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Recommended Citation

L. Biolsi and E. A. Mason, "Effect of Molecular Angular Momentum on the Thermal Conductivity of a Multicomponent Gas Mixture," *Journal of Chemical Physics*, vol. 63, no. 1, pp. 10-18, American Institute of Physics (AIP), Jul 1974.

The definitive version is available at <https://doi.org/10.1063/1.431060>

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Effect of molecular angular momentum on the thermal conductivity of a multicomponent gas mixture

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(Received 14 February 1975)

The effects of molecular angular momentum (spin polarization) on the thermal conductivity of a multicomponent gas mixture are considered. The Wang Chang-Uhlenbeck approach to the kinetic theory of gases with internal states is used. Formal results are obtained for the thermal conductivity of a gas mixture of uniform composition. These results are given in terms of the quantum mechanical degeneracy-averaged cross section.

The formal kinetic theory of a single-component gas composed of polyatomic molecules with internal states was first developed by Wang Chang and Uhlenbeck¹ and was extended to include polyatomic gas mixtures by Monchick, Yun, and Mason.² Later work³ showed that the assumption of detailed balance made by Wang Chang and Uhlenbeck is not, in general, correct but their results are valid if the internal states are nondegenerate or if the quantum mechanical cross section has been degeneracy averaged.

In 1961 Kagan and Afanas'ev⁴ showed that in a system of molecules possessing angular momentum, the perturbation part of the distribution function should be written in terms of the two independent vector quantities linear momentum and angular momentum. The angular momentum terms account for the polarization of the molecules caused by gradients in the gas and were not included in the work of Refs. 1 and 2. This "spin polarization" can affect the transport properties.^{5,6} For instance, Sandler and Dahler⁵ found, using a classical loaded-sphere model for a mixture of D₂ and HT, that spin polarization caused negligible changes for diffusion, appreciable changes for thermal conductivity, and changes up to 24% for thermal diffusion. McCourt and Snider⁷ developed a formal quantum mechanical approach to the spin polarization effect on thermal conductivity for a single-component polyatomic gas. The purpose of this paper is to extend the quantum mechanical treatment of the spin polarization effect on thermal conductivity to polyatomic gas mixtures, using the Wang Chang-Uhlenbeck approach.

I. THE SEMICLASSICAL BOLTZMANN EQUATION

The kinetic equation solved by Wang Chang and Uhlenbeck is¹

$$\frac{\partial f_{qi}}{\partial t} + \mathbf{v}_q \cdot \frac{\partial f_{qi}}{\partial \mathbf{r}} = \sum_{q'} \sum_{jkl} \int \cdots \int (f'_{q'h} f'_{1q'l} - f_{qi} f_{1q'j}) \times g I_{ij}^{kl}(g, \chi, \phi) \sin \chi d\chi d\phi d\mathbf{v}_{1q'} \quad (1)$$

where $f_{qi} = f_q(\mathbf{v}_q, E_{qi}, \mathbf{r}, t)$ is the singlet distribution function and E_{qi} is the internal energy of the q th chemical species in quantum state i . Also I_{ij}^{kl} is the differential scattering cross section for the process in which molecules q and q' , initially in internal states i and j , re-

spectively, go to final internal states k and l , respectively, the primes indicating post-collision values, and

$$\mathbf{g} = \mathbf{v}_q - \mathbf{v}_{1q'}$$

Equation (1) has been obtained by assuming the existence of symmetry between inverse processes; i. e.,

$$g I_{ij}^{kl}(g, \chi, \phi) = g' I_{kl}^{ij}(g', \chi, \phi) \quad (2)$$

This relation is strictly correct only if the internal states are nondegenerate or if the differential cross section has been degeneracy averaged. Equation (1) is called the semiclassical Boltzmann equation because the translational motion is treated classically and the internal motion is treated quantum mechanically.

In the perturbation solution of the Boltzmann equation, the left hand side of Eq. (1) is treated as the perturbation and the distribution function is written as

$$f_{qi} = f_{qi}^0 (1 + \Phi_{qi} + \cdots),$$

where f_{qi}^0 is the zero-order (equilibrium) distribution function and Φ_{qi} is the perturbation function.

Consider a system of rotating polyatomic molecules without any net macroscopic angular momentum; i. e., one in which no torques act on the gas. The zero order distribution function for this system is⁷

$$f_{qi}^{(0)} = \left[n_q \int \exp(-E_{qi} - \boldsymbol{\alpha} \cdot \mathbf{J}_q) / kT \right] (m_q / 2\pi kT)^{3/2} \times \exp(-m_q V_q^2 / 2 + E_{qi} + \boldsymbol{\alpha} \cdot \mathbf{J}_q) / kT \quad (3)$$

where \mathbf{J}_q is the internal angular momentum operator and

$$\mathbf{V}_q = \mathbf{v}_q - \mathbf{v}_0$$

in which \mathbf{v}_0 is the mass-average velocity. The vector $\boldsymbol{\alpha}$ represents the local average angular velocity,⁸ i. e., even when the net macroscopic angular velocity is zero, there can be a local angular velocity due to internal rotation.

The normalization conditions on f_{qi}^0 are

$$n_q = \sum_i \int f_{qi}^0 d\mathbf{v}_q \quad (4)$$

and

$$\rho \mathbf{v}_0 = \sum_q \sum_i m_q \int f_{qi}^0 \mathbf{v}_q d\mathbf{v}_q \quad (5)$$

where

$$\rho = \sum_q n_q m_q \quad (6)$$

Also

$$\rho U^0 = \rho U_{tr}^0 + \rho U_{int}^0 = \sum_q \sum_i \int f_{qi}^0 \left(\frac{m_q}{2} V_q^2 + E_{qi} \right) d\mathbf{v}_q \quad (7)$$

and

$$\mathbf{J} = \sum_q \sum_i \int f_{qi}^0 \mathbf{J}_q d\mathbf{v}_q \quad (8)$$

where n_q is the macroscopic number density, ρ is the macroscopic mass density, U^0 is the energy per gram, and \mathbf{J} is the angular momentum density.

The average internal angular momentum will be taken to be zero in which case α is also zero.⁷ Then Eq. (3) can be written as

$$f_{qi}^0 = \frac{n_q}{Q_q} \left(\frac{m_q}{2\pi kT} \right)^{3/2} \exp(-W_q^2 - \epsilon_{qi}) \quad (9)$$

where

$$\mathbf{w}_q = \sqrt{m_q/2kT} \mathbf{V}_q, \quad \epsilon_{qi} = E_{qi}/kT, \quad Q_q = \sum_i e^{-\epsilon_{qi}}$$

Gradients in α are necessary for the transport of angular momentum. However, when the average internal angular momentum is zero, individual molecules may still have polarized angular momenta.

