on $J$ and $M$ and, being eigenstates of $H_{rot}$, also on $\tau$.

$$\int d\omega \langle J M' \tau' | \omega \rangle \langle \omega | J M \tau \rangle = \delta_{\tau' \tau} \delta_{J M' M}, $$

with $d\omega = \sin \omega_2 d\omega_1 d\omega_2 d\omega_3$.

The Slater sum $W_{rot}^a = \langle \omega | e^{-\beta H_{rot}} | \omega \rangle$ is independent of $\omega$. This statement can be generalized to the operator

$$\rho = P(J_x, J_y, J_z) e^{-\beta H_{rot}}, $$

where $P(J_x, J_y, J_z)$ is a homogeneous polynomial. Since the $J_u$’s do not commute mutually we cannot use the same manner of proof as for the $p_a$’s. Therefore, we consider first

$$\sum_M \langle \omega | J M \tau \rangle \langle J M' \tau' | \omega \rangle = \sum_M \langle \omega | J M \tau \rangle P(J_x, J_y, J_z) \langle J M' \tau' | \omega \rangle $$

and

$$\sum_M \langle \omega | J M \tau \rangle P(J_x, J_y, J_z) e^{-\beta H_{rot}} | J M \tau \rangle = \sum_M \langle \omega | J M \tau \rangle D_{MK}^J(\omega)^* D_{MK}^J(\omega). $$

The dependence on $\omega$ has dropped out because of the homomorphism condition satisfied by the unitary $D$ matrices. Introduction of the resolution of the identity in the $JM \tau$ representation into $\langle \omega | \rho | \omega \rangle$ in three places, employment of the diagonality of $P(J_x, J_y, J_z)$ in $J$ and $M$ and the indepen-dence of its matrix elements on $M$ (because the body-fixed angular momenta commute with the space-fixed $J_u$, whose eigenvalue is $M$), taken together with the diagonality of $e^{-\beta H_{rot}}$ in $J, M$ and $\tau$ gives for $\langle \omega | \rho | \omega \rangle$ the result

$$\langle \omega | \rho | \omega \rangle = \sum_{JM \tau \tau' \tau''} \langle \omega | J M \tau \rangle \langle J M \tau | P(J_x, J_y, J_z) | J M' \tau' \rangle \langle J M' \tau' | D_{MK}^J(\omega)^* D_{MK}^J(\omega) \rangle $$

and

$$\sum_{JM \tau} \langle JM \tau | P(J_x, J_y, J_z) e^{-\beta H_{rot}} | JM \tau \rangle \langle \omega | JM \tau \rangle = \frac{1}{8 \pi^2} \sum_{JM \tau} \langle JM \tau | P(J_x, J_y, J_z) e^{-\beta H_{rot}} | JM \tau \rangle \langle \omega | JM \tau \rangle. $$

In particular,

$$W_{rot}^a = \langle \omega | e^{-\beta H_{rot}} | \omega \rangle = \frac{Q_{rot}^T}{8 \pi^2}. $$

The trace in Eq. (10) does not necessarily vanish for polynomials $P(J_x, J_y, J_z)$ of odd order. The asymmetric top Hamiltonian $H_{rot}$ belongs to the Abelian symmetry group $D_2$, which consists of rotations by $\pi$ around the three inertial
axes. A rotation around the x axis gives \( J_x \rightarrow -J_y, J_y \rightarrow J_x \), and \( J_z \rightarrow J_z \). The rotations around the y and z axis give the corresponding (cyclically permuted) maps. So, the three operators \( J_x, J_y, \) and \( J_z \) transform according to different irreducible representations (irreps) of \( D_2 \). Rigid rotor functions \( |JM \rangle \) belong to irreps of \( D_2 \). An expectation value (bra and ket the same) of an arbitrary operator with respect to rigid rotor functions is nonvanishing if and only if the operator transforms as the totally symmetric irrep \( A_1 \). Since \( J_x, J_y, \) and \( J_z \) do not transform as \( A_1 \) their expectation values vanish. In second order only the squares \( J_x^2, J_y^2, \) and \( J_z^2 \) transform as \( A_1 \), while out of all third-order monomials only the product \( J_xJ_yJ_z \) transforms as \( A_1 \). If higher than \( h^2 \) quantum corrections are contemplated this latter ternary product must not be overlooked, which is easy to do because its expectation value is zero in the case of the symmetric top with its much higher symmetry \( D_{\infty h} \).

