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Triple-Collision Operator for a Quantum Gas with Bound States

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The triple-collision operator of dense gas theory is analyzed for a quantum-mechanical gas obeying Boltzmann statistics. The contribution of two-body bound states is extracted by using Faddeev's representation of the three-body resolvent. The result is a binary atom–molecule collision operator which includes the effects of molecular formation and breakup, and inelastic and rearrangement collisions. An additional contribution is a modification of the Boltzmann collision operator due to the binding of one member of the colliding pair to a third particle. The analysis is carried out in the framework of the Green–Kubo formulas so the operators considered are linear and the results are in a form suitable for the evaluation of the transport coefficients.

KEY WORDS: Kinetic theory; triple collisions; polyatomic gases; inelastic collisions; reactions.

1. INTRODUCTION

The Boltzmann equation provides a sound basis for the description of processes in low-density monatomic gases in which the particles interact by binary elastic collisions. In a molecular gas there is the additional possibility of inelastic collisions and reactions.[2] A kinetic theory which includes inelastic collisions was presented by Wang-Chang, Uhlenbeck, and deBoer.$^{(2)}$ Their theory is based on a distribution function which depends on the position and velocity of the center of mass of a molecule, and on the quantum numbers which label the internal states. A more general theory was developed by Waldmann and Snider,[3] who took the distribution

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[2] Some discussion of kinetic theory for polyatomic gases can be found in Ref. 1.

[3] See Waldmann (Ref. 3). The Waldmann–Snider equation and its applications have been reviewed by Beenakker and McCourt and by Moraal (Ref. 3).

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function to be a density matrix with respect to the internal states. Their density matrix is diagonal in the internal molecular energies, but in case of degeneracy need not be fully diagonal. Reactions have been considered in the context of the Waldmann–Snider equation by Lowry and Snider,(4) and rearrangement collisions between an atom and a diatomic molecule have been discussed by Eu.(5) The approach generally has been to treat the molecule as a particle rather than a composite system. The existence of different internal states is allowed for, but collisions are assumed to occupy small intervals of space and time.

A different line of development has dealt with the kinetic theory for dense monatomic gases. A generalization of the Boltzmann equation to the dense hard-sphere gas was obtained by Enskog.(6) Enskog's equation contains a density-dependent correction to the collision frequency, and also takes account of the finite spatial extent of a collision and the collisional transfer of energy and momentum. A more general approach, initiated by Bogoliubov(7) and analyzed further by Green(8) and Cohen,(9) leads to a kinetic equation in which the binary collision operator is augmented by terms describing triple and, in principle, higher-order collisions. By now this theory has been extensively developed, particularly for classical gases with repulsive interactions.[4]

The approach developed in dense-gas theory should also be applicable when the interaction between particles can support bound states. Extraction of the bound-state contributions can then provide a description of molecular processes. In such an approach molecules will occur as an automatic consequence of the dynamics, and all effects associated with a given order in the density can be obtained together in a consistent way. The composite nature of the molecule is fully taken into account, as are its finite size and the finite extent of collisions. Such a derivation is the dynamic analog of the equilibrium virial expansion where the molecular contribution to the second virial coefficient is obtained as the bound-state part of the Beth–Uhlenbeck formula.[5]

In this paper the triple-collision operator of dense-gas theory will be analyzed with the purpose of extracting the contribution of bound states.[6] This provides a description of the molecular processes which can occur in a

[4] For a recent review see Ref. 10.

[5] Bound-state contributions in the equilibrium problem have been treated with techniques similar to those used here in Ref. 11.

[6] The triple-collision operator for a classical gas with attractive forces has been discussed by Kawasaki and Oppenheim (Ref. 12). Other work on the effect of attractive forces in classical theory includes Davis *et al.*, Kim and Ross, Dufty and Gubbins, and Marchetti and Dufty (Ref. 12).

system of three atoms, including collisions involving an atom and a diatomic molecule. The system considered is a quantum-mechanical gas of identical particles obeying Boltzmann statistics, and interacting by two-body central forces.

The triple collision operator to be analyzed is the linear operator obtained from the density expansion of the Green–Kubo formula for a transport coefficient. The fluxes occurring in the Green–Kubo formula are taken to be sums of single-particle operators. Hence the potential-energy terms which lead to collisional transfer of energy and momentum are not included. Methods are known[7] for dealing with collisional transfer in a monatomic gas, and its inclusion in the theory for a polyatomic gas is discussed briefly in the last section below.

The triple-collision operator depends on the time-development operator for the three-body system, and also contains repeated two-body time-development operators. Bound-state contributions to the latter lead to a modification of the Boltzmann collision operator in which one of the colliding particles is bound to a third particle; this modification is loosely analogous to Enskog's correction to the collision frequency. The remaining bound-state contributions are extracted by using Faddeev's representation of the three-body resolvent.(14) This results in a set of atom–molecule collision operators which describe molecular formation and dissociation, elastic and inelastic scattering, and rearrangement collisions.[8] These act on matrix elements (with respect to the molecular states) of two-body contributions to the fluxes in the Green–Kubo formula; as in Waldmann–Snider theory the matrices need not be diagonal but only elements which are diagonal in the molecular energy occur. In addition there occur terms in which the two fluxes are correlated over the molecular state; for the thermal conductivity and viscosity these terms depend on the correlation of an internal stress in the molecule.

Since the discussion is based on the Green–Kubo formulas, the results are in a form which would be convenient for the evaluation of the transport coefficients. However, such evaluation would require knowledge of the three-body scattering and reaction amplitudes which appear in the final form of the collision operators, and this problem is not considered here.[9] Detailed analysis of the three-body problem is of course difficult. (Even for classical hard spheres the calculation by Sengers and co-workers(17) of the

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[7] Collisional transfer in the Enskog hard-sphere theory is discussed in Ref. 6. Other treatments of collisional transfer in monatomic gases are given in Ref. 13.

[8] A preliminary report of some of the results obtained here has been given in Ref. 15.

[9] Recent discussions of three- (and more-) body collisions can be found in Ref. 16.

three-body contributions to the transport coefficients required heroic efforts.) However, the results obtained below at least provide a framework for input, from theory or experiment, on the amplitudes, and less-than-perfect input could lead to improved semiempirical formulas for the transport coefficients.

The complete triple-collision operator is obtained by adding the results obtained here to the collision operator for scattering of three free particles (that is, scattering in which neither initial nor final states contain bound particles). This operator, for the quantum-mechanical case, has been discussed by Resibois,(18) and the analysis given here has several points of similarity with that of Resibois. Actually the bound-state part is easier to analyze since binding partially reduces the three-body problem to a two-body problem. The free-to-free scattering leads to a long-time divergence of the contribution from reducible diagrams; this divergence is canceled by other contributions to the triple-collision operator but its treatment still requires care. Binding leads to a milder long-time dependence so that the various terms are individually convergent.