II. THE EQUATIONS OF CHANGE

The usual equations of change are obtained: the equation of continuity,

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial \mathbf{r}} \cdot \rho \mathbf{v}_0 = 0 \quad (10)$$

the equation of motion,

$$\rho \frac{\partial}{\partial t} \mathbf{v}_0 + \rho \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 = - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{p} \quad (11)$$

and the equation of energy balance,

$$\rho \frac{\partial}{\partial t} U^0 + \rho \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{r}} U^0 = - \mathbf{p} : \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{q} \quad (12)$$

In the equations above the pressure tensor \mathbf{p} is defined as

$$\mathbf{p} = \sum_q n_q m_q \langle \mathbf{V}_q \mathbf{V}_q \rangle \quad (13)$$

and the heat flux vector \mathbf{q} is defined as

$$\mathbf{q} = \sum_q n_q \langle (\frac{1}{2} m_q V_q^2 + E_{qi}) \mathbf{V}_q \rangle \quad (14)$$

where

$$\langle \psi_{qi}(\mathbf{r}, t) \rangle = \frac{1}{n_q} \int \psi_{qi}(\mathbf{r}, \mathbf{v}_q, t) f_{qi} d\mathbf{v}_q \quad (15)$$

In addition, there is an equation of change for internal angular momentum;

$$\frac{\partial}{\partial t} \sum_q n_q \langle \mathbf{J}_q \rangle + \frac{\partial}{\partial \mathbf{r}} \cdot \sum_q n_q \mathbf{v}_0 \langle \mathbf{J}_q \rangle = - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{L} \quad (16)$$

where the angular momentum flux tensor \mathbf{L} is defined

as⁷

$$\mathbf{L} = \sum_q n_q \langle \mathbf{V}_q \mathbf{J}_q \rangle \quad (17)$$

At equilibrium

$$\mathbf{L} = 0, \quad q = 0, \quad \mathbf{p} = p\mathbf{U}, \quad p = nkT,$$

where \mathbf{U} is the unit tensor.

III. THE LINEARIZED BOLTZMANN EQUATION

The set of integral equations for the perturbation function, Φ_{qi} , is given by

$$\begin{aligned} \sum_{q'} I(\Phi_{qi}) = f_{qi}^0 \left[2(\mathbf{w}_q \mathbf{w}_q - \frac{1}{3} \mathbf{w}_q^2 \mathbf{U}) : \mathbf{S} + \left\{ (w_q^2 - \frac{5}{2}) \right. \right. \\ \left. \left. + (\epsilon_{qi} - \bar{\epsilon}_q) \right\} \mathbf{V}_q \cdot \frac{\partial}{\partial \mathbf{r}} \ln T + \frac{c_{int}}{c_v} \left\{ \left(\frac{2}{3} \mathbf{w}_q^2 - 1 \right) \right. \right. \\ \left. \left. - \frac{k}{c_{int}} (\epsilon_{qi} - \bar{\epsilon}_q) \right\} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0 + \frac{n}{n_q} \mathbf{V}_q \cdot \mathbf{d}_q \right] \quad (18) \end{aligned}$$

where

$$\begin{aligned} I(\Phi_{qi}) = \sum_{jkl} \int \cdots \int f_{qi}^0 f_{lq'}^0 (\Phi_{qk} + \Phi_{q'l} - \Phi_{qi} - \Phi_{q'j}) \\ \times g I_{ij}^{kl}(g, \chi, \phi) \sin \chi d\chi d\phi d\mathbf{v}_{lq'} \quad (19) \end{aligned}$$

and

$$\bar{\epsilon}_q = \frac{1}{Q_q} \sum_i \epsilon_{qi} \exp(-\epsilon_{qi})$$

Also, c_v is the heat capacity per unit volume per molecule and the internal heat capacity per molecule, c_{int} , is given by

$$c_{int} = c_v - \frac{3}{2} k$$

In addition

$$\mathbf{S} = \frac{1}{2} \left(\frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 + \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0^t \right) - \frac{1}{3} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0 \mathbf{U}$$

and

$$\mathbf{d}_q = \frac{\partial}{\partial \mathbf{r}} \left(\frac{n_q}{n} \right) + \left(\frac{n_q}{n} - \frac{n_q m_q}{\rho} \right) \frac{\partial}{\partial \mathbf{r}} \ln p$$

where the superscript t denotes the transpose.

The form of Eq. (18) suggests that Φ_{qi} should be expanded in the linearly independent gradients of density, temperature, and velocity, i.e.,

$$\begin{aligned} \Phi_{qi} = - \mathbf{A}_{qi} \cdot \frac{\partial}{\partial \mathbf{r}} \ln T - \mathbf{B}_{qi} : \mathbf{S} + n \sum_{q'} (C_{q'}^{\alpha} \cdot \mathbf{d}_{q'}) \\ - D_q \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0 \quad (20) \end{aligned}$$

The first term in Eq. (20) is associated with thermal conductivity, the second term with shear viscosity, the third term with diffusion, and the fourth term with the volume (bulk) viscosity. If α had not been taken to be zero, there would also be a term involving the gradient of angular momentum.⁷

IV. THERMAL CONDUCTIVITY

Thermal conductivity is determined by the temperature gradient, associated with the \mathbf{A}_{qi} in Eq. (20). From Eqs. (18) and (20), the set of integral equations for the \mathbf{A}_{qi} is found to be

$$f_{q_i}^0 \left[(W_q^2 - \frac{5}{2}) + (\epsilon_{q_i} - \bar{\epsilon}_q) \right] \mathbf{V}_q = - \sum_{q'} I(A_{q_i}) \quad (21)$$

From Eqs. (14), (20), and (21), the heat flux vector can be written as

$$\mathbf{q} = \mathbf{q}_{tr} + \mathbf{q}_{int} \quad (22)$$

where

$$\mathbf{q}_{tr} = \frac{5}{2} kT \sum_q n_q \langle \mathbf{V}_q \rangle + kT \sum_q \sum_i \int \mathbf{V}_q f_{q_i}^0 (W_q^2 - \frac{5}{2}) \times \left[-A_{q_i} \cdot \frac{\partial}{\partial \mathbf{r}} \ln T + n \sum_{q'} (C_{q'}^{q'} \cdot \mathbf{d}_{q'}) \right] dV_q \quad (23)$$

and

$$\mathbf{q}_{int} = kT \sum_q n_q \bar{\epsilon}_q \langle \mathbf{V}_q \rangle + kT \sum_q \sum_i \int \mathbf{V}_q f_{q_i}^0 (\epsilon_{q_i} - \bar{\epsilon}_q) \times \left[-A_{q_i} \cdot \frac{\partial}{\partial \mathbf{r}} \ln T + n \sum_{q'} (C_{q'}^{q'} \cdot \mathbf{d}_{q'}) \right] dV_q \quad (24)$$

The first terms on the right in Eqs. (23) and (24) represent heat flux due to mass transport, and the second terms on the right represent the heat flux due to temperature gradients. A thermal conductivity coefficient for a mixture at uniform composition, λ_0 , is associated with the second terms.

The last terms in Eqs. (23) and (24) represent the heat flux due to diffusion forces; i.e., the effect of thermal diffusion. The diffusion forces, $\mathbf{d}_{q'}$, are conventionally eliminated by using the diffusion equation,^{2,9} leading to a new thermal conductivity coefficient, λ_∞ . In this paper it is assumed that the gas mixture maintains a uniform composition. Thus the last terms in Eqs. (23) and (24) do not contribute. This should be a reasonable assumption since, often, $\lambda_0 \approx \lambda_\infty$.^{2,10} Also, classical numerical model calculations of the effects of spin polarization on thermal conductivity involve calculations of λ_0 .⁵ Work is in progress on the spin polarization contribution to λ_∞ .

