

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 Pack² 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 for the N -body canonical partition function derived earlier by Friedmann³ for the special case of symmetric tops. The general expression for a partition function is

$$Q_N(T) \equiv \text{Tr} e^{-\beta H(1,2,\dots,N)}, \quad (1)$$

where $\beta=1/(k_B T)$, k_B is the Boltzmann constant, and $H(1,2,\dots,N)$ is the Hamiltonian of a system of N interacting rigid rotors. One of the purposes of this paper is to show that T Pack's equation is valid equally well for gases consisting of asymmetric tops. We will do this by deriving the first quantum correction to Q_N , or rather to Q_2 . Only the case $N=2$ is of importance for virial coefficients, since they may be obtained from⁴

$$B_2(T) = V \left(\frac{1}{2} - \frac{Q_2(T)}{Q_1(T)^2} \right), \quad (2)$$

where V is the volume of the vessel containing the gas.

In this paper we will follow an idea of Friedmann³ concerning the expansion of $\exp[-\beta H]$ in orders of \hbar . Friedmann considered the first (\hbar^2) quantum correction to Q_N for systems of N diatoms and N symmetric tops. His expansion will be applied below to Q_2 in a much simpler setting. Friedmann's approach is very complicated as he starts out from

the general Laplace–Beltrami–Podolsky^{5,6} form of the Hamiltonian valid for arbitrary coordinate systems (even for those with nondiagonal metric tensors, such as Euler angles). The inverse of the metric tensor, its derivatives, and its determinant appear in the Hamiltonian. After a quite complicated development Friedmann specialized his general theory to diatoms and symmetric tops, both of which have metric tensors that can be found in textbooks.⁷ However, both types of systems can be treated very well with angular momentum theory without any explicit reference to metric tensors. The metric tensor of an asymmetric top is somewhat more complicated than that of a symmetric top and Friedmann did not consider the former case. A compact derivation of quantum corrections to Q_N will be given that is more accessible than Friedmann's 30 odd pages. We will look at asymmetric tops using angular momentum operators instead of coordinate derivatives. The complicated Laplace–Beltrami–Podolsky Hamiltonian is replaced by the simple rigid-rotor Hamiltonian

$$H_{\text{rot}} = \frac{\mathcal{J}_x^2}{2I_x} + \frac{\mathcal{J}_y^2}{2I_y} + \frac{\mathcal{J}_z^2}{2I_z}, \quad (3)$$

where I_a is an inertia moment and \mathcal{J}_a ($a=x,y,z$) is a component of the body-fixed angular momentum operator.⁸ The symmetric top will follow as the special case that two out of the three inertia moments are equal.

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 \mathbf{r} of its center of mass, and its orientation, given by the three Euler angles $\boldsymbol{\omega} \equiv (\omega_1, \omega_2, \omega_3)$. Thus, a rotor has the coordinates $\mathbf{x} \equiv (\mathbf{r}, \boldsymbol{\omega})$. The quantum mechanical kinetic energy of a

rotor is a sum of a translational part $H_{\text{tr}} = \mathbf{p} \cdot \mathbf{p} / (2M)$, with M the mass of the rotor, and a rotational part H_{rot} [Eq. (3)]. The one-body partition function factorizes

$$Q_1 = \text{Tr}(e^{-\beta H_{\text{tr}}}) \text{Tr}(e^{-\beta H_{\text{rot}}}) \equiv Q_1^{\text{tr}} Q_1^{\text{rot}}.$$

The operator $p_a \equiv -i\hbar \partial / \partial r_a$ ($a=x, y, z$) 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 \mathcal{J}_x , \mathcal{J}_y , and \mathcal{J}_z are Hermitian since they act on periodic functions of the Euler angles. Note that while $[p_a, p_b] = 0$ ($a, b=x, y, z$), the body-fixed operators \mathcal{J}_a satisfy the well-known⁸ anomalous commutation relations.

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

$$Q_1^{\text{tr}} = \int_V d\mathbf{r} W_1^{\text{tr}}(\mathbf{r}) \quad \text{with } W_1^{\text{tr}}(\mathbf{r}) = \langle \mathbf{r} | e^{-\beta H_{\text{tr}}} | \mathbf{r} \rangle. \quad (4)$$

We assume on the one hand that the operators \mathbf{r} and \mathbf{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,⁹ the Slater sum is independent of \mathbf{r} and is related to de Broglie thermal length Λ by

$$W_1^{\text{tr}} = \Lambda^{-3} \equiv \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2}, \quad (5)$$

so that $Q_1^{\text{tr}} = V \Lambda^{-3}$.