The results obtained below apply to a gas with a low degree of association. If the concentration of molecules is significant, it becomes necessary to include molecule–molecule collisions. Their description, in the approach used here, would require analysis of the four-body collision operator of dense-gas theory.

Transport processes can of course be described by kinetic equations rather than with the correlation-function approach used here. Kinetic equations are needed particularly for the theory of chemical reaction rates as formulas of the Green–Kubo type are not available for this case. The construction of the kinetic equations for a gas with bound states will be discussed in a separate publication.(19)

2. TRIPLE-COLLISION OPERATOR

This section will provide a derivation of the triple-collision operator which is the object of interest in the remainder of the paper. The system considered is a quantum gas of identical particles obeying Boltzmann statistics. The derivation is based on the time-dependent cluster expansion(8,9,10) for a time-dependent correlation function.[10]

Let A_N be an operator on the Hilbert space for the N-particle system, which initially is assumed to be confined to a region of volume V. The

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[10] The cluster expansion for time-dependent correlation functions in quantum mechanics has been discussed in Ref. 20.

grand-canonical average is given by

$$\langle A\rangle = e^{-Q}\sum_{N=0}^{\infty}\frac{1}{N!}e^{\zeta N}\mathrm{Tr}_N e^{-\beta H_N}A_N \tag{1}$$

Here $\beta = 1/kT$ where k is Boltzmann's constant and T the Kelvin temperature, $\zeta = \beta\mu$ where μ is the chemical potential, H_N is the Hamiltonian operator for the N-particle system, and Tr_N denotes the trace associated with the N-particle Hilbert space. In addition the grand potential Q is determined by

$$e^{Q} = \sum_{N=0}^{\infty}\frac{1}{N!}e^{\zeta N}\mathrm{Tr}_N e^{-\beta H_N} \tag{2}$$

We assume two-body interactions, so H_N is

$$H_N = \sum_{\alpha=1}^{N}(p_\alpha^2/2m) + \frac{1}{2}\sum_{\alpha\beta}V_{\alpha\beta} \tag{3}$$

where p_α is the momentum of the αth particle, m is the mass, and $V_{\alpha\beta}$ is the potential energy of the pair α, β.

The transport coefficients can be obtained from time-dependent correlation functions by means of the Green–Kubo formulas whose general form is(21)

$$L_{AB} = \int_0^{\infty} dt\, C_{AB}(t) \tag{4}$$

where $C_{AB}(t)$ is the correlation function (per unit volume)

$$C_{AB}(t) = \lim_{V\to\infty} V^{-1}\left[\langle AB(t)\rangle - \langle A\rangle\langle B\rangle\right] \tag{5}$$

Here the time dependence is induced by the atomic equations of motion,

$$\begin{aligned} B_N(t) &= U_N^*(t)B_N U_N(t) \\ U_N(t) &= \exp(-itH_N/\hbar). \end{aligned} \tag{6}$$

where the asterisk denotes the adjoint. The quantities A, B are fluxes whose particular form depends on the transport coefficient being considered. For example, the thermal conductivity λ is given by

$$\lambda = (1/3kT^2)\int_0^{\infty} dt \lim_{V\to\infty} V^{-1}\langle \mathbf{S}'\cdot\mathbf{S}'(t)\rangle \tag{7}$$

where $\mathbf{S}'$ is the "subtracted" energy flux

$$\mathbf{S}' = \mathbf{S} - (h/\rho)\mathbf{P} \tag{8}$$

Here $\mathbf{S}$ is the total energy flux, (h/ρ) is the enthalpy per unit mass, and $\mathbf{P}$ is the total momentum. In terms of the atomic coordinates and momenta, $\mathbf{S}$ is given by(22)

$$S_i = \sum_\alpha \left\{ \frac{p_{\alpha i}}{m} \left[\frac{p_\alpha^2}{2m} + \frac{1}{2} \sum_\beta V_{\alpha\beta} \right] + \frac{1}{2} \sum_\beta (q_{\beta i} - q_{\alpha i}) \frac{p_{\alpha j}}{m} \frac{\partial V_{\alpha\beta}}{\partial q_{\alpha j}} \right\} \tag{9}$$

Formulas of the type (4) also hold for the coefficients of viscosity and diffusion.

Noncommutation of operators in quantum mechanics allows for the definition of several different correlation functions.(23) Frequently the "canonical correlation"

$$\langle A; B(t) \rangle = \beta^{-1} \int_0^\beta d\lambda \, C_{AB}(t - i\hbar\lambda) \tag{10}$$

is used, and the Green–Kubo formula written as

$$L'_{AB} = \int_0^\infty dt \langle A; B(t) \rangle \tag{11}$$

In most cases of interest, Eqs. (4) and (11) yield the same result. Suppose in particular the system to be invariant under space inversion and time reversal (which is the case for the gas considered here). Then

$$\begin{aligned} C_{AB}(t) &= \sigma_A \sigma_B C_{AB}(t) \\ &= \tau_A \tau_B C_{AB}(-t) \end{aligned} \tag{12}$$

where σ, τ denote the parity under inversion and time reversal. The fluxes of interest (namely, the fluxes for energy, momentum, and particle number) in fact each have the same space and time parity, $\sigma = \tau$. It follows that

$$C_{AB}(t) = C_{AB}(-t) \tag{13}$$

and similarly

$$\langle A; B(t) \rangle = \langle A; B(-t) \rangle \tag{14}$$

Hence we have

$$L_{AB} = \frac{1}{2} \int_{-\infty}^\infty dt \, C_{AB}(t), \quad L'_{AB} = \frac{1}{2} \int_{-\infty}^\infty dt \langle A; B(t) \rangle \tag{15}$$

and it follows immediately that $L_{AB} = L'_{AB}$. [This can also be seen by taking the zero-frequency limit in Eq. (6.18) of Ref. 23.] Here we will use the correlation $C_{AB}(t)$ since it is somewhat easier to deal with than $\langle A; B(t) \rangle$.