We will need expressions for \( \langle \omega | J_{ex}^2 e^{-\beta H_{rot}} | \omega \rangle \) \( (\omega = x, y, z) \). While the corresponding expressions for \( p_{xx}^2 \) \( [\text{Eq. (7)}] \) could be obtained by integration, there are no closed formulas for these expressions. Introducing the rotational temperature \( T=\frac{\hbar^2}{2I_k b} \) we can write, however,

\[
\frac{\langle \omega | J_{ex}^2 e^{-\beta H_{rot}} | \omega \rangle}{Q_1^{rot}} = -\frac{\partial \ln Q_{rot}^1}{\partial \Theta_{\omega}}, \quad \omega = x, y, z,
\]

and from Eq. (10)

\[
\langle \omega | J_{ex}^2 e^{-\beta H_{rot}} | \omega \rangle = -\frac{Q_1^{rot}}{2} \frac{\partial \ln Q_{rot}^1}{\partial \Theta_{\omega}}. \tag{11}
\]

Stripp and Kirkwood\(^{13}\) derived an approximation for \( Q_1^{rot} \) that consists of a sum of a classical and a first-order quantum term. The first term \( Q_1^{rot,cl} \) is an integral over phase space (premultiplied by \( h^2 \)), which can be computed analytically, giving

\[
Q_1^{rot,cl} = \left( \frac{\pi T^3}{\Theta_x \Theta_y \Theta_z} \right)^{1/2}. \tag{12}
\]

The second term is the first \([O(h^2)]\) quantum correction, which, according to Stripp and Kirkwood,\(^{13}\) is

\[
Q_1^{rot,qm(1)} = \frac{Q_1^{rot,cl}}{12T} \sum_{x,y,z \text{ cyclic}} \left[ 2\Theta_x - \Theta_y - \Theta_z \Theta_x \right]. \tag{13}
\]

Substitution of Eqs. (12) and (13) into Eq. (11) yields an expression that is valid through \( h^2 \), namely,

\[
\langle \omega | J_{ex}^2 e^{-\beta H_{rot}} | \omega \rangle = \frac{k_B T Q_1^{rot}}{8\pi^2} \left( -\frac{1}{2} - F_a(T) \right) + O(h^4) \tag{14}
\]

with \( F_a(T) \) given by \((a \neq b \neq c)\)

\[
F_a(T) = \frac{[\Theta_a(\Theta_b - \Theta_c)^2 - (\Theta_b \Theta_c)^2]}{P(T)}, \tag{15}
\]

in which \( P(T) \) is given as

\[
P(T) = -2\Theta_x \Theta_y \Theta_z (6T + \Theta_x + \Theta_y + \Theta_z) + \Theta_y^2 \Theta_z^2 + \Theta_z^2 \Theta_x^2 + \Theta_x^2 \Theta_y^2 + \Theta_y^2 \Theta_z^2.
\]

In the same \((O(h^2))\) approximation the quantum statistical average \( \langle H_{rot} \rangle \) of the rotational Hamiltonian is given by

\[
\langle H_{rot} \rangle = \frac{\text{Tr} H_{rot} e^{-\beta H_{rot}}}{Q_1^{rot}} = k_B \frac{T}{2} - \sum_{a=x,y,z} F_a(T). \tag{16}
\]

In the following section we will show that it is consistent to neglect \( F_x, F_y, \) and \( F_z \) in the first quantum correction of \( B_2(T) \).

By computing \( \text{Tr}[H_{rot} \exp(-\beta H_{rot})] \) and \( \text{Tr}[\exp(-\beta H_{rot})] \) numerically, one can approximate the value of \( \langle H_{rot} \rangle \) to any precision. This makes it possible to investigate how good an approximation Eq. (16) gives. Because the \( F_a(T) \)’s originate from a first-order quantum correction to the classical partition function, their sum gives only a first-order correction to \( \langle H_{rot} \rangle \). Upon recalling the definition of \( H_{rot} \) in Eq. (3), we note that the operation of \( J_a \) on the symmetric top wave functions \( D_{MK}^J(\omega) \) is well defined, and via the use of step-up(down) operators easily implemented. Thus, in the basis \( D_{MK}^J(\omega) \) \((J \text{ and } K \text{ running})\) the matrix of \( H_{rot} \) can be readily calculated. This matrix is block diagonal in \( J \) and independent of \( M \). After diagonalization of the subblocks, yielding the eigenvalues \( E_{J}\_\_ \) the matrices of \( \exp(-\beta H_{rot}) \) and \( H_{rot} \exp(-\beta H_{rot}) \) become diagonal and functions of \( E_{J}\_\_ \) so that their contributions to \( \langle H_{rot} \rangle \) are easily calculated. By increasing the maximum \( J \) in this procedure and monitoring convergence, the quantum statistical average of \( H_{rot} \) can be computed to any required precision.