In the following section we will meet the expression $\langle \mathbf{r} | p_a p_b \exp(-\beta H_{\text{tr}}) | \mathbf{r} \rangle$ 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 $P(p_x, p_y, p_z)$ and consider

$$\langle \mathbf{r} | P(p_x, p_y, p_z) e^{-\beta H_{\text{tr}}} | \mathbf{r} \rangle. \quad (6)$$

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 $P(p_x, p_y, p_z)$ 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 \mathbf{p} representation and $\langle \mathbf{r} | \mathbf{p} \rangle = h^{-3/2} \exp(i\mathbf{r} \cdot \mathbf{p})$, so that $\langle \mathbf{r} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{r} \rangle = h^{-3}$, we find by simple integration,

$$\frac{1}{2M} \langle \mathbf{r} | p_a p_b e^{-\beta H_{\text{tr}}} | \mathbf{r} \rangle = \delta_{ab} \frac{k_B T}{2} \Lambda^{-3} = \delta_{ab} \frac{k_B T}{2} \frac{Q_1^{\text{tr}}}{V}, \quad (7)$$

where the Kronecker δ is due to reflection symmetry in \mathbf{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 ob-

tained by diagonalizing H_{rot} on the space spanned by the elements (symmetric top eigenfunctions¹⁰) in row M of the complex conjugate of a Wigner D matrix.¹¹ The result is independent of M . That is, the eigenfunctions belonging to the $(2J+1)$ -degenerate energy $E_{J\tau}$ are

$$\langle \boldsymbol{\omega} | JM\tau \rangle = \sqrt{\frac{2J+1}{8\pi^2}} \sum_{K=-J}^J c_{K\tau} D_{MK}^J(\boldsymbol{\omega})^*, \quad M = -J, \dots, J,$$

where $D_{MK}^J(\boldsymbol{\omega})^*$ 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 $\text{SO}(3)$] shows that the states are orthogonal on J and M and, being eigenstates of H_{rot} , also on τ ,

$$\int d\boldsymbol{\omega} \langle J'M'\tau' | \boldsymbol{\omega} \rangle \langle \boldsymbol{\omega} | JM\tau \rangle = \delta_{J'J} \delta_{M'M} \delta_{\tau'\tau}, \quad (8)$$

with $d\boldsymbol{\omega} = \sin \omega_2 d\omega_1 d\omega_2 d\omega_3$.

The Slater sum $W_1^{\text{rot}} = \langle \boldsymbol{\omega} | e^{-\beta H_{\text{rot}}} | \boldsymbol{\omega} \rangle$ is independent of $\boldsymbol{\omega}$. This statement can be generalized to the operator

$$\rho \equiv P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z) e^{-\beta H_{\text{rot}}},$$

where $P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z)$ is a homogeneous polynomial. Since the \mathcal{J}_a 's do not commute mutually we cannot use the same manner of proof as for the p_a 's. Therefore, we consider first

$$\begin{aligned} & \sum_M \langle \boldsymbol{\omega} | JM\tau \rangle \langle JM\tau' | \boldsymbol{\omega} \rangle \\ &= \frac{2J+1}{8\pi^2} \sum_{KK'} c_{K\tau} c_{K'\tau'}^* \sum_M D_{MK}^J(\boldsymbol{\omega})^* D_{MK'}^J(\boldsymbol{\omega}) \\ &= \frac{2J+1}{8\pi^2} \sum_K c_{K\tau} c_{K\tau'}^* = \frac{2J+1}{8\pi^2} \delta_{\tau\tau'}. \end{aligned} \quad (9)$$

The dependence on $\boldsymbol{\omega}$ 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 $\langle \boldsymbol{\omega} | \rho | \boldsymbol{\omega} \rangle$ in three places, employment of the diagonality of $P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z)$ in J and M and the independence of its matrix elements on M (because the body-fixed angular momenta commute with the space-fixed J_z , whose eigenvalue is M), taken together with the diagonality of $\exp[-\beta H_{\text{rot}}]$ in J , M and τ gives for $\langle \boldsymbol{\omega} | \rho | \boldsymbol{\omega} \rangle$ the result

$$\begin{aligned} \langle \boldsymbol{\omega} | \rho | \boldsymbol{\omega} \rangle &= \sum_{JM\tau\tau'} \langle \boldsymbol{\omega} | JM\tau \rangle \langle JM\tau' | P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z) | JM\tau' \rangle \\ &\quad \times \langle JM\tau' | e^{-\beta H_{\text{rot}}} | JM\tau'' \rangle \langle JM\tau'' | \boldsymbol{\omega} \rangle \\ &= \frac{1}{8\pi^2} \sum_{JM\tau} \langle JM\tau | P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z) e^{-\beta H_{\text{rot}}} | JM\tau \rangle. \end{aligned} \quad (10)$$

In particular,

$$W_1^{\text{rot}} = \langle \boldsymbol{\omega} | e^{-\beta H_{\text{rot}}} | \boldsymbol{\omega} \rangle = \frac{Q_1^{\text{rot}}}{8\pi^2}.$$