There are several auxiliary conditions on the perturbation function. These are a consequence of the fact that the local values of density, energy, and linear and angular momentum must be determined by the local equilibrium distribution function. The auxiliary conditions are

$$\sum_i \int f_{q_i}^0 A_{q_i} dV_q = 0 \quad (25)$$

$$\sum_q \sum_i m_q \int f_{q_i}^0 \mathbf{v}_q A_{q_i} dV_q = 0 \quad (26)$$

$$\sum_q \sum_i \int f_{q_i}^0 \left(\frac{m_q}{2} V_q^2 + E_{q_i} \right) A_{q_i} dV_q = 0 \quad (27)$$

and

$$\sum_q \sum_i \int f_{q_i}^0 \mathbf{J}_q A_{q_i} dV_q = 0 \quad (28)$$

Four independent polar vectors can be constructed from \mathbf{W}_q and \mathbf{J}_q .⁷ These are

$$\mathbf{W}_q \quad [\mathbf{J}_q; \mathbf{J}_q \cdot \mathbf{W}_q], \quad [\mathbf{J}_q; \mathbf{J}_q \cdot \mathbf{W}_q], \quad \mathbf{J}_q \times \mathbf{W}_q$$

Since it can be shown that the last two terms do not contribute to the expression for \mathbf{q} ,⁷ the operator A_{q_i} can be

written in the Hermitian form

$$A_{q_i} + A_{q_i}^1 \mathbf{W}_q + \frac{1}{4} \{ [\mathbf{J}_q; \mathbf{J}_q \cdot \mathbf{W}_q], A_{q_i}^2 \} \quad (29)$$

using the polar vectors, where

$$A_{q_i}^1 = \sum_{n,l,m} a_{q_{nlm}}^1 S_{3/2}^{(n)}(W_q^2) R_p^{(0)}(\epsilon_{q_i}) P_l^{(0)}(m^2) \quad (30)$$

and

$$A_{q_i}^2 = \sum_{n,l,m} a_{q_{nlm}}^2 S_{3/2}^{(n)}(W_q^2) R_p^{(0)}(\epsilon_{q_i}) P_l^{(1)}(m^2) \quad (31)$$

The $a_{q_{nlm}}^1$ and $a_{q_{nlm}}^2$ are expansion coefficients to be determined. The effect of spin polarization is included in the second term on the right in Eq. (29).

The polynomial $S_{3/2}^{(n)}(W_q^2)$ is a Sonine polynomial,¹¹ $R_p^{(0)}(\epsilon_{q_i})$ is the polynomial introduced by Wang Chang and Uhlenbeck,¹ and $P_l^{(0)}(m^2)$ and $P_l^{(1)}(m^2)$ are the quantum mechanical analogs⁷ of the polynomials introduced by Kagan and Afanas'ev.⁴ Only the first few polynomials will be used. These are given by

$$S_{3/2}^{(0)}(W_q^2) = 1, \quad S_{3/2}^{(1)}(W_q^2) = \frac{5}{2} - W_q^2, \\ R_0^{(0)}(\epsilon_{q_i}) = 1, \quad R_1^{(0)}(\epsilon_{q_i}) = \epsilon_{q_i} - \bar{\epsilon}_q, \\ P_0^{(0)}(m^2) = 1, \quad P_0^{(1)}(m^2) = [l(l+1)]^{-1},$$

where l is the angular momentum quantum number and m is the z component of angular momentum quantum number. Thus the index i stands for the indices l and m and $\epsilon_{q_i} = \epsilon_{q_i}$. The orthonormality conditions on these polynomials are

$$\int_0^\infty x^m e^{-x} S_m^{(n)}(x) S_m^{(n')}(x) dx = \frac{(m+n)!}{n!} \delta_{nm}, \\ \sum_i (2l+1) \frac{e^{-\epsilon_{q_i}}}{Q_q} R_p^{(0)}(\epsilon_{q_i}) R_{p'}^{(0)}(\epsilon_{q_i}) = \left(\frac{C_{q_{int}}}{k} \right)^p \delta_{pp'}, \\ \sum_m P_0^{(0)}(m^2) P_l^{(0)}(m^2) = (2l+1) \delta_{0l},$$

and

$$\sum_m m^2 P_0^{(1)}(m^2) P_l^{(1)}(m^2) = \frac{(2l+1)}{3l(l+1)} \delta_{0l}.$$

Let the direction of \mathbf{W}_q be the z axis. Then, upon substituting Eqs. (29), (30), and (31) in Eqs. (23) and (24) and using the properties of the polynomials, it can be shown that

$$\mathbf{q}_{tr} = \frac{5}{2} kT \sum_q n_q \langle \mathbf{V}_q \rangle - \lambda_{0tr} \frac{\partial}{\partial \mathbf{r}} T \quad (32)$$

and

$$\mathbf{q}_{int} = kT \sum_q n_q \bar{\epsilon}_q \langle \mathbf{V}_q \rangle - \lambda_{0int} \frac{\partial}{\partial \mathbf{r}} T \quad (33)$$

assuming that the contribution to thermal conductivity due to thermal diffusion is small. The translational and internal contributions to the thermal conductivity in a multicomponent gas mixture of uniform composition are given by

$$\lambda_{0tr} = -\frac{5}{2} k \sum_q n_q \sqrt{\frac{2kT}{m_q}} (a_{q_{100}}^1 + \frac{1}{3} a_{q_{100}}^2) \quad (34)$$

and

$$\lambda_{0int} = \frac{1}{2} \sum_q n_q \sqrt{\frac{2kT}{m_q}} c_{eint} (a_{q010}^1 + \frac{1}{3} a_{q010}^2), \quad (35)$$

respectively. It can also be shown that the auxiliary condition on the expansion coefficients is

$$\sum_q n_q \sqrt{m_q} (a_{q000}^1 + \frac{1}{3} a_{q000}^2) = 0. \quad (36)$$

The a_q 's in Eqs. (34), (35), and (36) must now be determined.

V. CALCULATION OF THE EXPANSION COEFFICIENTS

The expansion coefficients are obtained through the use of the variational principle. This has been discussed by Hirschfelder, Curtiss, and Bird¹¹ and by McCourt and Snider.⁷ In order to calculate the coefficients, a trial function for A_{qi} is necessary. Let

$$T_{np't}^{(3/2)0f} = S_{3/2}^{(n)}(W_q^2) R_p^{(0)}(\epsilon_{qi}) P_t^{(f)}(m^2). \quad (37)$$

Then the trial function used in this paper can be written as

$$\begin{aligned} A_{qi} = & a_{q000}^1 T_{00}^{(3/2)00} W_q + (a_{q100}^1 T_{100}^{(3/2)00} + a_{q010}^1 T_{010}^{(3/2)00}) W_q \\ & + \frac{1}{2} a_{q000}^2 T_{000}^{(3/2)01} [J_q; J_q \cdot W_q]_+ + \frac{1}{2} (a_{q100}^2 T_{100}^{(3/2)01} \\ & + a_{q010}^2 T_{010}^{(3/2)01}) [J_q; J_q \cdot W_q]_+; \end{aligned} \quad (38)$$

i. e., the trial function contains terms with

$$n=p=t=0 \quad n=t=0; p=1 \quad p=t=0; n=1 \quad (39)$$

Equation (38) is similar to the trial function used by McCourt and Snider⁷ and contains more terms than have been used in the analogous classical calculations.⁴⁻⁶ The smallest number of terms necessary to give all the physical effects have been used in the trial function.