In order to illustrate the magnitude of \( F_x, F_y, \) and \( F_z \) and the error that their neglect will introduce, we consider the \( \text{H}_2\text{O} \) and \( \text{SO}_2 \) molecules as typical examples of asymmetric tops. From \( mT=1.007 \, 825 \, 2 \, u, mO=15.994 \, 915 \, 0 \, u, mS =31.972 \, 070 \, 69 \, u, r_{OH}=0.9572 \, Å, \ r_{SO}=1.4321 \, Å, \ \angle\text{H–O–H}=104.5°, \ \angle\text{O–S–O}=119.5°, \) we obtain the following rotational temperatures \((\text{the molecules are in the } xy \text{ plane, the } yz \text{ plane is the symmetry plane})\):

\[
\text{H}_2\text{O}: \Theta_x=39.455 \, K, \quad \Theta_y=21.007 \, K, \quad \text{and} \quad \Theta_z=13.708 \, K.
\]

\[
\text{SO}_2: \Theta_x=2.9176 \, K, \quad \Theta_y=0.4952 \, K, \quad \text{and} \quad \Theta_z=0.4234 \, K.
\]

The symmetry number \( \sigma \) \((\text{number of equivalent conformations})\) which is 2, does not play a role here. See Table I for some results. For water, which is a relatively light molecule, we find after applying the first quantum correction the following errors:

\begin{itemize}
  \item for 50 K 0.94%, for 100 K 0.24%, and for 500 K 0.01%.
  \item For the much heavier molecule \( \text{SO}_2 \) the error is \((\text{within four digit accuracy})\) zero for the four temperatures listed.
\end{itemize}

That is, the first quantum correction gives essentially the exact result. It is important for the present development that the classical approximation to \( \langle H_{rot} \rangle \) \( \text{[and accordingly also the left-hand side of Eq. (14)]} \) is very good and that neglect of \( F_x \) and \( F_y \) does not introduce any error \((\text{within four decimal digits})\), while neglect of \( F_z \) introduces a small error \((6\% \text{ at } \text{50 K})\) for \( \text{H}_2\text{O} \) and hardly any \((0.2\% \text{ at } \text{50 K})\) for \( \text{SO}_2 \).

Finally, combining Eqs. (5) and (10), we find an expression for the total one-rotor Slater sum \( W_1 \) that is very important for the development in Sec. IV.
TABLE I. Approximate quantum correction to $\langle H_{a\alpha} \rangle/(k_B T)$ in column labeled “Approx,” see Eq. (16) for its definition. See Eq. (15) for the definition of $F_s$, $F_r$, and $F_\ell$. $T$ is in kelvin. Column labeled “Exact” gives exact values of $\langle H_{a\alpha} \rangle/(k_B T)$ obtained from converged numerical calculations.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$F_s$</th>
<th>$F_r$</th>
<th>$F_\ell$</th>
<th>Approx.</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0837</td>
<td>1.4163</td>
<td>1.4031</td>
</tr>
<tr>
<td>100</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0437</td>
<td>1.4563</td>
<td>1.4528</td>
</tr>
<tr>
<td>500</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0091</td>
<td>1.4909</td>
<td>1.4908</td>
</tr>
<tr>
<td>1000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0045</td>
<td>1.4955</td>
<td>1.4954</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
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<td>0.0000</td>
<td>0.0028</td>
<td>1.4972</td>
<td>1.4972</td>
</tr>
<tr>
<td>100</td>
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<td>0.0000</td>
<td>0.0014</td>
<td>1.4986</td>
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<tr>
<td>500</td>
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<td>0.0000</td>
<td>0.0003</td>
<td>1.4997</td>
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<tr>
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<td>0.0000</td>
<td>0.0001</td>
<td>1.4999</td>
<td>1.4999</td>
</tr>
<tr>
<td>SO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where $a^s$ and $s$ denote symmetric and antisymmetric functions, respectively.