The trace in Eq. (10) does not necessarily vanish for polynomials $P(\mathcal{J}_x, \mathcal{J}_y, \mathcal{J}_z)$ of odd order. The asymmetric top Hamiltonian H_{rot} belongs to the Abelian symmetry group D_2 , which consists of rotations by π around the three inertial

axes. A rotation around the x axis gives $\mathcal{J}_y \mapsto -\mathcal{J}_y$, $\mathcal{J}_z \mapsto -\mathcal{J}_z$, and $\mathcal{J}_x \mapsto \mathcal{J}_x$. The rotations around the y and z axis give the corresponding (cyclically permuted) maps. So, the three operators \mathcal{J}_x , \mathcal{J}_y , and \mathcal{J}_z transform according to different irreducible representations (irreps) of D_2 .¹² Rigid rotor functions $|JM\tau\rangle$ 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 \mathcal{J}_x , \mathcal{J}_y , and \mathcal{J}_z do not transform as A_1 their expectation values vanish. In second order only the squares \mathcal{J}_x^2 , \mathcal{J}_y^2 , and \mathcal{J}_z^2 transform as A_1 , while out of all third-order monomials only the product $\mathcal{J}_x\mathcal{J}_y\mathcal{J}_z$ transforms as A_1 . If higher than \hbar^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_∞ .

We will need expressions for $\langle \boldsymbol{\omega} | \mathcal{J}_a^2 e^{-\beta H_{\text{rot}}} | \boldsymbol{\omega} \rangle$ ($a = x, y, z$). While the corresponding expressions for p_a^2 [Eq. (7)] could be obtained by integration, there are no closed formulas for these expressions. Introducing the rotational temperature $\Theta_a = \hbar^2 / (2I_a k_B)$ we can write, however,

$$\frac{\text{Tr}(\mathcal{J}_a^2 e^{-\beta H_{\text{rot}}})}{Q_1^{\text{rot}}} = -T\hbar^2 \frac{\partial \ln Q_1^{\text{rot}}}{\partial \Theta_a}, \quad a = x, y, z,$$

and from Eq. (10)

$$\langle \boldsymbol{\omega} | \mathcal{J}_a^2 e^{-\beta H_{\text{rot}}} | \boldsymbol{\omega} \rangle = -\frac{Q_1^{\text{rot}} T \hbar^2 \partial \ln Q_1^{\text{rot}}}{2 \partial \Theta_a}. \quad (11)$$

Stripp and Kirkwood¹³ derived an approximation for Q_1^{rot} that consists of a sum of a classical and a first-order quantum term. The first term $Q_1^{\text{rot,class}}$ is an integral over phase space (premultiplied by h^{-3}), which can be computed analytically, giving

$$Q_1^{\text{rot,class}} = \left(\frac{\pi T^3}{\Theta_x \Theta_y \Theta_z} \right)^{1/2}. \quad (12)$$

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

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

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

$$\langle \boldsymbol{\omega} | \frac{\mathcal{J}_a^2}{2I_a} e^{-\beta H_{\text{rot}}} | \boldsymbol{\omega} \rangle = \frac{k_B T Q_1^{\text{rot}}}{8\pi^2} \left(\frac{1}{2} - F_a(T) \right) + O(\hbar^4) \quad (14)$$

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

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

in which $P(T)$ is given as

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

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

$$\langle\langle H_{\text{rot}} \rangle\rangle = \frac{\text{Tr} H_{\text{rot}} e^{-\beta H_{\text{rot}}}}{Q_1^{\text{rot}}} = k_B T \left(\frac{3}{2} - \sum_{a=x,y,z} F_a(T) \right). \quad (16)$$

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 $\text{Tr}[H_{\text{rot}} \exp(-\beta H_{\text{rot}})]$ and $\text{Tr}[\exp(-\beta H_{\text{rot}})]$ numerically, one can approximate the value of $\langle\langle H_{\text{rot}} \rangle\rangle$ 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 $\langle\langle H_{\text{rot}} \rangle\rangle$. Upon recalling the definition of H_{rot} in Eq. (3), we note that the operation of \mathcal{J}_a on the symmetric top wave functions $D_{MK}^J(\boldsymbol{\omega})^*$ is well defined, and via the use of step-up(down) operators easily implemented. Thus, in the basis $D_{MK}^J(\boldsymbol{\omega})^*$ (J and K 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 $E_{J\tau}$, the matrices of $\exp(-\beta H_{\text{rot}})$ and $H_{\text{rot}} \exp(-\beta H_{\text{rot}})$ become diagonal and functions of $E_{J\tau}$, so that their contributions to $\langle\langle H_{\text{rot}} \rangle\rangle$ 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 H_2O and SO_2 molecules as typical examples of asymmetric tops. From $m_{\text{H}} = 1.007\,825\,2$ u, $m_{\text{O}} = 15.994\,915\,0$ u, $m_{\text{S}} = 31.972\,070\,69$ u, $r_{\text{OH}} = 0.9572$ Å, $r_{\text{SO}} = 1.4321$ Å, $\angle \text{H-O-H} = 104.5^\circ$, $\angle \text{O-S-O} = 119.5^\circ$, we obtain the following rotational temperatures (the molecules are in the xy plane, the yz plane is the symmetry plane):