A set of six equations for the six unknown expansion coefficients a_{q000}^1 , a_{q000}^2 , a_{q100}^1 , a_{q100}^2 , a_{q010}^1 , and a_{q010}^2 is obtained by taking integral moments of each term in trial function (38) with Eq. (21). These equations can be written in the form

$$\begin{aligned} R_{qnp't} = & \sum_{q'} \sum_{np't} \sum_{n'p't'} \{ a_{q'n'p't'}^1 \bar{Q}_{qq'}^{np't, n'p't'} \\ & + a_{q'n'p't'}^2 \bar{Q}_{qq'}^{np't, n'p't'} \} \end{aligned} \quad (40)$$

and

$$\begin{aligned} \frac{1}{3} R_{qnp't} = & \sum_{q'} \sum_{np't} \sum_{n'p't'} \{ a_{q'n'p't'}^1 Q_{qq'}^{np't, n'p't'} \\ & + a_{q'n'p't'}^2 Q_{qq'}^{np't, n'p't'} \} \end{aligned} \quad (41)$$

subject to the constraints on n , p , t and n' , p' , t' in expressions (39). Also the R 's and Q 's are defined as

$$R_{qnp't} = -n_q \sqrt{\frac{2kT}{m_q}} \left[\frac{15}{4} \delta(np't, 100) - \frac{3}{2} \frac{c_{eint}}{k} \delta(np't, 010) \right], \quad (42)$$

$$\begin{aligned} Q_{qq'}^{np't, n'p't'} = & \sum_{q''} n_q n_{q''} \{ \delta_{qq''} [T_{np't}^{(3/2)00} W_q; T_{n'p't'}^{(3/2)00} W_{q''}]_{qq''} \\ & + \delta_{q''q'} [T_{np't}^{(3/2)00} W_q; T_{n'p't'}^{(3/2)00} W_{q''}]_{qq''} \}, \end{aligned} \quad (43)$$

$$\begin{aligned} Q_{qq'}^{np't, n'p't'} = & \frac{1}{2} \sum_{q''} n_q n_{q''} \{ \delta_{qq''} [T_{np't}^{(3/2)00} W_q \\ & \times T_{n'p't'}^{(3/2)01} [J_q; J_q \cdot W_q]_{qq''} + \delta_{q''q'} [T_{np't}^{(3/2)00} W_q; T_{n'p't'}^{(3/2)01} \\ & \times [J_q; J_q \cdot W_q]_{qq''}]_{qq''} \}, \end{aligned} \quad (44)$$

$$\begin{aligned} Q_{qq'}^{np't, n'p't'} = & \frac{1}{4} \sum_{q''} n_q n_{q''} \{ \delta_{qq''} [T_{np't}^{(3/2)01} [J_q; J_q \cdot W_q]_{+}; \\ & \times T_{n'p't'}^{(3/2)01} [J_q; J_q \cdot W_q]_{+}]_{qq''} + \delta_{q''q'} [T_{np't}^{(3/2)01} [J_q; J_q \cdot W_q]_{+}; \\ & \times T_{n'p't'}^{(3/2)01} [J_q; J_q \cdot W_q]_{+}]_{qq''} \}, \end{aligned} \quad (45)$$

where the bracket integrals, $[]_{qq''}$, are evaluated in the Appendix. In addition

$$\bar{Q}_{qq'}^{000,000} = Q_{qq'}^{000,000} - \frac{n_q \sqrt{m_q}}{n_{q'} \sqrt{m_{q'}}} Q_{qq'}^{000,000}, \quad (46)$$

$$\bar{Q}_{qq'}^{000,000} = Q_{qq'}^{000,000} - \frac{n_q \sqrt{m_q}}{n_{q'} \sqrt{m_{q'}}} Q_{qq'}^{000,000}, \quad (47)$$

and

$$\bar{Q}_{qq'}^{np't, n'p't'} = Q_{qq'}^{np't, n'p't'}, \quad (48)$$

$$\bar{Q}_{qq'}^{np't, n'p't'} = Q_{qq'}^{np't, n'p't'},$$

when n , p , t , n' , p' , and t' are not all zero.

The auxiliary condition given by Eq. (36) has been included in this set of equations. The form has been chosen so that the results reduce to those obtained in Ref. 2 in the absence of spin polarization.

Now define matrix elements L by⁹

$$Q_{qq'}^{np't, n'p't'} = -\frac{k}{12} \frac{g_{qnp't} g_{q'n'p't'}}{x_q x_{q'}} L_{qq'}^{np't, n'p't'}, \quad (49)$$

with an exactly similar definition of $\bar{L}_{qq'}^{np't, n'p't'}$ in terms of $\bar{Q}_{qq'}^{np't, n'p't'}$, where

$$\begin{aligned} g_{qnp't} = & n_q \sqrt{\frac{2kT}{m_q}} \left[\frac{15}{4} \delta(np't, 000) + \frac{15}{4} \delta(np't, 100) \right. \\ & \left. - \frac{3}{2} \frac{c_{eint}}{k} \delta(np't, 010) \right]. \end{aligned} \quad (50)$$

When Eq. (49) is substituted in Eqs. (40) and (41), a set of linear equations in terms of the $L_{qq'}^{np't, n'p't'}$ is obtained. This set of equations is solved for the expansion coefficients. Then Eq. (34) becomes

$L_{aa'00}^{100,010}$ and $L_{aa'00}^{010,100}$ (see Ref. 2) vanish.

Since $\Delta\epsilon_{aa'}$ can be either positive or negative, the linear terms in $\Delta\epsilon_{aa'}$ should be nearly zero on averaging over all collisions.¹² Thus the inelastic collision processes depend on terms of order $\Delta\epsilon_{aa'}^2$. Mason and Monchick^{12,13} showed that for a single-component gas without spin polarization, these terms can be expressed in terms of the relaxation time, a quantity that is often experimentally measurable. Inelastic collision processes in a gas possessing spin polarization should also be related to relaxation times and work is in progress on this point.

The results given here are quite formal and one might wonder if the spin polarization effects on thermal conductivity are important. The classical model calculations mentioned previously^{5,6} indicate that spin polarization

contributes significantly to transport properties that depend sensitively on inelastic collisions. Thermal conductivity is such a transport property.² The assumption of inverse collisions is correct if the internal states are nondegenerate or if the cross section is degeneracy averaged. Does this degeneracy averaging "wash out" spin polarization effects? A complete answer is not possible at this point. However loaded spheres have inverse collisions but still show a definite spin polarization effect.^{5,6}

ACKNOWLEDGMENTS

This work was supported in part by NASA Grant NGL-40-002-059 at Brown University and the University of Missouri Assistant Professor Research Fund.