\( W_1 = \langle \hat{x} | \text{e}^{-\beta H_0 + H_{a\alpha}} | x \rangle = \frac{Q^a_q \ Q^rot}{V \ 8 \pi^2} = \frac{Q_t}{V 8 \pi^2}. \) (17)

\[ \tilde{U} = \{ \tilde{\nabla}_a, \tilde{U} \} \]

and

\[ \tilde{U}_{aa} = \{ \tilde{\nabla}_a, \tilde{U}_a \}. \]

III. THE EXPANSION OF $\text{e}^{-\beta H_0 + U}$

To simplify and unify notation we define

\[ \nabla_a(i) = \begin{cases} (2M)^{-1/2} p_a(i) & \text{for } a = 1, 2, 3, \\ (2J_a(i))^{-1/2} J_a(i) & \text{for } a = 4, 5, 6. \end{cases} \] (18)

The operator $\nabla_a(i)$ is Hermitian. The pair potential is $U(x_1, x_2)$ and the two-body Hamiltonian becomes $\hat{H} = \hat{H}_0 + \hat{U}$, with $\hat{H}_0 = \sum_i [H_{a\alpha}(i) + H_{a\beta}(i)]$. We will write

\[ \hat{H}_0 = \nabla_a \nabla_a = \sum_{a=1}^{12} \sum_{i=1}^{6} \nabla_a(i) \nabla_a(i), \]

where a sum over two particles and six components per particle is implied for two repeated Greek indices. Further, we write

\[ \tilde{U} = \beta U \]

and

\[ \tilde{H}_0 = \tilde{\nabla}_a \tilde{\nabla}_a \]

with

\[ \tilde{\nabla}_a = \sqrt{\beta} \nabla_a. \]

Note that $\tilde{U}$ and $\tilde{H}_0$ are dimensionless, as is $\tilde{\nabla}_a$. Define, following Friedmann,\(^3\) the operator $T$ by

\[ T = e^{\tilde{U}} e^{-\beta H_0} e^{\tilde{H}_0} \Leftrightarrow e^{-\beta H_0 + U} = e^{-\beta U} T e^{-\beta H_0} \] (19)

and expand it

\[ T = 1 + T^{(1)} + T^{(2)} + \cdots, \]

where $T^{(k)}$ is of order $\tilde{H}_0^k$, i.e., of order $\tilde{\nabla}_a^k$. We will give expressions for $T^{(1)}$ and $T^{(2)}$ in terms of $(\alpha \tilde{U})^k \tilde{H}_0$, where

\[ (\alpha \tilde{U})^k \tilde{H}_0 = \left[ \tilde{U}, \left[ \tilde{U}, \left[ \tilde{U}, \cdots \left[ \tilde{U}, \tilde{H}_0 \right] \cdots \right] \right] \right], \]

where $U$ is the summation of all possible $k$ nested pairs of operators $\tilde{U}$ such that \( k \) times nested

We define first and second derivatives

\[ e^{\tilde{U}} \tilde{H}_0 e^{-\beta \tilde{U}} = (e^{\beta \tilde{U}} \tilde{H}_0) = \sum_{k=0}^{\infty} \frac{\tilde{U}^k}{k!} (\alpha \tilde{U})^k \tilde{H}_0, \]

so that

\[ \frac{dV}{dt} = -\tilde{U} e^{-\beta \tilde{U}} T(t) e^{-\beta \tilde{H}_0} e^{-\beta \tilde{U}} T(t) - e^{-\beta \tilde{U}} T(t) e^{-\beta \tilde{U}} T(t) e^{-\tilde{U} \tilde{H}_0} + e^{-\beta \tilde{U}} \frac{dT}{dt} e^{-\beta \tilde{H}_0}. \] (22)

Multiplication by $e^{\beta \tilde{U}}$ on the left and $e^{-\beta \tilde{U}}$ on the right gives

\[ \frac{dT}{dt} = T(t) \tilde{H}_0 - e^{-\beta \tilde{U}} \tilde{H}_0 e^{-\beta \tilde{U}} T(t). \]

Introduce the following commutator expansion:\(^14\)

\[ e^{\beta \tilde{U}} \tilde{H}_0 e^{-\beta \tilde{U}} = (e^{\beta \tilde{U}} \tilde{H}_0) = \sum_{k=0}^{\infty} \frac{\tilde{U}^k}{k!} (\alpha \tilde{U})^k \tilde{H}_0, \]

so that
where the summation ends at $k = 2$, as we saw above, because $\tilde{H}_0$ is a second-order differential operator. The terms in the summation are given by Eqs. (20) and (21). We solve this equation by iteration and the master recursion relation becomes

$$dT^{(n+1)}(t) = [T^{(n)}(t), \tilde{H}_0] + \left\{ \frac{2}{k!} (\text{ad} \tilde{U})^k \tilde{H}_0 \right\} T(t),$$  

(23)

with $T^{(0)} = 1$.