The expression (9) for **S** contains kinetic terms (which depend only on the momenta), and terms depending on the potential energy. The potential terms lead to collisional-transfer contributions to the thermal conductivity. The potential terms are usually analyzed(13) by methods which are somewhat different from those for the kinetic terms; as mentioned in the Introduction, here we will only consider the kinetic terms. Thus we simplify

A and B to sums of single-particle functions of the momenta,

$$A_N = \sum_{\alpha=1}^{N} a(\mathbf{p}_\alpha), \qquad B_N = \sum_{\alpha=1}^{N} b(\mathbf{p}_\alpha) \tag{16}$$

We have defined $C_{AB}(t)$ with the assumption that A, B are self-adjoint, as is the case for the fluxes of interest. For non-self-adjoint operators the natural choice is

$$C_{AB}(t) = \lim_{V\to\infty} V^{-1}\left[\langle A^* B(t)\rangle - \langle A^*\rangle\langle B\rangle\right] \tag{17}$$

It is readily confirmed that $C_{AB}(0)$, considered as a functional of a, b, has the properties of an inner product. Hence we write it as (a,b),

$$\begin{aligned}(a,b) &= C_{AB}(0)\\ &= \lim_{V\to\infty} V^{-1}\left[\langle A^* B\rangle - \langle A^*\rangle\langle B\rangle\right]\end{aligned} \tag{18}$$

This equation converts the algebra of single-particle operators into a Hilbert space, $\mathcal{H}$. Considered as a functional of a and b, $C_{AB}(t)$ then defines a linear operator $\Lambda(t)$ on $\mathcal{H}$:

$$C_{AB}(t) = (a, \Lambda(t) b) \tag{19}$$

It is straightforward to show that $C_{AA}(t)$ is bounded by its initial value, and so $\Lambda(t)$ is a contraction,

$$|(a, \Lambda(t) a)| \leqslant (a,a) \tag{20}$$

As a consequence the Laplace transform

$$\tilde{\Lambda}(s) = \int_0^\infty dt\, e^{-st}\Lambda(t) \tag{21}$$

exists throughout the right half plane $\operatorname{Re} s \geqslant 0$. The Green–Kubo formula can be written as a limit for $s\to 0$,

$$L_{AB} = \lim_{s\to 0}(a, \tilde{\Lambda}(s) b) \tag{22}$$

Henceforth a and b will be assumed to be self-adjoint.

Following Zwanzig,$^{(24)}$ we define a memory function by

$$\tilde{\Lambda}(s) = \left[s + M(s)\right]^{-1} \tag{23}$$

The collision operator I is then given by

$$I = \lim_{s\to 0} M(s) \tag{24}$$

Our purpose now is to obtain a density expansion for I. Actually, however, we will work with the fugacity expansion, which is readily converted into a density expansion.

By writing out the sums in Eqs. (1) and (2), it is straightforward to obtain the expansion

$$(a,b)=\lim_{V\to\infty}(zV_0/V)\Big\{\mathrm{Tr}_1e^{-\beta H_1}ab+\tfrac{1}{2}zV_0\mathrm{Tr}_2\big[e^{-\beta H_2}-e^{-\beta H_0}\big]A_2B_2$$
$$+\frac{1}{3!}(zV_0)^2\mathrm{Tr}_3\Big[e^{-\beta H_3}-\sum_\mu e^{-\beta H_\mu}+2e^{-\beta H_0}\Big]A_3B_3+\cdots\Big\} \tag{25}$$

Here we have introduced

$$z=e^{\zeta}/V_0, \qquad V_0=h^3(2\pi mkT)^{-3/2} \tag{26}$$

and H_0 denotes the free-particle Hamiltonian (regardless of the number of particles). In addition μ has been used to denote a pair, and H_μ is the Hamiltonian for a three-particle system in which only the pair μ interacts,

$$H_\mu=H_0+V_\mu \tag{27}$$

Since the operators being dealt with commute with the total momentum, the energy of the center of mass can be factored out. Let $\mathbf{P}$ be the total momentum,

$$\mathbf{P}=\sum_{\alpha=1}^{N}\mathbf{p}_\alpha \tag{28}$$

and K_N the center-of-mass energy,

$$K_N=P^2/(2Nm) \tag{29}$$

For large volume the density of states for momentum is V/h^3 and taking the thermodynamic limit term-by-term in Eq. (25) we get

$$(a,b)=(zV_0/h^3)\Big\{\mathrm{tr}_1e^{-\beta H_1}ab+\tfrac{1}{2}zV_0\mathrm{tr}_2e^{-\beta K_2}$$
$$\times\big[e^{-\beta h_2}-e^{-\beta h_0}\big]A_2B_2+\frac{1}{3!}(zV_0)^2\mathrm{tr}_3e^{-\beta K_3}$$
$$\times\Big[e^{-\beta h_3}-\sum_\mu e^{-\beta h_\mu}+2e^{-\beta h_0}\Big]A_3B_3+\cdots\Big\} \tag{30}$$

The Hamiltonian operators in the center-of-mass frame have been denoted by lower case letters,

$$h_N=H_N-K_N, \qquad h_\mu=H_\mu-K_3 \tag{31}$$

The momentum $\mathbf{P}$ is treated as a parameter so h_N acts on the Hilbert space for N particles moving in infinite space with fixed $\mathbf{P}$; tr_N denotes the trace associated with this Hilbert space followed by an integration over $\mathbf{P}$. (In other words, tr_N means integrate over the diagonal matrix elements but leave out an overall momentum-conserving delta function.)

A similar treatment of the time-dependent correlation function yields the expansion

$$\begin{aligned}(a,\Lambda(t)b) = (zV_0/h^3)\Big\{ &\mathrm{tr}_1 e^{-\beta H_1} ab + \tfrac{1}{2} zV_0 \mathrm{tr}_2 e^{-\beta K_2} \\ &\times\left[e^{-\beta h_2} A_2 S_2(t) B_2 - e^{-\beta h_0} A_2 B_2\right] + \frac{1}{3!}(zV_0)^2 \mathrm{tr}_3 e^{-\beta K_3} \\ &\times\Big[e^{-\beta h_3} A_3 S_3(t) B_3 - \sum_\mu e^{-\beta h_\mu} A_3 S_\mu(t) B_3 \\ &\quad + 2e^{-\beta h_0} A_3 B_3\Big] + \cdots \Big\}\end{aligned} \tag{32}$$

Here we have introduced streaming operators $S_N(t)$ defined by $B_N(t) = S_N(t)B$; $S_\mu(t)$ denotes the streaming operator for the three-particle system in which only the pair μ interacts:

$$S_\mu(t)B_3 = U_\mu^*(t) B_3 U_\mu(t), \qquad U_\mu(t) = \exp(-itH_\mu/\hbar) \tag{33}$$

Since B_N commutes with the total momentum, all of the time-displacement operators in (32) can be written with h's instead of H's.