APPENDIX

Using Eqs. (43) through (50), the $L_{aa'ab}^{np t, n' p' t'}$ can be written in terms of the bracket integrals. The results are

$$\bar{L}_{aa'00}^{000,000} = -\frac{32x_a x_{a'} \sqrt{m_a m_{a'}}}{75k^2 T n_{a'}} \sum_{a''} n_{a''} \left\{ \delta_{aa''} [W_a; W_a]_{aa''} + \delta_{a'a''} [W_a; W_{a'}]_{aa''} - \frac{n_{a'} \sqrt{m_{a'}}}{n_{a'} \sqrt{m_a}} \{ [W_a; W_a]_{aa''} + \delta_{aa''} [W_a; W_{a'}]_{aa''} \} \right\} \quad (A1)$$

and

$$\bar{L}_{aa'00}^{np t, n' p' t'} = -\frac{6x_a x_{a'} \sqrt{m_a m_{a'}}}{k^2 T n_{a'} g_{anp t} g_{a'n' p' t'}} \sum_{a''} n_{a''} \{ \delta_{aa''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)00} W_a]_{aa''} + \delta_{a'a''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)00} W_{a'}]_{aa''} \} \quad (A2)$$

when $n, p, t, n', p',$ and t' are not all zero. Also

$$\begin{aligned} \bar{L}_{aa'01}^{000,000} = & -\frac{16x_a x_{a'} \sqrt{m_a m_{a'}}}{75k^2 T n_{a'}} \sum_{a''} n_{a''} \left\{ \delta_{aa''} [W_a; P_0^{(1)}(m_a^2) [J_a; J_a \cdot W_a]_{aa''} + \delta_{a'a''} [W_a; P_0^{(1)}(m_a^2) [J_{a'}; J_{a'} \cdot W_{a'}]_{aa''} \right. \\ & \left. - \frac{1}{3} \frac{n_{a'} \sqrt{m_{a'}}}{n_{a'} \sqrt{m_a}} \{ [W_a; W_a]_{aa''} + \delta_{aa''} [W_a; W_{a'}]_{aa''} \} \right\} \quad (A3) \end{aligned}$$

and

$$\begin{aligned} \bar{L}_{aa'01}^{np t, n' p' t'} = & \frac{-3x_a x_{a'} \sqrt{m_a m_{a'}}}{k^2 T n_{a'} g_{anp t} g_{a'n' p' t'}} \sum_{a''} n_{a''} \{ \delta_{aa''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)01} [J_a; J_a \cdot W_a]_{aa''} \\ & + \delta_{a'a''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)01} [J_{a'}; J_{a'} \cdot W_{a'}]_{aa''} \} \quad (A4) \end{aligned}$$

when $n, p, t, n', p',$ and t' are not all zero. In addition

$$\begin{aligned} L_{aa'01}^{np t, n' p' t'} = & -\frac{3x_a x_{a'} \sqrt{m_a m_{a'}}}{k^2 T n_{a'} g_{anp t} g_{a'n' p' t'}} \sum_{a''} n_{a''} \{ \delta_{aa''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)01} [J_a; J_a \cdot W_a]_{aa''} \\ & + \delta_{a'a''} [T_{np t}^{(3/2)00} W_a; T_{n' p' t'}^{(3/2)01} [J_{a'}; J_{a'} \cdot W_{a'}]_{aa''} \} \quad (A5) \end{aligned}$$

and

$$\begin{aligned} L_{aa'11}^{np t, n' p' t'} = & -\frac{3x_a x_{a'} \sqrt{m_a m_{a'}}}{2k^2 T n_{a'} g_{anp t} g_{a'n' p' t'}} \sum_{a''} n_{a''} \{ \delta_{aa''} [T_{np t}^{(3/2)01} [J_a; J_a \cdot W_a]_{aa''}; T_{n' p' t'}^{(3/2)01} [J_a; J_a \cdot W_a]_{aa''} \\ & + \delta_{a'a''} [T_{np t}^{(3/2)01} [J_a; J_a \cdot W_a]_{aa''}; T_{n' p' t'}^{(3/2)01} [J_{a'}; J_{a'} \cdot W_{a'}]_{aa''} \} \quad (A6) \end{aligned}$$

for all combinations of $n, p, t, n', p',$ and t' subject to the constraints in expressions (39).

The bracket integrals can be written as

$$[]_{aa''} = \frac{8}{Q_a Q_{a'}} \sqrt{\frac{kT}{2\pi\mu}} \sum_{ijkt} \int \dots \int e^{-(v^2 + \epsilon_{ai} + \epsilon_{aj})} F_{\beta\alpha} \bar{I}_{ij}^{kt}(\gamma, \chi, \phi) (2l_a + 1)(2l_{a'} + 1) \gamma^3 \sin\chi d\chi d\phi d\gamma, \quad (A7)$$

where the $F_{\beta\alpha}$ depend on the specific bracket integral and

$$\mu = m_a m_{a'} / (m_a + m_{a'}) \quad \gamma = \sqrt{\mu / 2kT} g.$$

In evaluating the bracket integrals, it has been assumed that either the internal states are nondegenerate or that the degeneracy averaged cross section, $\bar{I}_{ij}^{kl}(\gamma, \chi, \phi)$, is used. This is defined by¹⁴

$$\bar{I}_{ij}^{kl}(\gamma, \chi, \phi) = \frac{1}{(2I_q + 1)(2I_{q''} + 1)} \sum_{\text{K-component states}} I_{ij}^{kl}(\gamma, \chi, \phi). \quad (\text{A8})$$

The expressions for $\bar{L}_{aa'00}^{n''p'',n'p't'}$ were evaluated by Monchick, Yun, and Mason. The results are given by Eqs. (82) through (90d) in Ref. 2.

The results for the $\bar{L}_{aa'01}^{n''p'',n'p't'}$ and $L_{aa'01}^{n''p'',n'p't'}$ are given below:

$$\begin{aligned} \bar{L}_{aa'01}^{000,000} = & -\frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \sum \int d\bar{\Omega}_{aa''} \{ \delta_{aa''} [\bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''})] + \delta_{q'q''} \sqrt{m_q/m_{q''}} [\bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''}) \right. \\ & \left. - \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q'})] \} - \frac{4}{3} \frac{n_{q'} \sqrt{m_{q'}}}{n_q \sqrt{m_q}} \Omega_{aa''}^{(1,1)} \right\}, \end{aligned} \quad (\text{A9})$$

where $L_{aa'01}^{000,000}$ is given by Eq. (A9) with the last term omitted. Also