Integration over $t'$ from 0 to $t$ yields the expansion

$$T^{(1)}(t) = -\sum_{k=1}^{\infty} \frac{f^{k+1}}{(k+1)!} (\text{ad} \tilde{U})^k \tilde{H}_0.$$  

(25)

Hence $T^{(1)}(1)$ becomes

$$T^{(1)} = \frac{1}{2} \tilde{U}_{\alpha \beta} + \tilde{U}_{\alpha \beta} \tilde{x}_\alpha - \frac{1}{3} \tilde{U}_{\alpha \beta}.$$  

(26)

Substitution of Eq. (25) into Eq. (23) and integration gives

$$T^{(2)}(t) = -\sum_{k=1}^{\infty} \frac{f^{k+2}}{(k+2)!} [(\text{ad} \tilde{U})^k \tilde{H}_0]$$  

$$\times \frac{1}{k! (k+1)!} (\text{ad} \tilde{U})^k \tilde{H}_0.$$  

(27)

This expansion gives $T^{(2)}$ after substitution $t = 1$. After some straightforward but tedious algebra we find that the operator $T^{(2)}$ can be determined to be

$$T^{(2)} = \frac{1}{2} \tilde{U}_{\alpha \beta \gamma} + \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma}$$  

$$- \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha - \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha$$  

$$+ \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha + \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha$$  

$$+ \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha + \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{U}_{\gamma} \tilde{x}_\alpha$$  

$$- \frac{1}{2} \tilde{U}_{\alpha \beta} \tilde{x}_\alpha.$$  

(28)

At this point we can show that only $T^{(1)}$ and $T^{(2)}$ contribute to the first quantum correction of $B_2$. The quantum corrections due to $T^{(k)}$ contain by definition $(2k)$th derivatives. We see in Eq. (26) that the terms appearing for $k = 1$ are multiples of $(\tilde{x}_\alpha \tilde{U})$ and $(\tilde{x}_\alpha \tilde{U})(\tilde{U} \tilde{U})$, but also that a term $(\tilde{x}_\alpha \tilde{U})$ with trailing operator $\tilde{x}_\alpha$ appears. In general the $T^{(n)}$ terms have trailing polynomials $P(\tilde{x})$ of different order and we will see below that these arise in $\langle \tilde{x}\rangle | P(\tilde{x}) \rangle \times \text{exp}(-\tilde{H}_0) | \tilde{x}\rangle$. We discussed in the preceding section that many such expectation values vanish because of time reversal or $D_2$ symmetry and so does the one with $P(\tilde{x}) = \tilde{x}_\alpha$. Consequently, the term with trailing $\tilde{x}_\alpha$ in $T^{(1)}$ does not contribute to $Q_2$. The remaining terms in $T^{(1)}$ do contribute to $h^2$ terms.

The terms of $T^{(2)}$ are by definition fourth order in the components of $\tilde{x}$. In Eq. (28) we see $h^4$ terms of the type

$$\langle \tilde{x}_\alpha \tilde{U} \rangle (\tilde{x}_\alpha \tilde{U}) (\tilde{x}_\alpha \tilde{U})$$  

$$= \langle \tilde{x}_\alpha \tilde{U} \rangle (\tilde{x}_\alpha \tilde{U}) (\tilde{x}_\alpha \tilde{U})$$  

and also terms with trailing operators. At first sight it seems as if $T^{(2)}$ is of highest order 3 in the trailing operators, because of the presence of $[\tilde{x}_\alpha, \tilde{x}_\alpha]$. The linear momenta commute with themselves and also with the angular momenta, so that only the case $[\tilde{U}, \tilde{U}]$ and $[\tilde{U}, \tilde{U}]$ is of concern. In general, the commutation relations of $J_\alpha$’s imply that the commutator $[J_{\alpha 0} J_{\alpha_0} \cdots J_{\alpha_n}]$ is of order $n+1$ in the operators $J_\alpha$, $J_\alpha$, and $J_\alpha$ so that $T^{(2)}$ is of maximum order 2 in the trailing operators.