We next expand Λ,

$$\Lambda = \Lambda_0 + z\Lambda_1 + z^2\Lambda_2 + \cdots \tag{34}$$

On writing Eq. (30) with Λb in place of b and comparing with (32), we get

$$\begin{aligned}\Lambda_0 &= 1 \\ \mathrm{tr}_1 e^{-\beta H_1} a\Lambda_1 b &= \tfrac{1}{2} V_0 \mathrm{tr}_2 e^{-\beta H_2} A_2(S_2 - 1)B_2 \\ \mathrm{tr}_1 e^{-\beta H_1} a\Lambda_2 b &= \frac{1}{3!} V_0^2 \mathrm{tr}_3 e^{-\beta K_3}\Big[e^{-\beta h_3} A_3(S_3 - 1)B_3 \\ &\qquad - \sum_\mu e^{-\beta h_\mu} A_3(S_\mu - 1)B_3\Big] \\ &\quad - \tfrac{1}{2} V_0 \mathrm{tr}_2 e^{-\beta K_2}\left[e^{-\beta h_2} - e^{-\beta h_0}\right] A_2 \Lambda_1 B_2\end{aligned} \tag{35}$$

Here we have used the abbreviation $(\Lambda_1 B_2)(1,2) = (\Lambda_1 b)(1) + (\Lambda_1 b)(2)$.

The transformed operator $\tilde{\Lambda}$ has the expansion

$$\tilde{\Lambda} = \tilde{\Lambda}_0 + z\tilde{\Lambda}_1 + z^2\tilde{\Lambda}_2 + \cdots \tag{36}$$

It follows from the first of Eqs. (35) that $\tilde{\Lambda}_0 = s^{-1}$. Introducing the expansion into Eq. (23) we get

$$M = zM_1 + z^2 M_2 + \cdots \tag{37}$$

where

$$M_1 = -s^2\tilde{\Lambda}_1$$
$$M_2 = -s^2\tilde{\Lambda}_2 + s^3\tilde{\Lambda}_1^2 \tag{38}$$

Finally the collision operator I is given by

$$I = zI_1 + z^2I_2 + \cdots \tag{39}$$

where

$$\begin{aligned} I_1 &= -\lim_{s\to 0} s^2\tilde{\Lambda}_1 \\ I_2 &= -\lim_{s\to 0}\left[s^2\tilde{\Lambda}_2 - s^3\tilde{\Lambda}_1^2\right] \end{aligned} \tag{40}$$

If the above formula for I_1 is worked out, the result, as shown in the Appendix, is the linearized Boltzmann collision operator(6)

$$(I_1b)(\mathbf{p}_1) = \int d\mathbf{p}_2\,\varphi(p_2)\int d\Omega'\, g\sigma(\mathbf{g}',\mathbf{g})\left[b(\mathbf{p}_1) + b(\mathbf{p}_2) - b(\mathbf{p}_1') - b(\mathbf{p}_2')\right] \tag{41}$$

Here $\mathbf{p}_1', \mathbf{p}_2'$ denote momenta after a collision with initial momenta $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{g}$ and $\mathbf{g}'$ are the relative velocities before and after the collision, σ is the cross section, and $d\Omega'$ is an element of solid angle about the direction of $\mathbf{g}'$. In addition, φ denotes the Maxwell–Boltzmann distribution function,

$$\varphi = (2\pi mkT)^{-3/2}\exp(-p^2/2mkT) \tag{42}$$

The last term in Eq. (35) for Λ_2 gives a contribution to I_2 which can be expressed immediately in terms of I_1. Hence we write

$$I_2 = I_2' + I_2'' \tag{43}$$

where I_2'' is obtained from the last term in Eq. (35). Using the first of Eqs. (40) we get

$$\mathrm{tr}_1 e^{-\beta H_1} a I_2'' b = -\tfrac{1}{2} V_0 \mathrm{tr}_2 e^{-\beta K_2}\left[e^{-\beta h_2} - e^{-\beta h_0}\right] A_2 I_1 B_2 \tag{44}$$

The remaining part, I_2', is determined by

$$I_2' = -\lim_{s\to 0}\left[s^2\tilde{\Lambda}_2' - s^3\tilde{\Lambda}_1^2\right] \tag{45}$$

where $\tilde{\Lambda}_2'$ is the Laplace transform of the operator Λ_2' determined by

$$\begin{aligned} \mathrm{tr}_1 e^{-\beta H_1} a \Lambda_2' b = {} & \frac{1}{3!} V_0^2 \mathrm{tr}_3 e^{-\beta K_3} \\ & \times\left[e^{-\beta h_3} A_3(S_3 - 1)B_3 - \sum_{\mu} e^{-\beta h_\mu} A_3(S_\mu - 1)B_3\right] \end{aligned} \tag{46}$$

As is well known,(10) divergences occur in the density expansion for the collision operator and it is necessary to perform a resummation of ring diagrams if the expansion is carried to higher order. However, the divergence first occurs (in three dimensions) at the next order beyond that considered here, and plays no role in our discussion.

3. TWO-BODY PART

For small s, $\tilde{\Lambda}_1$ is singular as $s^{-2}I_1$. Hence the last term in Eq. (45) is singular as s^{-1}. It works out that $\tilde{\Lambda}_2'$ has an s^{-3} singularity such that the combination of terms in (45) has a well-defined limit. In order to break the calculation down into parts, it is convenient to write

$$I_2' = F + G \tag{47}$$

where

$$\begin{aligned} F &= -\lim_{s\to 0}\left[s^2\tilde{\Lambda}_2' - s^{-1}I_1^2\right] \\ G &= \lim_{s\to 0}\left[s^3\tilde{\Lambda}_1^2 - s^{-1}I_1^2\right] \end{aligned} \tag{48}$$

Each of the above limits exists separately so this division of I_2' makes sense.

The operator G involves only two-body dynamics and so its analysis is relatively straightforward. The remainder of this section will be devoted to G.