$$\begin{aligned} \bar{L}_{aa'01}^{000,100} = L_{aa'01}^{000,100} = & -\frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{aa''} \{ \delta_{aa''} [(\frac{5}{2} - \frac{5}{2}M_q - M_{q''} \gamma^2) \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) \\ & - (\frac{5}{2} - \frac{5}{2}M_q - M_{q''} \gamma'^2) \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''})] + \delta_{q'q''} \sqrt{m_q/m_{q''}} [(\frac{5}{2} - \frac{5}{2}M_{q''} - M_q \gamma'^2) \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''}) \\ & - (\frac{5}{2} - \frac{5}{2}M_{q''} + M_q \gamma^2) \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q'})] \}, \end{aligned} \quad (\text{A10})$$

$$\begin{aligned} \bar{L}_{aa'01}^{000,010} = L_{aa'01}^{000,010} = & \frac{16x_q x_{q'} \sqrt{m_q m_{q'}}}{15k T n_{q'} c_{q' \text{int}}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \delta_{aa''} \left[\sum \int d\bar{\Omega}_{aa''} (\epsilon_{q_i} - \bar{\epsilon}_q) \{ \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_{q'} \gamma_{q'}) \} - 4 \frac{m_q}{m_{q''}} \langle \Delta \epsilon_{aa''} \rangle_{aa''} \right] \right. \\ & \left. + \delta_{q'q''} \sqrt{m_q/m_{q''}} \left[\sum \int d\bar{\Omega}_{aa''} (\epsilon_{q''_j} - \bar{\epsilon}_{q''}) \{ \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) - \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q'}) \} + 4 \langle \Delta \epsilon_{aa''} \rangle_{aa''} \right] \right\}, \end{aligned} \quad (\text{A11})$$

$$\begin{aligned} \bar{L}_{aa'01}^{100,000} = L_{aa'01}^{100,000} = & -\frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{aa''} \{ (\frac{5}{2} - \frac{5}{2}M_q - M_{q''} \gamma^2) \{ \delta_{aa''} [\bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''})] \\ & + \delta_{q'q''} \sqrt{m_q/m_{q''}} [\bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''})] \} \}, \end{aligned} \quad (\text{A12})$$

$$\begin{aligned} \bar{L}_{aa'01}^{010,000} = L_{aa'01}^{010,000} = & \frac{16x_q x_{q'} \sqrt{m_q m_{q'}}}{15k T n_{q'} c_{q' \text{int}}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{aa''} (\epsilon_{q_i} - \bar{\epsilon}_q) \{ \delta_{aa''} [\bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q''})] \\ & + \delta_{q'q''} \sqrt{m_q/m_{q''}} [\bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''})] \}, \end{aligned} \quad (\text{A13})$$

$$\begin{aligned} \bar{L}_{aa'01}^{100,100} = L_{aa'01}^{100,100} = & -\frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \delta_{aa''} \left[\sum \int d\bar{\Omega}_{aa''} \{ \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) \left[\frac{25}{4} m_q/m_{q''} - 15M_q + \frac{29}{2} M_q^2 - 5M_{q''} \gamma^2 \right. \right. \right. \\ & + 9M_q M_{q''} \gamma^2 + M_{q''} \gamma^4 - M_q M_{q''} \gamma'^2 + \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) \left[\frac{25}{2} M_q - \frac{25}{4} - \frac{43}{4} M_q^2 - M_{q''}^2 \gamma^2 \gamma'^2 - 2M_q M_{q''} \gamma \gamma' \cos \chi + \frac{5}{2} M_q^2 \gamma'^2 \right. \\ & \left. \left. + \frac{5}{2} M_{q''}^2 \gamma^2 + \bar{I}_{ij}^{kl}(\gamma_{q'} \gamma_{q'}) \left[\frac{5}{2} m_q/m_{q''} - \gamma^2 - \frac{5}{2} M_q \right] + 2M_q M_{q''} \langle \Delta \epsilon_{aa''}^2 \rangle_{aa''} + 8M_{q''}^2 \Omega_{aa''}^{(1,1)} \right] \right. \\ & \left. + \delta_{q'q''} \sqrt{m_q/m_{q''}} \left[\sum \int d\bar{\Omega}_{aa''} \{ \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) \left[5M_q^2 + 5M_{q''}^2 - \frac{5}{2} - \frac{43}{4} M_q M_{q''} - 2M_q M_{q''} \gamma'^2 \right. \right. \right. \\ & - M_q M_{q''} \gamma^4 - \frac{7}{2} M_q^2 \gamma^2 - \frac{7}{2} M_{q''}^2 \gamma^2 + 6M_q M_{q''} \gamma^2 + \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) \left[\frac{7}{2} M_q^2 \gamma^2 - \frac{5}{2} - M_q M_{q''} \gamma^2 \gamma'^2 \right. \\ & \left. \left. + \frac{63}{4} M_q M_{q''} - M_{q''} \gamma^2 + \frac{7}{2} M_q^2 \gamma'^2 - M_q \gamma'^2 - 2M_q M_{q''} \gamma \gamma' \cos \chi + \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) M_q M_{q''} [5 - 2\gamma^2] \right. \right. \\ & \left. \left. + 2M_q M_{q''} \langle \Delta \epsilon_{aa''}^2 \rangle_{aa''} - 8M_q M_{q''} \Omega_{aa''}^{(1,1)} \right] \right\}, \end{aligned} \quad (\text{A14})$$

$$\begin{aligned} \bar{L}_{aa'01}^{100,010} = L_{aa'01}^{100,010} = & \frac{16x_q x_{q'} \sqrt{m_q m_{q'}}}{15k T n_{q'} c_{q' \text{int}}} \sum_{q'' \neq q} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \delta_{aa''} \left[4 \frac{m_q}{m_{q''}} \langle (M_{q''} \gamma^2 + \frac{5}{2} M_q - \frac{5}{2}) \Delta \epsilon_{aa''} \rangle_{aa''} + \sum \int d\bar{\Omega}_{aa''} \{ \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) \right. \right. \\ & \left. \left. \times [(\epsilon_{q_i} - \bar{\epsilon}_q) (\frac{5}{2} - \frac{7}{2} M_q - M_{q''} \gamma^2) + M_q (\epsilon_{q_h} - \bar{\epsilon}_q)] - \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) (\epsilon_{q_h} - \bar{\epsilon}_q) (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) \right] \right. \\ & \left. + \delta_{q'q''} \sqrt{m_q/m_{q''}} \left[4 \langle (M_{q''} \gamma^2 + \frac{5}{2} M_q - \frac{5}{2}) \Delta \epsilon_{aa''} \rangle_{aa''} + \sum \int d\bar{\Omega}_{aa''} \{ \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) \left[M_{q''} (\epsilon_{q''_i} - \bar{\epsilon}_{q''}) \right. \right. \right. \\ & \left. \left. - (\epsilon_{q''_j} - \bar{\epsilon}_{q''}) (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) + \bar{I}_{ij}^{kl}(\gamma_{q''} \gamma_{q''}) (\epsilon_{q''_i} - \bar{\epsilon}_{q''}) (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) \right] \right\}, \end{aligned} \quad (\text{A15})$$