$$\text{H}_2\text{O}: \Theta_x = 39.455 \text{ K}, \quad \Theta_y = 21.007 \text{ K}, \quad \text{and}$$

$$\Theta_z = 13.708 \text{ K},$$

$$\text{SO}_2: \Theta_x = 2.9176 \text{ K}, \quad \Theta_y = 0.4952 \text{ K}, \quad \text{and}$$

$$\Theta_z = 0.4234 \text{ K}.$$

The symmetry number σ (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: for 50 K 0.94%, for 100 K 0.24%, and for 500 K 0.01%. For the much heavier molecule SO_2 the error is (within four digit accuracy) zero for the four temperatures listed. That is, the first quantum correction gives essentially the exact result. It is important for the present development that the classical approximation to $\langle\langle H_{\text{rot}} \rangle\rangle$ [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 (within four decimal digits), while neglect of F_z introduces a small error (6% at 50 K) for H_2O and hardly any (0.2% at 50 K) for 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 $\langle\langle H_{\text{rot}}\rangle\rangle/(k_B T)$ in column labeled ‘‘Approx,’’ see Eq. (16) for its definition. See Eq. (15) for the definition of F_x , F_y , and F_z . T is in kelvin. Column labeled ‘‘Exact’’ gives exact values of $\langle\langle H_{\text{rot}}\rangle\rangle/(k_B T)$ obtained from converged numerical calculations.

T	F_x	F_y	F_z	Approx.	Exact
H ₂ O					
50	0.0000	0.0000	0.0837	1.4163	1.4031
100	0.0000	0.0000	0.0437	1.4563	1.4528
500	0.0000	0.0000	0.0091	1.4909	1.4908
1000	0.0000	0.0000	0.0045	1.4955	1.4954
SO ₂					
50	0.0000	0.0000	0.0028	1.4972	1.4972
100	0.0000	0.0000	0.0014	1.4986	1.4986
500	0.0000	0.0000	0.0003	1.4997	1.4997
1000	0.0000	0.0000	0.0001	1.4999	1.4999

$$W_1 \equiv \langle \mathbf{x} | e^{-\beta(H_{\text{tr}} + H_{\text{rot}})} | \mathbf{x} \rangle = \frac{Q_1^{\text{tr}} Q_1^{\text{rot}}}{V 8 \pi^2} = \frac{Q_1}{V 8 \pi^2}. \quad (17)$$

$$\tilde{U}_\alpha = [\tilde{\nabla}_\alpha, \tilde{U}]$$

and

$$\tilde{U}_{\alpha\alpha} = [\tilde{\nabla}_\alpha, \tilde{U}_\alpha].$$

It is easy to show that

$$\text{ad } \tilde{U} \tilde{H}_0 = \tilde{\nabla}_\alpha (\text{ad } \tilde{U} \tilde{\nabla}_\alpha) + (\text{ad } \tilde{U} \tilde{\nabla}_\alpha) \tilde{\nabla}_\alpha = -\tilde{U}_{\alpha\alpha} - 2\tilde{U}_\alpha \tilde{\nabla}_\alpha, \quad (20)$$

and, by applying $\text{ad } \tilde{U}$ again,

$$(\text{ad } \tilde{U})^2 \tilde{H}_0 = 2(U_\alpha)^2, \quad (\text{ad } \tilde{U})^3 \tilde{H}_0 = 0. \quad (21)$$

The latter property restricts expansions containing $(\text{ad } \tilde{U})^k \tilde{H}_0$ to $k=2$.

Consider now

$$V(t) \equiv e^{-t(\tilde{U} + \tilde{H}_0)} = e^{-t\tilde{U}} T(t) e^{-t\tilde{H}_0}$$

and note that for $t=1$ we get the relation of Eq. (19), i.e., $T(1)$ is the operator we wish to expand, while $T(0)=1$. Differentiation gives

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

Multiplication by $\exp(t\tilde{U})$ on the left and $\exp(t\tilde{H}_0)$ on the right gives

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

Introduce the following commutator expansion:¹⁴

$$e^{t\tilde{U}} \tilde{H}_0 e^{-t\tilde{U}} = (e^{t \text{ad } \tilde{U}}) \tilde{H}_0 = \sum_{k=0}^{\infty} \frac{t^k}{k!} (\text{ad } \tilde{U})^k \tilde{H}_0,$$

so that

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

To simplify and unify notation we define

$$\nabla_a(i) \equiv \begin{cases} (2M)^{-1/2} p_a(i) & \text{for } a=1,2,3, \\ (2I_{a-3})^{-1/2} \mathcal{J}_{a-3}(i) & \text{for } a=4,5,6. \end{cases} \quad (18)$$