Let G be rewritten as

$$G = \frac{1}{2}\lim_{s\to 0} s^{-1}\left\{\left[s^2\tilde{\Lambda}_1 - I_1\right]\left[s^2\tilde{\Lambda}_1 + I_1\right] + \left[s^2\tilde{\Lambda}_1 + I_1\right]\left[s^2\tilde{\Lambda}_1 - I_1\right]\right\} \tag{49}$$

Using Eq. (40) for I_1, we get

$$G = I_1 U + U I_1 \tag{50}$$

where

$$U = -\lim_{s\to\infty}\left[s\tilde{\Lambda}_1 + s^{-1}I_1\right] \tag{51}$$

As remarked in the Introduction, the large t divergence is weakened by binding. In particular the bound-state contribution to $\Lambda_1(t)$ is a bounded function of t. (Actually it contains terms which oscillate with the characteristic molecular frequencies.) Hence the bound-state contribution to $\tilde{\Lambda}_1$ is singular for small s only as s^{-1}, and we may separate U into the two parts

$$U = Y + V \tag{52}$$

where

$$\begin{aligned} Y &= -\lim_{s\to 0} s(\tilde{\Lambda}_1)_b \\ V &= -\lim_{s\to 0}\left[s(\tilde{\Lambda}_1)_f + s^{-1}I_1\right] \end{aligned} \tag{53}$$

Here the subscripts b and f denote the bound and free (i.e., unbound) parts. Our concern is only with Y, and V will not be considered further.

It is now necessary to work out $\tilde{\Lambda}_1$ in detail. Equation (35) for Λ_1 can be rewritten as

$$(a, \Lambda_1 b)_0 = (V_0^2/2h^3)\mathrm{tr}_2 e^{-\beta K} A_2 [u_2^*(t), B_2] u_2(t) e^{-\beta h_2} \tag{54}$$

where brackets [,] denote the commutator and

$$u_2(t) = \exp(-ith_2/\hbar) \tag{55}$$

For brevity K has been written instead of K_2. In addition brackets $(\, , \,)_0$ denote the Maxwellian average,

$$(a, b)_0 = \int dp \, \varphi ab \tag{56}$$

The extraction of the bound-state part of Λ_1 amounts to picking out the contribution of the eigenvalues of h_2. This can be done directly from Eq. (54) but we will follow an approach which will be useful below, and which is also applicable to the evaluation of V.

The last two factors in Eq. (54) can be written as

$$u_2(t) e^{-\beta h_2} = -(1/2\pi i) \int_C dw \, R_2(w) \exp(-\beta - it/\hbar) w \tag{57}$$

Here R_2 is the resolvent for h_2,

$$R_2(w) = (h_2 - w)^{-1} \tag{58}$$

and the contour C encloses the spectrum of h_2. We assume the latter to consist of a continuous spectrum along the positive real axis, plus a finite number of eigenvalues (corresponding to bound states) at $-e_i$, $i = 1, 2, \ldots$, with $e_i > 0$.

Equation (57) is to be introduced into (54) and the Laplace transform taken. We suppose that $\hbar s > \mathrm{Im}\, w$ on C so that the time integral can be taken inside the contour integral. The result is

$$(a, \tilde{\Lambda}_1 b)_0 = -(V_0^2/8\pi^2 h^2) \int_C dw \, e^{-\beta w} \mathrm{tr}_2 e^{-\beta K} A_2 [R_2(w - i\lambda), B_2] R_2(w) \tag{59}$$

where we have set $\lambda = \hbar s$. The transition operator $t(w)$ is defined by

$$R_2(w) = R_0(w) - R_0(w) t(w) R_0(w) \tag{60}$$

where R_0 is the noninteracting resolvent,

$$R_0(w) = (h_0 - w)^{-1} \tag{61}$$

Using the fact that R_0 commutes with A_2, B_2, and K we can reduce Eq.

(59) to

$$(a,\tilde{\Lambda}_1 b)_0 = -\left(V_0^2/8\pi^2 h^2\right)\int_C dw\, e^{-\beta w}\mathrm{tr}_2 e^{-\beta K} R_0(w) R_0(w-i\lambda) A_2 \times\left[t(w-i\lambda), B_2\right] R_0(w) R_0(w-i\lambda) t(w) \tag{62}$$

Let $\mathbf{q}$ denote the relative momentum

$$\mathbf{q} = \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2) \tag{63}$$

In momentum representation $R_0(w)$ amounts to multiplication by

$$r_0(w,\mathbf{q}) = (u-w)^{-1} \tag{64}$$

where u is the kinetic energy of the relative motion,

$$u = q^2/m \tag{65}$$

The transition operator is represented by the kernel $t(w,\mathbf{q},\mathbf{q}')$:

$$(t(w)f)(\mathbf{q}) = \int d\mathbf{q}'\, t(w,\mathbf{q},\mathbf{q}') f(\mathbf{q}') \tag{66}$$

With the matrix elements written out, Eq. (62) becomes

$$(a,\tilde{\Lambda}_1 b)_0 = -\left(V_0^2/8\pi^2 h^2\right)\int_c dw\, e^{-\beta w}\int d\mathbf{P}\, d\mathbf{q}\, d\mathbf{q}'\, e^{-\beta K} A_2(\mathscr{P}) \times\left[B_2(\mathscr{P}') - B_2(\mathscr{P})\right] r_0(w,\mathbf{q}) r_0(w,\mathbf{q}') t(w,\mathbf{q}',\mathbf{q}) r_0(w-i\lambda,\mathbf{q}') \times r_0(w-i\lambda,\mathbf{q}) t(w-i\lambda,\mathbf{q},\mathbf{q}') \tag{67}$$

Here we have used $\mathscr{P}$ to denote the pair $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathscr{P}'$ denotes $\mathbf{p}_1'$, $\mathbf{p}_2'$ which are determined by

$$\begin{aligned} \mathbf{P} &= \mathbf{P}' = \mathbf{p}_1' + \mathbf{p}_2' \\ \mathbf{q}' &= \tfrac{1}{2}(\mathbf{p}_1' - \mathbf{p}_2') \end{aligned} \tag{68}$$

As a function of the complex variable w, the transition operator has singularities which are exhibited by the formula

$$t(w,\mathbf{q},\mathbf{q}') = \sum_i \frac{(u+e_i)(u'+e_i)}{e_i+w}\psi_i(\mathbf{q})\bar{\psi}_i(\mathbf{q}') + \hat{t}\,(w,\mathbf{q},\mathbf{q}') \tag{69}$$

The first term contains the bound-state poles at $w = -e_i$; ψ_i denotes the ith eigenfunction and it is assumed (in case of degeneracy) that the set ψ_i is orthonormal:

$$\int d\mathbf{q}\,\bar{\psi}_i(\mathbf{q})\psi_j(\mathbf{q}) = \delta_{ij} \tag{70}$$

The function $\hat{t}$ is analytic in w except for a branch cut along the positive real axis, and has finite limiting values as w approaches the branch cut from above or below. (These statements regarding t have been proven by Faddeev subject to certain reasonable restrictions on the potential energy.)