Noting that $\langle \tilde{x}_\alpha \tilde{U} \rangle (\tilde{x}_\alpha \tilde{U}) \exp(-\tilde{H}_0) | \tilde{x}\rangle$ vanishes, as do the cross terms $\tilde{x}_\alpha \tilde{x}_\beta$, we see that $T^{(2)}$ contributes only terms of the type $\langle \tilde{x}_\alpha \tilde{U} \rangle (\tilde{x}_\alpha \tilde{U})$ and $\langle \tilde{x}_\alpha \tilde{U} \rangle (\tilde{x}_\alpha \tilde{U})$ to the first quantum correction, together with the $O(h^2)$ term of $\langle \tilde{x}\tilde{U}\rangle \times \exp(-\tilde{H}_0) | \tilde{x}\rangle$. The first-order $O(h^1)$ term in the latter expectation value is given in Eq. (14). Obviously this term contributes $O(h^2)$ to $B_2$ and can consistently be neglected. (In the preceding section the size of this term was discussed for $H_2$ and $H_3$ as examples of asymmetric top molecules.) In conclusion, in order to compute the first-order quantum correction we need at least $T^{(1)}$ and $T^{(2)}$.

By the principle of mathematical induction we show that $T^{(n+1)}$ is of maximum order $n+1$ in the trailing operators. Assume that to that end the trailing polynomial of $T^{(n)}$ is of maximum order $n$ in the components of $\tilde{x}$. We have seen that this is true for $n=0$, 1, and 2. From the master relation $[\tilde{H}_0, T^{(n)}] = 0$ follows that $dT^{(n+1)}/dt$ is of order $n+1$ in the $\tilde{x}_\alpha$’s, since we have just argued that $[T^{(n)}(t), \tilde{H}_0]$ is of order $n+1$. Furthermore, integration does not change this order, and so $T^{(n+1)}$ is of maximum order $n+1$ in the components of $\tilde{x}$. For $T^{(3)}$ this implies that the maximum order of its trailing operator is 3, so that the derivatives of the potential are of minimum order 3 and contribute to $h^3$ terms. By the same argument the elements $T^{(k)}$ for $k > 3$ do not give $h^3$ contributions, which is why only $T^{(1)}$ and $T^{(2)}$ contribute in order $h^2$.

### IV. CONTRIBUTIONS TO $B_2$

In this section the classical and first quantum contribution to the second virial coefficient $B_2(T)$ will be given. We reiterate that only $Q_2$ is needed. Using the general expression for $Q_N$ valid in the Boltzmann limit (no exchange), we write

$$Q_2 = \frac{1}{2!} \int \langle x_1, x_2 \rangle e^{-\beta U(x_1, x_2)} dx_1 \, dx_2$$  

$$= \frac{1}{2!} \int e^{-\beta U(x_1, x_2)} \langle x_1, x_2 \rangle [T e^{-\beta U(x_1, x_2)}] dx_1 \, dx_2.$$  

(29)

Since $U$ is a local function of $x_1$ and $x_2$ we were able to use here

$$\langle x_1, x_2 \rangle [e^{-\beta U(x_1, x_2)}] = \delta(x_1 - x_1) \delta(x_2 - x_2) e^{-\beta U(x_1, x_2)}.$$
A. Contributions from $T^0$

Insert $T^0=1$ and twice the Slater sum [Eq. (17)] into Eq. (29) and we get the classical contribution to the two-body partition function,

$$Q_2^{(0)} = \frac{1}{2!} \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int dx_1 dx_2 e^{-\beta U(x_1, x_2)}. \quad (30)$$

Using Eq. (2) it follows that the classical contribution to $B_2$ for a gas consisting of interacting asymmetric tops is

$$B_2^{(0)} = \frac{1}{V 128 \pi^4} \int \left[ 1 - e^{-\beta U(x_1, x_2)} \right] dx_1 dx_2. \quad (31)$$

B. Contributions from $T^1$

From Eq. (26) we get the contribution $Q_2^{(1)}$ to $Q_2$ arising from $T^1$

$$Q_2^{(1)} = \frac{1}{2!} \int e^{-\beta U(x_1, x_2)} \left[ \frac{1}{2} \bar{U}_{aa}(x_1, x_2) - \frac{1}{3} \bar{U}_a(x_1, x_2) \right]^2$$

$$\times \langle x_1, x_2 | e^{-\beta H} | x_1, x_2 \rangle dx_1 dx_2. \quad (32)$$