The operator $\nabla_a(i)$ is Hermitian. The pair potential is $U(\mathbf{x}_1, \mathbf{x}_2)$ and the two-body Hamiltonian becomes $H=H_0+U$, with $H_0=\sum_i [H_{\text{tr}}(i)+H_{\text{rot}}(i)]$. We will write

$$H_0 = \nabla_\alpha \nabla_\alpha \equiv \sum_{\alpha=1}^{12} \nabla_\alpha \nabla_\alpha \equiv \sum_{i=1}^2 \sum_{a=1}^6 \nabla_a(i) \nabla_a(i),$$

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

$$\tilde{H}_0 = \tilde{\nabla}_\alpha \tilde{\nabla}_\alpha$$

with

$$\tilde{\nabla}_\alpha = \sqrt{\beta} \nabla_\alpha.$$

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

$$T \equiv e^{\tilde{U}} e^{-\tilde{U}-\tilde{H}_0} e^{\tilde{H}_0} \Leftrightarrow e^{-\beta(H_0+U)} = e^{-\beta U} T e^{-\beta H_0} \quad (19)$$

and expand it

$$T = 1 + T^{(1)} + T^{(2)} + \dots,$$

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

$$(\text{ad } \tilde{U})^k \tilde{H}_0 = \underbrace{[\tilde{U}, [\tilde{U}, [\dots [\tilde{U}, \tilde{H}_0]] \dots]]}_{k \text{ times nested}}.$$

We define first and second derivatives

$$\frac{dT(t)}{dt} = [T(t), \tilde{H}_0] - \left\{ \sum_{k=1}^2 \frac{t^k}{k!} (\text{ad } \tilde{U})^k \tilde{H}_0 \right\} T(t), \quad (23)$$

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

$$\frac{dT^{(n+1)}}{dt} = [T^{(n)}(t), \tilde{H}_0] + [t(\tilde{U}_{\alpha\alpha} + 2\tilde{U}_{\alpha}\nabla_{\alpha}) - t^2\tilde{U}_{\alpha}^2]T^{(n)}, \quad (24)$$

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

Integration over t' from 0 to t yields the expansion

$$T^{(1)}(t) = - \sum_{k=1}^2 \frac{t^{k+1}}{(k+1)!} (\text{ad } \tilde{U})^k \tilde{H}_0. \quad (25)$$

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

$$T^{(1)} = \frac{1}{2}\tilde{U}_{\alpha\alpha} + \tilde{U}_{\alpha}\tilde{\nabla}_{\alpha} - \frac{1}{3}\tilde{U}_{\alpha}^2. \quad (26)$$

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

$$\begin{aligned} T^{(2)}(t) = & - \sum_{k=1}^2 \frac{t^{k+2}}{(k+2)!} [(\text{ad } \tilde{U})^k \tilde{H}_0, \tilde{H}_0] \\ & + \sum_{k_1, k_2=1}^2 \frac{t^{k_1+k_2+2}}{(k_1+k_2+2)k_1!(k_2+1)!} (\text{ad } \tilde{U})^{k_1} \\ & \times \tilde{H}_0 (\text{ad } \tilde{U})^{k_2} \tilde{H}_0. \end{aligned} \quad (27)$$

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

$$\begin{aligned} T^{(2)} = & -\frac{1}{6}\tilde{U}_{\alpha\alpha\beta\beta} + \frac{1}{8}\tilde{U}_{\alpha\alpha}\tilde{U}_{\beta\beta} + \frac{1}{6}\tilde{U}_{\alpha\beta}\tilde{U}_{\alpha\beta} + \frac{5}{12}\tilde{U}_{\alpha}\tilde{U}_{\alpha\beta\beta} \\ & - \frac{1}{6}\tilde{U}_{\alpha}\tilde{U}_{\alpha}\tilde{U}_{\beta\beta} - \frac{4}{15}\tilde{U}_{\alpha}\tilde{U}_{\beta}\tilde{U}_{\alpha\beta} + \frac{1}{18}\tilde{U}_{\alpha}\tilde{U}_{\alpha}\tilde{U}_{\beta}\tilde{U}_{\beta} \\ & - \frac{2}{3}\tilde{U}_{\alpha\alpha\beta}\tilde{\nabla}_{\beta} + \frac{1}{2}\tilde{U}_{\alpha\alpha}\tilde{U}_{\beta}\tilde{\nabla}_{\beta} + \frac{5}{6}\tilde{U}_{\alpha}\tilde{U}_{\alpha\beta}\tilde{\nabla}_{\beta} \\ & - \frac{1}{3}\tilde{U}_{\alpha}\tilde{U}_{\alpha}\tilde{U}_{\beta}\tilde{\nabla}_{\beta} - \frac{2}{3}\tilde{U}_{\alpha\beta}\tilde{\nabla}_{\alpha}\tilde{\nabla}_{\beta} + \frac{1}{2}\tilde{U}_{\alpha}\tilde{U}_{\beta}\tilde{\nabla}_{\alpha}\tilde{\nabla}_{\beta} \\ & - \frac{1}{3}\tilde{U}_{\alpha}[\tilde{\nabla}_{\beta}^2, \tilde{\nabla}_{\alpha}]. \end{aligned} \quad (28)$$