Since the poles in (69) are separated from the branch cut, their contribution to the integral (67) can be evaluated immediately to give the bound-state contribution to $\tilde{\Lambda}_1$:

$$\begin{aligned}(a,(\tilde{\Lambda}_1)_b b)_0 = &-i\left(V_0^2/4\pi h^2\right)\int d\mathbf{P}\,d\mathbf{q}\,d\mathbf{q}'\,e^{-\beta K}A_2(\mathcal{P})\left[B_2(\mathcal{P}')-B_2(\mathcal{P})\right]\\ &\times\sum_i e^{\beta e_i}\psi_i(\mathbf{q}')\bar{\psi}_i(\mathbf{q})(u+e_i+i\lambda)^{-1}\\ &\times(u'+e_i+i\lambda)^{-1}t(-e_i-i\lambda,\mathbf{q},\mathbf{q}')\end{aligned}\tag{71}$$

(Note that the factor $t(w-i\lambda,\mathbf{q},\mathbf{q}')$ in Eq. (67) is analytic within the contour.) We write the remaining t matrix in the form (69), using a subscript j to label the poles. In the limit $\lambda\to 0$ all terms remain finite except for those with $e_j=e_i$ which contribute a factor $(-i\lambda)^{-1}$. The result for Y is

$$\begin{aligned}(a,Yb)_0 = &-\left(V_0^2/2h^3\right)\sum_i e^{\beta e_i}\int d\mathbf{P}\,d\mathbf{q}\,d\mathbf{q}'\,e^{-\beta K}A_2(\mathcal{P})\left[B_2(\mathcal{P}')-B_2(\mathcal{P})\right]\\ &\times\psi_i(\mathbf{q}')\bar{\psi}_i(\mathbf{q})\sum_{j/i}\psi_j(\mathbf{q})\bar{\psi}_j(\mathbf{q}')\end{aligned}\tag{72}$$

Here the notation j/i means that the sum is to extend over those values of j for which $e_j=e_i$.

Equation (72) can be rewritten as[11]

$$(a,Yb)_0=\sum_i K_i\int d\mathbf{P}\,\varphi_m(P)\left[\langle A_2B_2\rangle_{ii}-\sum_{j/i}\langle A_2\rangle_{ij}\langle B_2\rangle_{ji}\right]\tag{73}$$

Here φ_m denotes the Maxwell–Boltzmann distribution function for the molecule,

$$\varphi_m=2^{-3/2}\left(V_0/h^3\right)e^{-\beta K}\tag{74}$$

The brackets $\langle\ \rangle_{ij}$ denote matrix elements with respect to the set ψ_i, e.g.,

$$\langle A_2\rangle_{ij}=\int d\mathbf{q}\,A_2\bar{\psi}_i(\mathbf{q})\psi_j(\mathbf{q})\tag{75}$$

Of course in this and similar formulas A_2 is to be considered as a function of $\mathbf{P}$, $\mathbf{q}$ rather than of $\mathbf{p}_1$, $\mathbf{p}_2$, and the matrix element is a function of $\mathbf{P}$. The factor K_i is the reaction constant,

$$K_i=2^{1/2}V_0e^{\beta e_i}\tag{76}$$

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[11] In Ref. 15 the equation corresponding to (73) was written only for the special case of nondegenerate energy eigenvalues.

In the expansion (39) Y is multiplied by z^2. The resulting combination

$$n_i = K_i z^2 \tag{77}$$

is just the density of molecules in the state ψ_i. [Equation (76) is valid for a Boltzmann gas. Usually the reaction constant is evaluated with quantum statistics, and the formula (76) then has $2^{3/2}$ in place of $2^{1/2}$.]

We return briefly to the operator I_2'' defined in Eq. (44). This equation can be rewritten as

$$(a, I_2'' b)_0 = -2^{1/2} V_0 \int d\mathbf{P}\, \varphi_m(P) \int d\mathbf{q} \left[e^{-\beta h_2} - e^{-\beta h_0} \right] A_2 I_1 B_2 \tag{78}$$

This can be reduced further by equilibrium techniques such as are used to derive the Beth–Uhlenbeck formula. The bound-state contribution, $(I_2'')_b$, can be obtained immediately by projection onto the eigenvalues of h_2. The result is

$$(a, (I_2'')_b b)_0 = -\sum_i K_i \int d\mathbf{P}\, \varphi_m(P) \langle A_2 I_1 B_2 \rangle_{ii} \tag{79}$$

This has an evident similarity to the result (73).

4. THREE-BODY DYNAMICS

The evaluation of F involves three-body dynamics. In this section the pertinent results for the three-body problem, as developed particularly by Faddeev,(14) will be briefly summarized.

Let $\mathcal{P}$ now denote a set of three momenta $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$. The total momentum is

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 \tag{80}$$

while the kinetic energy and center-of-mass energy are

$$E_{\mathcal{P}} = \left(p_1^2 + p_2^2 + p_3^2\right)/2m, \qquad K = P^2/6m \tag{81}$$

A pair can be labeled by the two particles in it or by the third particle. Thus for example $\alpha = 1, 2$ and $\alpha = 3$ can both be used to denote the pair 1, 2 as well as particle 3. Let $\mathbf{q}_\alpha$ be the relative momentum of the pair α, so for example

$$\mathbf{q}_{12} = \mathbf{q}_3 = \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2) \tag{82}$$

In addition, let $\mathbf{k}_\alpha$ denote the relative momentum of particle α with respect to the pair α, e.g.,

$$\begin{aligned} \mathbf{k}_{12} = \mathbf{k}_3 &= \tfrac{2}{3}\mathbf{p}_3 - \tfrac{1}{3}(\mathbf{p}_1 + \mathbf{p}_2) \\ &= \mathbf{p}_3 - \tfrac{1}{3}\mathbf{P} \end{aligned} \tag{83}$$

We also introduce the kinetic energies of the relative motion of the pair α, and of particle α with respect to pair α,

$$u_\alpha = q_\alpha^2/m, \qquad \kappa_\alpha = 3k_\alpha^2/4m \tag{84}$$

It follows that

$$E_{\mathscr{P}} - K = u_1 + \kappa_1 = u_2 + \kappa_2 = u_3 + \kappa_3 \tag{85}$$

The three momenta $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$ can be expressed in terms of $\mathbf{P}$ and any pair $\mathbf{q}_\alpha$, $\mathbf{k}_\alpha$; furthermore

$$\begin{aligned} d\mathscr{P} &= d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 \\ &= d\mathbf{P} d\mathbf{q}_\alpha d\mathbf{k}_\alpha \end{aligned} \tag{86}$$

We will frequently use $\mathbf{q}, \mathbf{k}$ to denote any of the equivalent pairs $\mathbf{q}_\alpha, \mathbf{k}_\alpha$, and $u_\alpha + \kappa_\alpha$ will be abbreviated as $u + \kappa$.