$$\begin{aligned} \bar{L}_{qq'01}^{010,100} = L_{qq'01}^{010,100} = \frac{16x_q x_{q'} \sqrt{m_q m_{q'}}}{15k^2 T n_{q'} c_{q'} \text{int}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \delta_{qq''} \left[\sum \int d\bar{\Omega}_{qq''} (\epsilon_{q_i} - \bar{\epsilon}_q) \{ \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) (\frac{5}{2} - \frac{1}{2} M_q - M_{q'} \gamma^2) \right. \right. \\ \left. \left. - \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) (\frac{5}{2} - \frac{5}{2} M_q - M_{q'} \gamma'^2) + M_{q'} \bar{I}_{ij}^{kl}(\gamma_q' \gamma_{q'}) \right] + M_q \langle \Delta \epsilon_{qq''}^2 \rangle_{qq''} \right\} + \delta_{q'q''} \sqrt{m_q/m_{q''}} \left[\sum \int d\bar{\Omega}_{qq''} (\epsilon_{q_i} - \bar{\epsilon}_q) \right. \\ \left. \times \left\{ \bar{I}_{ij}^{kl}(\gamma_{q'} \gamma_{q''}) (\frac{5}{2} - \frac{5}{2} M_{q'} - M_q \gamma'^2) - \bar{I}_{ij}^{kl}(\gamma_{q'} \gamma_{q''}) (\frac{5}{2} - \frac{5}{2} M_{q'} + M_q - M_q \gamma^2) + M_q \bar{I}_{ij}^{kl}(\gamma_{q'}' \gamma_{q''}') \right\} + M_q \langle \Delta \epsilon_{qq''}^2 \rangle_{qq''} \right\} \end{aligned} \quad (A16)$$

and

$$\begin{aligned} \bar{L}_{qq'01}^{010,010} = L_{qq'01}^{010,010} = - \frac{8x_q x_{q'} \sqrt{m_q m_{q'}}}{3T n_{q'} c_{q'} \text{int} c_{q'} \text{int}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \left\{ \delta_{qq''} \left[\sum \int d\bar{\Omega}_{qq''} (\epsilon_{q_i} - \bar{\epsilon}_q)^2 \{ \bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) - \bar{I}_{ij}^{kl}(\gamma_q' \gamma_{q'}) \} \right. \right. \\ \left. \left. - 4 \frac{m_q}{m_{q''}} \langle (\epsilon_{q_i} - \bar{\epsilon}_q) \Delta \epsilon_{qq''} \rangle_{qq''} \right] + \delta_{q'q''} \sqrt{m_q/m_{q''}} \left[\sum \int d\bar{\Omega}_{qq''} (\epsilon_{q_i} - \bar{\epsilon}_q) (\epsilon_{q'_j} - \bar{\epsilon}_{q'}) \right. \right. \\ \left. \left. \times \left\{ \bar{I}_{ij}^{kl}(\gamma_{q'}' \gamma_{q''}') - \bar{I}_{ij}^{kl}(\gamma_{q'} \gamma_{q''}) \right\} - 4 \langle (\epsilon_{q_i} - \bar{\epsilon}_q) \Delta \epsilon_{q'q''} \rangle_{q'q''} \right] \right\} \end{aligned} \quad (A17)$$

where

$$\begin{aligned} M_q &= m_q / (m_q + m_{q'}), & M_{q'} &= m_{q'} / (m_q + m_{q'}), \\ \Delta \epsilon_q &= \epsilon_{qk} - \epsilon_{qi}, & \Delta \epsilon_{q'} &= \epsilon_{q'j} - \epsilon_{q'i}, \\ \Delta \epsilon_{qq''} &= \Delta \epsilon_q + \Delta \epsilon_{q''}, = \gamma^2 - \gamma'^2, \end{aligned}$$

$$\Omega_{qq'}^{(1,1)} = \frac{1}{Q_q Q_{q'}} \sqrt{\frac{kT}{2\pi u}} \sum_{ijkl} \int \dots \int d\gamma d\phi \sin\chi d\chi \gamma^3 e^{-(\gamma^2 + \epsilon_{qi} + \epsilon_{q'i})} \bar{I}_{ij}^{kl}(\gamma, \chi, \phi) (2l_q + 1)(2l_{q'} + 1) (\gamma^2 - \gamma\gamma' \cos\chi),$$

$$\langle F(\Delta\epsilon) \rangle_{qq'} = \frac{1}{Q_q Q_{q'}} \sqrt{\frac{kT}{2\pi u}} \sum_{ijkl} \int \dots \int d\gamma d\phi \sin\chi d\chi \gamma^3 e^{-(\gamma^2 + \epsilon_{qi} + \epsilon_{q'i})} \bar{I}_{ij}^{kl}(\gamma, \chi, \phi) (2l_q + 1)(2l_{q'} + 1) F(\Delta\epsilon),$$

$$\sum \int d\bar{\Omega}_{qq''} F = \frac{8}{Q_q Q_{q''}} \sqrt{\frac{kT}{2\pi u}} \sum_{ijkl} \int \dots \int d\gamma d\phi \sin\chi d\chi \gamma^3 e^{-(\gamma^2 + \epsilon_{qi} + \epsilon_{q'i})} (2l_q + 1)(2l_{q''} + 1) F,$$

and

$$\bar{I}_{ij}^{kl}(\gamma_q \gamma_{q'}) = \frac{1}{(2l_q + 1)(2l_{q'} + 1)} \sum_{\text{e-component states}} \frac{1}{2J_q^2} [\gamma \cdot J_q J_{q'} \gamma' + \gamma' \cdot J_q J_q \gamma] \bar{I}_{ij}^{kl}(\gamma, \chi, \phi). \quad (A18)$$

The results for the $L_{qq'11}^{nq', n'q'}$ are given below:

$$\begin{aligned} L_{qq'11}^{000,000} = - \frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{qq''} \left\{ \delta_{qq''} [\bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma) - \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma')] \right. \\ \left. + \delta_{q'q''} \sqrt{\frac{m_q}{m_{q''}}} [\bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma') - \bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma)] \right\} \end{aligned} \quad (A19)$$

$$\begin{aligned} L_{qq'11}^{100,000} = L_{qq'11}^{000,100} = - \frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{qq''} \left\{ \delta_{qq''} (\frac{5}{2} - \frac{5}{2} M_q - M_{q'} \gamma^2) [\bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma) - \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma')] \right. \\ \left. + \delta_{q'q''} \sqrt{m_q/m_{q''}} [\bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma') - \bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma)] \right\} \end{aligned} \quad (A20)$$

$$\begin{aligned} L_{qq'11}^{010,000} = L_{qq'11}^{000,010} = \frac{16x_q x_{q'} \sqrt{m_q m_{q'}}}{15k^2 T n_{q'} c_{q'} \text{int}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{qq''} \left\{ \delta_{qq''} (\epsilon_{q_i} - \bar{\epsilon}_q) [\bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma) - \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma')] \right. \\ \left. + \delta_{q'q''} \sqrt{\frac{m_q}{m_{q''}}} (\epsilon_{q'_j} - \bar{\epsilon}_{q'}) [\bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma') - \bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma)] \right\} \end{aligned} \quad (A21)$$