At this point we can show that *only* $T^{(1)}$ and $T^{(2)}$ contribute to the first quantum correction of $B_2(T)$. 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 $(\tilde{\nabla}_{\alpha}\tilde{\nabla}_{\alpha}\tilde{U})$ and $(\tilde{\nabla}_{\alpha}\tilde{U})(\tilde{\nabla}_{\alpha}\tilde{U})$, but also that a term $(\tilde{\nabla}_{\alpha}\tilde{U})\tilde{\nabla}_{\alpha}$ with trailing operator $\tilde{\nabla}_{\alpha}$ appears. In general the $T^{(n)}$ terms have trailing polynomials $P(\tilde{\nabla})$ of different order and we will see below that these arise in $\langle \mathbf{x} | P(\tilde{\nabla}) \times \exp(-\tilde{H}_0) | \mathbf{x} \rangle$. 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 $P(\tilde{\nabla}) \equiv \tilde{\nabla}_{\alpha}$. Consequently, the term with trailing $\tilde{\nabla}_{\alpha}$ in $T^{(1)}$ does not contribute to Q_2 . The remaining terms in $T^{(1)}$ do contribute to \hbar^2 terms.

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

$$(\tilde{\nabla}_{\alpha}\tilde{U})(\tilde{\nabla}_{\alpha}\tilde{U})(\tilde{\nabla}_{\beta}\tilde{\nabla}_{\beta}\tilde{U}), \quad (\nabla_{\alpha}\nabla_{\alpha}\nabla_{\beta}\nabla_{\beta}\tilde{U}) \text{ etc.},$$

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 $[\tilde{\nabla}_{\beta}^2, \tilde{\nabla}_{\alpha}]$. The linear momenta commute with themselves and also with the angular momenta, so that only the case $\tilde{\nabla}_{\beta}^2 \propto \mathcal{J}_b^2$ and $\tilde{\nabla}_{\alpha} \propto \mathcal{J}_a$ is of concern. In general, the commutation relations of \mathcal{J}_a 's imply that the commutator $[\mathcal{J}_b^2, \mathcal{J}_{a_1}\mathcal{J}_{a_2}\cdots\mathcal{J}_{a_n}]$ is of order $n+1$ in the operators $\mathcal{J}_x, \mathcal{J}_y,$ and \mathcal{J}_z so that $T^{(2)}$ is of maximum order 2 in the trailing operators.

Noting that $\langle \mathbf{x} | [\tilde{\nabla}_{\beta}^2, \tilde{\nabla}_{\alpha}] \exp(-\tilde{H}_0) | \mathbf{x} \rangle$ vanishes, as do the cross terms $\tilde{\nabla}_{\alpha}\tilde{\nabla}_{\beta}$, we see that $T^{(2)}$ contributes only terms of the type $(\tilde{\nabla}_{\alpha}\tilde{\nabla}_{\alpha}\tilde{U})$ and $(\tilde{\nabla}_{\alpha}\tilde{U})(\tilde{\nabla}_{\alpha}\tilde{U})$ to the first quantum correction, together with the $O(\hbar^0)$ term of $\langle \boldsymbol{\omega} | \mathcal{J}_a^2 \times \exp(-\tilde{H}_0) | \boldsymbol{\omega} \rangle$. The first-order $[O(\hbar^2)]$ term in the latter expectation value is given in Eq. (14). Obviously this term contributes $O(\hbar^4)$ to $B_2(T)$ and can consistently be neglected. (In the preceding section the size of this term was discussed for H_2O and SO_2 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 to that end that the trailing polynomial of $T^{(n)}$ is of maximum order n in the components of $\tilde{\nabla}$. We have seen that this is true for $n=0, 1,$ and 2 . From the master relation [Eq. (24)] follows that $dT^{(n+1)}/dt$ is of order $n+1$ in the $\tilde{\nabla}_{\alpha}$'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 $\tilde{\nabla}$. 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 \hbar^3 terms. By the same argument the elements $T^{(k)}$ for $k>3$ do not give \hbar^2 contributions, which is why *only* $T^{(1)}$ and $T^{(2)}$ contribute in order \hbar^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

$$\begin{aligned} Q_2 = & \frac{1}{2!} \int \langle \mathbf{x}_1, \mathbf{x}_2 | e^{-\beta H} | \mathbf{x}_1, \mathbf{x}_2 \rangle d\mathbf{x}_1 d\mathbf{x}_2 \\ = & \frac{1}{2!} \int e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)} \langle \mathbf{x}_1, \mathbf{x}_2 | T e^{-\beta H_0} | \mathbf{x}_1, \mathbf{x}_2 \rangle d\mathbf{x}_1 d\mathbf{x}_2. \end{aligned} \quad (29)$$