We used here that $\bar{U}_{aa}$ and $\bar{U}_a^2$ are local and hence diagonal in the $x$ representation. We dropped the term with trailing $\bar{V}_a$, because it gives a vanishing contribution. Using Eq. (17) for the Slater sum gives

$$Q_2^{(1)} = \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int e^{-\beta U(x_1, x_2)} \left[ \frac{1}{4} \bar{U}_{aa}(x_1, x_2) \right.$$ 

$$- \frac{1}{6} \bar{U}_a(x_1, x_2) \left. \right]^2 dx_1 dx_2.$$

Knowing that $\bar{V}_a$ is Hermitian and purely imaginary, we can rewrite the second derivative as a product of two first derivatives, namely,

$$\int e^{-\beta \bar{V}_a \bar{V}_a} d\bar{U} dx_1 dx_2 = \int (\bar{V}_a \exp(-\beta \bar{U}))^2 \bar{V}_a \exp(-\beta \bar{U}) d\bar{U} dx_1 dx_2$$

$$= \int (e^{-\beta \bar{V}_a} \bar{V}_a)^2 \bar{V}_a \exp(-\beta \bar{U}) d\bar{U} dx_1 dx_2$$

$$= e^{-\beta \bar{V}_a \bar{V}_a} \bar{U}_a dx_1 dx_2.$$

This result may be summarized by the effective [valid inside the integral with kernel $\exp(-\beta \bar{U})$] equation

$$H_0 U = \bar{V}_a \bar{V}_a U = \beta (\bar{V}_a U)(\bar{V}_a U). \quad (33)$$

Using this in Eq. (32), we get the final contribution to $Q_2^{(1)}$ from $T^1$

$$Q_2^{(1)} = \frac{1}{12} \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int e^{-\beta U(x_1, x_2)} \bar{U}_a(x_1, x_2)^2 dx_1 dx_2. \quad (34)$$

Anticipating that the contribution from $T^2$ has the same form, the adding of this result to $B_2^{(0)}$ will be postponed to the last section.

C. Contributions from $T^2$

As discussed in the preceding section, only the second derivatives of the potential arising in Eq. (28) need be considered in the $\hbar^2$ approximation. These terms contain trailing polynomials bilinear in $\bar{V}_a \bar{V}_b$ (or $\bar{V}_a \bar{V}_b$) with different particle index $i \neq j$ vanish. For equal particle index only the diagonal terms $\bar{V}_a \bar{V}_a$ survive; this is true for the translational as well as for the rotational derivatives. Hence $T^2$ contributes:

$$Q_2^{(2)} = \frac{1}{2} \int e^{-\beta U(x_1, x_2)} \left[ \frac{1}{8} \bar{U}_a(x_1, x_2)^2 - \frac{1}{3} \bar{U}_{aa}(x_1, x_2) \right]$$

$$\times \langle x_1, x_2 | \bar{V}_a \bar{V}_a e^{-\beta H} | x_1, x_2 \rangle dx_1 dx_2. \quad (35)$$

Recalling that the summation convention is employed (sum over two particles and six degrees of freedom per particle), it is easily shown that for the second derivatives of an arbitrary function $\bar{V}(x_1, x_2)$

$$\bar{V}_{aa}(x_1, x_2) \bar{V}_a \bar{V}_a e^{-\beta H} | x_1, x_2 \rangle = \frac{1}{2} \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \bar{V}_{aa}$$

holds. Note that this is equally valid for translational [cf. Eq. (7)] as well as rotational [with neglect of $F_{ai}$, cf. Eq. (14)] derivatives. Hence

$$Q_2^{(2)} = \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int e^{-\beta U(x_1, x_2)} \left[ \frac{1}{8} \bar{U}_a(x_1, x_2)^2$$

$$- \frac{1}{6} \bar{U}_{aa}(x_1, x_2) \right] dx_1 dx_2$$

$$= \frac{1}{24} \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int e^{-\beta U(x_1, x_2)} \bar{U}_a(x_1, x_2)^2 dx_1 dx_2. \quad (36)$$

where for the second equality Eq. (33) has been employed. Adding this expressions to Eq. (34) and reintroducing summations give finally the total correction of order $\hbar^2$ to the partition function $Q_2$ as

$$Q_2^{(1+2)} = \frac{1}{24} \left( \frac{Q_1}{V 8 \pi^2} \right)^2 \int e^{-\beta U(x_1, x_2)}$$

$$\times \sum_{i=1}^{2} \sum_{a=1}^{6} [\bar{V}_a(i) \bar{U}_a(x_1, x_2)]^2 dx_1 dx_2. \quad (37)$$

Upon recalling the definition of $\bar{V}_a(i)$ from Eq. (18), we have a result for asymmetric rotors that is the same as that obtained earlier by Friedmann for symmetric rotors (two equal inertia moments).