Let $R(w)$ be the resolvent for the three-body Hamiltonian in the center-of-mass frame,

$$R(w) = (h_3 - w)^{-1} \tag{87}$$

The noninteracting resolvent, now for three particles rather than two, will again be denoted by $R_0(w)$. Its kernel (in the Hilbert space for relative motion) is

$$R_0(w, \mathbf{kq}, \mathbf{k}'\mathbf{q}') = r_0(w, \mathbf{kq})\delta(\mathbf{k} - \mathbf{k}')\delta(\mathbf{q} - \mathbf{q}') \tag{88}$$

where

$$r_0(w, \mathbf{kq}) = (u + \kappa - w)^{-1} \tag{89}$$

In addition let $R_\alpha(w)$ denote the resolvent for the three-body system in which only the pair α interacts,

$$R_\alpha(w) = (h_\alpha - w)^{-1} \tag{90}$$

A three-body transition operator T can be defined in analogy to Eq. (60) by

$$R = R_0 - R_0 T R_0 \tag{91}$$

However, T contains disconnected contributions which arise from purely two-body collisions. The connected transition operator τ is defined by

$$R = R_0 - R_0 \sum_\alpha T_\alpha R_0 - R_0 \tau R_0 \tag{92}$$

Here T_α satisfies

$$R_\alpha = R_0 - R_0 T_\alpha R_0 \tag{93}$$

and is related to the two-body transition operator defined in Eq. (60) by

$$T_\alpha(w, \mathbf{kq}, \mathbf{k}'\mathbf{q}') = \delta(\mathbf{k}_\alpha - \mathbf{k}'_\alpha)t(w - \kappa_\alpha, \mathbf{q}_\alpha, \mathbf{q}'_\alpha) \tag{94}$$

Clearly

$$\tau = T - \sum_\alpha T_\alpha \tag{95}$$

Let $M_{\alpha\beta}$ be defined by

$$M_{\alpha\beta} = \delta_{\alpha\beta} V_\alpha - V_\alpha R V_\beta \tag{96}$$

where V_α is the potential energy for the αth pair. It is straightforward to show that

$$T = \sum_{\alpha,\beta} M_{\alpha\beta} \tag{97}$$

In addition we define

$$W_{\alpha\beta} = M_{\alpha\beta} - \delta_{\alpha\beta} T_\alpha \tag{98}$$

Then

$$\tau = \sum_{\alpha,\beta} W_{\alpha\beta} \tag{99}$$

As shown by Faddeev, $M_{\alpha\beta}$ satisfies

$$M_{\alpha\beta} = \delta_{\alpha\beta} T_\alpha - T_\alpha R_0 \sum_{\gamma \neq \alpha} M_{\gamma\beta} \tag{100}$$

Iteration of this equation yields the binary-collision expansion,

$$M_{\alpha\beta} = \delta_{\alpha\beta} T_\alpha - T_\alpha R_0 T_\beta (1 - \delta_{\alpha\beta}) + T_\alpha R_0 {\sum_\mu}' T_\mu R_0 T_\beta - \cdots \tag{101}$$

Here the prime on the sum means that no two consecutive subscripts are to be the same.

Of primary interest for our purposes is the analytic structure of $R(w)$. Since it is the resolvent of a self-adjoint operator, it must be analytic if w is not on the real axis. One expects a branch cut along the positive real axis; this is associated with the energy $u + \kappa$ for the motion of three free (i.e., unbound) particles. Superimposed on this is another branch cut extending from $-e_i$ to ∞; this cut corresponds to the energy $\kappa_\alpha - e_i$ of bound-pair α plus the third particle. Three-body bound states will introduce poles into $R(w)$; however, these need not concern us here since they can be shown to have no effect on the final form of the collision operator. (In the three-body problem a triatomic molecule will have nothing left to collide with.)

To describe the analytic structure in detail, note that from Eqs. (98) and (101), $W_{\alpha\beta}$ contains factors T_α and T_β on the extreme left and right, respectively. Each of these can be separated into bound-state and continuum contributions according to Eq. (69). The result is a division of $W_{\alpha\beta}$ into four parts (called components by Faddeev):

$$\begin{aligned} W_{\alpha\beta}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) = {} & W^0_{\alpha\beta}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) + \sum_i (w + e_i - \kappa'_\alpha)^{-1} W^1_{\alpha i,\beta}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) \\ & + \sum_j (w + e_j - \kappa_\beta)^{-1} W^2_{\alpha,\beta i}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) \\ & + \sum_{i,j} (w + e_i - \kappa'_\alpha)^{-1}(w + e_j - \kappa_\beta)^{-1} W^3_{\alpha i,\beta j}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) \end{aligned} \tag{102}$$

The coefficients $W^0_{\alpha\beta}, \ldots, W^3_{\alpha i,\beta j}$, as functions of w, are analytic except for a branch cut on the real axis, extending to the left as far as the lowest of the energies $-e_i$. They have finite limiting values as w approaches the bound-state poles at $\kappa_\beta - e_j$ and $\kappa'_\alpha - e_i$.

The dependence on the internal variable $\mathbf{q}$ for a bound pair can be completely factored out, and $W^1_{\alpha i,\beta}, \ldots, W^3_{\alpha i,\beta_j}$ take the form

$$\begin{aligned} W^1_{\alpha i,\beta}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= (u'_\alpha + e_i)\psi_i(\mathbf{q}'_\alpha)A^1_{\alpha i,\beta}(w,\mathbf{k}'_\alpha,\mathbf{kq}) \\ W^2_{\alpha,\beta j}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= (u_\beta + e_j)\bar{\psi}_j(\mathbf{q}_\beta)A^2_{\alpha,\beta j}(w,\mathbf{k}'\mathbf{q}',\mathbf{k}_\beta) \\ W^3_{\alpha i,\beta j}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= (u'_\alpha + e_i)(u_\beta + e_j)\psi_i(\mathbf{q}'_\alpha)\bar{\psi}_j(\mathbf{q}_\beta)A^3_{\alpha i,\beta j}(w,\mathbf{k}'_\alpha,\mathbf{k}_\beta) \end{aligned} \tag{103}$$

Self-adjointness of the Hamiltonian implies a certain behavior under complex conjugation. We note in particular that

$$\bar{\tau}(w,\mathbf{kq},\mathbf{k}'\mathbf{q}') = \tau(\bar{w},\mathbf{k}'\mathbf{q}',\mathbf{kq}) \tag{104}$$