Since U is a local function of \mathbf{x}_1 and \mathbf{x}_2 we were able to use here

$$\langle \mathbf{x}_1, \mathbf{x}_2 | e^{-\beta U} | \mathbf{x}'_1, \mathbf{x}'_2 \rangle = \delta(\mathbf{x}'_1 - \mathbf{x}_1) \delta(\mathbf{x}'_2 - \mathbf{x}_2) e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)}.$$

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,

$$Q_2^{(0)} = \frac{1}{2!} \left(\frac{Q_1}{V8\pi^2} \right)^2 \int d\mathbf{x}_1 d\mathbf{x}_2 e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)}. \quad (30)$$

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

$$B_2^{(0)} = \frac{1}{V128\pi^4} \int [1 - e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)}] d\mathbf{x}_1 d\mathbf{x}_2. \quad (31)$$

B. Contributions from $T^{(1)}$

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

$$Q_2^{(1)} = \frac{1}{2!} \int e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)} \left[\frac{1}{2} \tilde{U}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_2) - \frac{1}{3} \tilde{U}_{\alpha}(\mathbf{x}_1, \mathbf{x}_2)^2 \right] \times \langle \mathbf{x}_1, \mathbf{x}_2 | e^{-\tilde{H}_0} | \mathbf{x}_1, \mathbf{x}_2 \rangle d\mathbf{x}_1 d\mathbf{x}_2. \quad (32)$$

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

$$Q_2^{(1)} = \left(\frac{Q_1}{V8\pi^2} \right)^2 \int e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)} \left[\frac{1}{4} \tilde{U}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_2) - \frac{1}{6} \tilde{U}_{\alpha}(\mathbf{x}_1, \mathbf{x}_2)^2 \right] d\mathbf{x}_1 d\mathbf{x}_2.$$

Knowing that $\tilde{\nabla}_{\alpha}$ is Hermitian and purely imaginary, we can rewrite the second derivative as a product of two first derivatives, namely,

$$\begin{aligned} \int e^{-\tilde{U}} \tilde{\nabla}_{\alpha} \tilde{\nabla}_{\alpha} \tilde{U} d\mathbf{x}_1 d\mathbf{x}_2 &= \int (\tilde{\nabla}_{\alpha} e^{-\tilde{U}})^* (\tilde{\nabla}_{\alpha} \tilde{U}) d\mathbf{x}_1 d\mathbf{x}_2 \\ &= - \int (e^{-\tilde{U}} \tilde{\nabla}_{\alpha} \tilde{U})^* (\tilde{\nabla}_{\alpha} \tilde{U}) d\mathbf{x}_1 d\mathbf{x}_2 \\ &= \int e^{-\tilde{U}} \tilde{U}_{\alpha} \tilde{U}_{\alpha} d\mathbf{x}_1 d\mathbf{x}_2. \end{aligned}$$

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

$$H_0 U \equiv \nabla_{\alpha} \nabla_{\alpha} U = \beta (\nabla_{\alpha} U) (\nabla_{\alpha} U). \quad (33)$$

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

$$Q_2^{(1)} = \frac{1}{12} \left(\frac{Q_1}{V8\pi^2} \right)^2 \int e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} [\tilde{U}_{\alpha}(\mathbf{x}_1, \mathbf{x}_2)]^2 d\mathbf{x}_1 d\mathbf{x}_2. \quad (34)$$

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 $\tilde{\nabla}_{\alpha} \tilde{\nabla}_{\beta}$. Terms of the type $\nabla_a(i) \nabla_b(j)$ with different particle index $i \neq j$ vanish. For equal particle index only the diagonal terms $\tilde{\nabla}_{\alpha} \tilde{\nabla}_{\alpha}$ survive; this is true for the translational as well as the rotational derivatives. Hence $T^{(2)}$ contributes:

$$Q_2^{(2)} = \frac{1}{2} \int e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} \left(\frac{1}{2} \tilde{U}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_2)^2 - \frac{2}{3} \tilde{U}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_2) \right) \times \langle \mathbf{x}_1, \mathbf{x}_2 | \tilde{\nabla}_{\alpha} \tilde{\nabla}_{\alpha} e^{-\tilde{H}_0} | \mathbf{x}_1, \mathbf{x}_2 \rangle d\mathbf{x}_1 d\mathbf{x}_2. \quad (35)$$