D. Virial coefficient $B_2$

If we now add the classical contribution [Eq. (30)] to $Q_2^{(1+2)}$ [Eq. (37)] and use this in Eq. (2), we obtain the second virial coefficient correct through $\hbar^2$, namely,
\[ B_2 = \frac{1}{128V^2} \int \left[ 1 - e^{-\tilde{U}(x_1x_2)} \right] \times \left( 1 + \frac{\beta}{12} \sum_{a=1}^{2} \sum_{i=1}^{6} \left[ \tilde{V}_a(i) \tilde{U}(x_1x_2) \right]^2 \right) dx_1 dx_2. \]

Using Eq. (33) we can rewrite this equation thus
\[ B_2(T) = \frac{1}{128V^2} \int \cdots \left[ 1 - e^{-\beta \tilde{U}(x_1x_2)} \right] \times \left[ 1 + \frac{\beta^2}{12} \hat{H}_0(U) \right] dx_1 dx_2, \]

which has precisely the same form as the equation previously derived by T Pack\(^2\) for a gas of symmetric rotors. (Note that T Pack defines \(B_2\) as a molar property, whereas here it is a molecular property, the difference being a factor \(N_A\), which is Avogadro’s number.)

To simplify the integrals somewhat, we introduce
\[ \mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \]
and
\[ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \]
and assume that \(U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{\omega}_1, \mathbf{\omega}_2)\) does not depend on the position \(\mathbf{R}\) of the dimer mass center, but only on the distance \(\mathbf{r}\) and \(\mathbf{\omega}_1, \mathbf{\omega}_2\). Use
\[ d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{R} d\mathbf{r} \]
and
\[ d\mathbf{R} = V. \]

Let \(\mathbf{P}\) and \(\mathbf{p}\) be conjugate to \(\mathbf{R}\) and \(\mathbf{r}\), then it is well known that
\[ \frac{p(1)^2}{2M} + \frac{p(2)^2}{2M} = \frac{P^2}{4M} + \frac{p^2}{M}, \]
where \(\mathbf{P}\) and \(\mathbf{p}\) are the linear momentum of the dimer center of mass and the dimer relative particle (with reduced mass \(M/2\)), respectively. Noting that \(P^2U=0\) we obtain finally an expression for \(B_2(T)\) correct through \(\hbar^2\),
\[ B_2(T) = \frac{1}{128V^2} \int \left[ 1 - e^{-\beta \tilde{U}(\mathbf{\omega}_2, \mathbf{\omega}_2)} \right] \times \left( 1 + \frac{\beta^2}{12M} \sum_{a=1}^{3} \left[ p_a \tilde{U}(\mathbf{\omega}_1, \mathbf{\omega}_2) \right]^2 \right) d\mathbf{r} d\mathbf{\omega}_1 d\mathbf{\omega}_2. \]

The quantum correction contains an inner product of forces,
\[ \sum_{i=1}^{2} \sum_{a=4}^{6} \left[ \tilde{V}_a(i) \tilde{U}(\mathbf{\omega}_1, \mathbf{\omega}_2) \right]^2 \]
and of torques,
\[ \sum_{i=1}^{2} \sum_{a=4}^{6} \left[ \tilde{V}_a(i) \tilde{U}(\mathbf{\omega}_1, \mathbf{\omega}_2) \right]^2 \frac{1}{2M} \left[ \mathcal{J}_a(i) U \right]^2. \]

Both contributions are dimensionless. The quantum correction is purely dynamic as it does not contain kinetic energy terms.

V. SUMMARY

We have drastically simplified Friedmann’s approach to the quantum correction of canonical partition functions of symmetric tops. This was achieved by considering body-fixed angular momenta instead of derivatives with respect to Euler angles. The simplification reduced the length of the derivations considerably and it gives as an extra bonus the first quantum correction for asymmetric tops. The partition function was applied in the derivation of the second virial coefficient \(B_2\). The virial coefficient obtained has exactly the same form as the one published by T Pack,\(^2\) but without the restriction of its applicability to symmetric tops only. For further discussion and application of the formula for \(B_2\) to actual systems we refer to T Pack’s paper. Suffice it to say that the final equation is most easily applied when the intermolecular potential \(U(\mathbf{r}, \mathbf{\omega}_1, \mathbf{\omega}_2)\) is expanded in a product of \(D\) matrices and spherical harmonics: \(D_{m_k l}^l (\mathbf{\omega}_1)D_{m_k l}^l (\mathbf{\omega}_2)Y_{L}^j (\hat{r})\), see e.g., Ref. 15. The action of \(\mathcal{J}_a, \mathcal{J}_b, \mathcal{J}_c\) is easy after expressing these operators (that act on the column indices of the \(D\) matrices) in terms of shift operators. Expression of \(\mathbf{p}\) in spherical polar coordinates makes the action on \(Y_{L}^j (\hat{r})\) also well defined and easy.