$$\begin{aligned} L_{qq'11}^{100,100} = \frac{32x_q x_{q'} \sqrt{m_q m_{q'}}}{75k^2 T n_{q'}} \sum_{q''} \frac{n_{q''} m_{q''}}{(m_q + m_{q''})} \sum \int d\bar{\Omega}_{qq''} \left\{ \delta_{qq''} [\bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma) (\frac{1}{2} M_q M_{q'} \gamma^4 - \frac{5}{4} M_q M_{q'} \gamma^2 + M_q^2 \gamma^2 + \frac{5}{4} M_q M_{q'} \gamma'^2 - \frac{1}{2} M_q M_{q'} \gamma^2 \gamma^2 \right. \\ \left. - M_q^2 \gamma\gamma' \cos\chi) + \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma) (\frac{25}{4} + M_q^2 \gamma^4 - 5M_{q'} \gamma^2 - 15M_q + \frac{53}{4} M_q^2 + 9M_q M_{q'} \gamma^2 - M_q M_{q'} \gamma'^2) \right. \\ \left. + \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma\gamma') (\frac{5}{2} M_{q'} \gamma^2 - \frac{25}{4} - M_{q'}^2 \gamma^2 \gamma'^2 + \frac{5}{2} M_{q'} \gamma'^2 + \frac{25}{2} M_q - \frac{39}{4} M_q^2 - \frac{5}{2} M_q M_{q'} \gamma^2 - \frac{5}{2} M_q M_{q'} \gamma'^2 - 2M_q M_{q'} \gamma\gamma' \cos\chi) \right. \\ \left. - M_q M_{q'} \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma'\gamma) + M_q (\frac{5}{2} - \frac{5}{2} M_q - M_{q'} \gamma^2) \bar{I}_{ij}^{kl}(J_q J_{q'}; \gamma'\gamma') \right] + \delta_{q'q''} \sqrt{m_q/m_{q''}} [\bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma) (\frac{1}{2} M_q M_{q''} \gamma^4 - \frac{5}{4} M_q M_{q''} \gamma^2 \\ + \frac{5}{4} M_q \gamma'^2 - \frac{1}{2} M_q M_{q''} \gamma^2 \gamma'^2 + \frac{5}{4} M_q^2 \gamma^2 - \frac{5}{4} M_q^2 \gamma'^2 - M_q M_{q''} \gamma^2 + M_q M_{q''} \gamma\gamma' \cos\chi) + \bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma) \\ \times (\frac{5}{2} M_{q''} \gamma^2 - \frac{25}{4} - M_q M_{q''} \gamma^4 + \frac{5}{2} M_q \gamma^2 + \frac{5}{2} M_q^2 + \frac{25}{4} M_{q''} - \frac{43}{4} M_q M_{q''} + \frac{15}{4} M_q + 4M_q M_{q''} \gamma^2 - \frac{5}{2} M_q^2 \gamma^2 - \frac{5}{2} M_q^2 \gamma'^2 - M_q M_{q''} \gamma'^2) \\ \left. + \bar{I}_{ij}^{kl}(J_q J_{q''}; \gamma\gamma') (\frac{25}{4} + M_q M_{q''} \gamma^2 \gamma'^2 - \frac{25}{4} M_{q''} + \frac{39}{4} M_q M_{q''} - \frac{25}{4} M_q - \frac{5}{2} M_q \gamma^2 + \frac{5}{2} M_q^2 \gamma^2 - \frac{5}{2} M_q \gamma'^2 + \frac{5}{2} M_q^2 \gamma'^2) \right\} \end{aligned}$$

$$-2M_q M_{q''} \gamma \gamma' \cos \chi) + M_q M_{q''} \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma' \gamma) + \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma' \gamma') M_q (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) \}, \quad (\text{A22})$$

$$L_{qq''11}^{100,010} = L_{qq''11}^{010,100} = \frac{4x_q x_{q''} \sqrt{m_q m_{q''}}}{15kT n_{q''} c_{q''} \text{int } q''} \sum_{q''} \frac{n_q \cdot m_{q''}}{(m_q + m_{q''})} \sum \int d\tilde{\Omega}_{qq''} \{ \delta_{qq''} [\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma)] (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) (\epsilon_{qi} - \bar{\epsilon}_q) + M_q \Delta \epsilon_q \} \\ - \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma') (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) (\epsilon_{qk} - \bar{\epsilon}_q) + \frac{1}{2} M_q \Delta \epsilon_{qq''} \cdot \Delta \epsilon_q \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}) + \delta_{q''q} \sqrt{m_q/m_{q''}} [\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma)] \{ \Delta \epsilon_{qq''} \\ - (\frac{5}{2} - \frac{5}{2} M_q - M_{q''} \gamma^2) (\epsilon_{q''j} - \bar{\epsilon}_{q''}) \} + \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma') (\epsilon_{q''i} - \bar{\epsilon}_{q''}) + \frac{1}{2} M_{q''} \Delta \epsilon_{qq''} \cdot \Delta \epsilon_{q''} \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}) \}, \quad (\text{A23})$$

and

$$L_{qq''11}^{010,010} = -\frac{2x_q x_{q''} \sqrt{m_q m_{q''}}}{3T n_q \cdot c_q \text{int } c_{q''} \text{int } q''} \sum_{q''} \frac{n_q \cdot m_{q''}}{(m_q + m_{q''})} \sum \int d\tilde{\Omega}_{qq''} \cdot (\epsilon_{qi} - \bar{\epsilon}_q) \{ \delta_{qq''} [\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma)] (\epsilon_{qi} - \bar{\epsilon}_q) - \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma') (\epsilon_{qk} - \bar{\epsilon}_q) \\ - \frac{1}{2} (m_q/m_{q''}) \Delta \epsilon_q \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}) + \delta_{q''q} \sqrt{m_q/m_{q''}} [\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma') (\epsilon_{q''i} - \bar{\epsilon}_{q''}) - \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma) (\epsilon_{q''j} - \bar{\epsilon}_{q''}) \\ - \frac{1}{2} \Delta \epsilon_{q''} \tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}) \} \}, \quad (\text{A24})$$

where

$$\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}; \gamma \gamma') = \frac{1}{(2l_q + 1)(2l_{q''} + 1)} \sum_{z\text{-component states}} \frac{1}{J_q^2 J_{q''}^2} [\mathbf{J}_q \mathbf{J}_q \cdot \mathbf{J}_{q''} \mathbf{J}_{q''}; \gamma \gamma' + \mathbf{J}_q \mathbf{J}_{q''} \cdot \gamma' \gamma \mathbf{J}_{q''} \cdot \mathbf{J}_q] \tilde{I}_{ij}^{kl}(\gamma, \chi, \phi) \quad (\text{A25})$$

and

$$\tilde{I}_{ij}^{kl}(\mathbf{J}_q \mathbf{J}_{q''}) = \frac{1}{(2l_q + 1)(2l_{q''} + 1)} \sum_{z\text{-component states}} \frac{1}{J_q^2 J_{q''}^2} [\mathbf{J}_q \mathbf{J}_q : \mathbf{J}_{q''} \mathbf{J}_{q''}] I_{ij}^{kl}(\gamma, \chi, \phi). \quad (\text{A26})$$

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