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 $V(\mathbf{x}_1, \mathbf{x}_2)$

$$\tilde{\nabla}_{\alpha\alpha} \langle \mathbf{x}_1, \mathbf{x}_2 | \tilde{\nabla}_{\alpha} \tilde{\nabla}_{\alpha} e^{-\tilde{H}_0} | \mathbf{x}_1, \mathbf{x}_2 \rangle = \frac{1}{2} \left(\frac{Q_1}{V8\pi^2} \right)^2 \tilde{\nabla}_{\alpha\alpha}$$

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

$$\begin{aligned} Q_2^{(2)} &= \left(\frac{Q_1}{V8\pi^2} \right)^2 \int e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} \left(\frac{1}{8} \tilde{U}_{\alpha}(\mathbf{x}_1, \mathbf{x}_2)^2 - \frac{1}{6} \tilde{U}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_2) \right) d\mathbf{x}_1 d\mathbf{x}_2 \\ &= - \frac{1}{24} \left(\frac{Q_1}{V8\pi^2} \right)^2 \int e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} \tilde{U}_{\alpha}(\mathbf{x}_1, \mathbf{x}_2)^2 d\mathbf{x}_1 d\mathbf{x}_2, \quad (36) \end{aligned}$$

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

$$Q_2^{(1+2)} = \frac{1}{24} \left(\frac{Q_1}{V8\pi^2} \right)^2 \int e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} \times \sum_{i=1}^2 \sum_{a=1}^6 [\tilde{\nabla}_a(i) \tilde{U}(\mathbf{x}_1, \mathbf{x}_2)]^2 d\mathbf{x}_1 d\mathbf{x}_2. \quad (37)$$

Upon recalling the definition of $\nabla_a(i)$ 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,

$$B_2 = \frac{1}{128V\pi^4} \int \left[1 - e^{-\tilde{U}(\mathbf{x}_1, \mathbf{x}_2)} \right. \\ \left. \times \left(1 + \frac{1}{12} \sum_{i=1}^2 \sum_{a=1}^6 [\tilde{\nabla}_a(i) \tilde{U}(\mathbf{x}_1, \mathbf{x}_2)]^2 \right) \right] d\mathbf{x}_1 d\mathbf{x}_2.$$

Using Eq. (33) we can rewrite this equation thus

$$B_2(T) = \frac{1}{128V\pi^4} \int \dots \int \left\{ 1 - e^{-\beta U(\mathbf{x}_1, \mathbf{x}_2)} \right. \\ \left. \times \left[1 + \frac{\beta^2}{12} H_0(U) \right] \right\} d\mathbf{x}_1 d\mathbf{x}_2,$$

which has precisely the same form as the equation previously derived by T Pack² 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 $U(\mathbf{r}_1, \mathbf{r}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ does not depend on the position \mathbf{R} of the dimer mass center, but only on the distance \mathbf{r} and $\boldsymbol{\omega}_1, \boldsymbol{\omega}_2$. Use

$$d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{R} d\mathbf{r}$$

and

$$\int d\mathbf{R} = V.$$

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 $P^2 U = 0$ we obtain finally an expression for $B_2(T)$ correct through \hbar^2 ,

$$B_2(T) = \frac{1}{128\pi^4} \int \left[1 - e^{-\tilde{U}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)} \right. \\ \times \left(1 + \frac{\beta}{12M} \sum_{a=1}^3 [p_a \tilde{U}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]^2 \right. \\ \left. \left. + \frac{1}{12} \sum_{i=1}^2 \sum_{a=4}^6 [\tilde{\nabla}_a(i) \tilde{U}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]^2 \right) \right] d\mathbf{r} d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2.$$

The quantum correction contains an inner product of forces,

$$\frac{\beta}{12M} \sum_{a=1}^3 [p_a \tilde{U}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]^2 = - \frac{\hbar^2 \beta^3}{M} \sum_{a=x,y,z} \left(\frac{\partial U}{\partial r_a} \right)^2$$

and of torques,

$$\sum_{i=1}^2 \sum_{a=4}^6 [\tilde{\nabla}_a(i) \tilde{U}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]^2 = \beta^3 \sum_{i=1}^2 \sum_{a=x,y,z} \frac{1}{2I_a} [\mathcal{J}_a(i) U]^2.$$

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 $U(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ is expanded in a product of D matrices and spherical harmonics: $D_{m_1 k_1}^{l_1}(\boldsymbol{\omega}_1) D_{m_2 k_2}^{l_2}(\boldsymbol{\omega}_2) Y_M^L(\hat{\mathbf{r}})$, see e.g., Ref. 15. The action of $\mathcal{J}_x, \mathcal{J}_y$, and \mathcal{J}_z , 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 $Y_M^L(\hat{\mathbf{r}})$ also well defined and easy.

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