It can also be shown that

$$\begin{aligned} \overline{W}^1_{\alpha i,\beta}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= W^2_{\beta,\alpha i}(\bar{w},\mathbf{kq},\mathbf{k}'\mathbf{q}') \\ \overline{W}^3_{\alpha i,\beta j}(w,\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= W^3_{\beta j,\alpha i}(\bar{w},\mathbf{kq},\mathbf{k}'\mathbf{q}') \end{aligned} \tag{105}$$

These equations imply that

$$\begin{aligned} \bar{A}^1_{\alpha i,\beta}(w,\mathbf{k}'_\alpha,\mathbf{kq}) &= A^2_{\beta,\alpha i}(\bar{w},\mathbf{kq},\mathbf{k}'_\alpha) \\ \bar{A}^3_{\alpha i,\beta j}(w,\mathbf{k}'_\alpha,\mathbf{k}_\beta) &= A^3_{\beta j,\alpha i}(\bar{w},\mathbf{k}_\beta,\mathbf{k}'_\alpha) \end{aligned} \tag{106}$$

The A coefficients, when evaluated on the energy shell, are essentially reaction and scattering amplitudes for the various processes. This identification is provided by the S matrix, which has been worked out by Faddeev. Let α, i, $\mathbf{k}_\alpha$ denote the state in which pair α is bound with wave function $\psi_i(\mathbf{q}_\alpha)$, the third particle having relative momentum $\mathbf{k}_\alpha$. Similarly, let a state with no bound pairs be labeled by its momenta, say $\mathbf{k}'\mathbf{q}'$. Collision-induced dissociation is a transition α, i, $\mathbf{k}_\alpha \to \mathbf{k}'\mathbf{q}'$, and the S matrix for this transition is

$$S(\alpha, i, \mathbf{k}_\alpha \to \mathbf{k}'\mathbf{q}') = -2\pi i \delta(u' + \kappa' - \kappa_\alpha + e_i) T_i^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_\alpha) \tag{107}$$

where

$$T_i^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_\alpha) = \sum_\beta \left[A^2_{\beta,\alpha i}(\kappa_\alpha - e_i + i0, \mathbf{k}'\mathbf{q}', \mathbf{k}_\alpha) \right. \\ \left. + \sum_j \psi_j(\mathbf{q}'_\beta) A^3_{\beta j,\alpha i}(\kappa_\alpha - e_i + i0, \mathbf{k}'_\beta, \mathbf{k}_\alpha) \right] \tag{108}$$

The S matrix for molecular formation is

$$S(\mathbf{kq} \to \alpha, i, \mathbf{k}'_\alpha) = -2\pi i \delta(u + \kappa - \kappa'_\alpha + e_i) T_i^F(\mathbf{k}'_\alpha, \mathbf{kq}) \tag{109}$$

where

$$T_i^F(\mathbf{k}'_\alpha, \mathbf{kq}) = \sum_\beta \left[A^1_{\alpha i,\beta}(\kappa'_\alpha - e_i + i0, \mathbf{k}'_\alpha, \mathbf{kq}) \right. \\ \left. + \sum_j \bar{\psi}_j(\mathbf{q}_\beta) A^3_{\alpha i,\beta j}(\kappa'_\alpha - e_i + i0, \mathbf{k}'_\alpha, \mathbf{k}_\beta) \right] \tag{110}$$

For atom–molecule scattering (without rearrangement, but including inelastic collisions) the S matrix is

$$S(\alpha, i, \mathbf{k}_\alpha \to \alpha, j, \mathbf{k}'_\alpha) = \delta_{ij}\delta(\mathbf{k}_\alpha - \mathbf{k}'_\alpha) - 2\pi i \delta(\kappa_\alpha - e_i - \kappa'_\alpha + e_j) T^S_{ji}(\mathbf{k}'_\alpha, \mathbf{k}_\alpha) \tag{111}$$

where

$$T^S_{ji}(\mathbf{k}'_\alpha, \mathbf{k}_\alpha) = A^3_{\alpha j,\alpha i}(\kappa_\alpha - e_i + i0, \mathbf{k}'_\alpha, \mathbf{k}_\alpha) \tag{112}$$

For a rearrangement collision we have

$$S(\alpha, i, \mathbf{k}_\alpha \to \beta, j, \mathbf{k}'_\beta) = -2\pi i \delta(\kappa_\alpha - e_i - \kappa'_\beta + e_j) T^R_{ji}(\mathbf{k}'_\beta, \mathbf{k}_\alpha) \tag{113}$$

where

$$T^R_{ji}(\mathbf{k}'_\beta, \mathbf{k}_\alpha) = A^3_{\beta j,\alpha i}(\kappa_\alpha - e_i + i0, \mathbf{k}'_\beta, \mathbf{k}_\alpha) \tag{114}$$

5. BOUND-STATE CONTRIBUTIONS

We now return to the evaluation of F, given by the first of Eqs. (48). It is necessary to work out the operator $\tilde{\Lambda}'_2$, which is determined by Eq. (46).

A straightforward calculation along the lines of Section 3 shows that

$$(a, \tilde{\Lambda}_2' b)_0 = -\left(V_0^3/24\pi^2 h^2\right)\int_C dw\, e^{-\beta w} X(w) \tag{115}$$

where

$$X(w) = \mathrm{tr}_3 e^{-\beta K} A_3 \Big\{ \left[R(w - i\lambda), B_3 \right] R(w) - \sum_\alpha \left[R_\alpha(w - i\lambda), B_3 \right] R_\alpha(w) \Big\} \tag{116}$$

Let Eqs. (92) and (93) be substituted into this expression. The leading terms give no contribution since R_0 commutes with A_3, B_3, and K, and the result is

$$\begin{aligned} X(w) = {} & \mathrm{tr}_3 e^{-\beta K} A_3 R_0^- R_0 \\ & \times \Big\{ \left[\tau^-, B_3 \right] R_0^- R_0 \tau + \left[\tau^-, B_3 \right] R_0^- R_0 \sum_\alpha T_\alpha \\ & + \sum_\alpha \left[T_\alpha^-, B_3 \right] R_0^- R_0 \tau + \sum_{\alpha,\beta}{}' \left[T_\alpha^-, B_3 \right] R_0^- R_0 T_\beta \Big\} \end{aligned} \tag{117}$$

Here for brevity we have written R_0, τ, T_α when the argument is w, while $R_0^-, \tau^-, T_\alpha^-$ have $w - i\lambda$ for their argument. Actually the last term above vanishes. This can be seen by writing out the matrix elements, which gives a factor $B_3(\mathcal{P}') - B_3(\mathcal{P})$; the requirement $\alpha \neq \beta$ combined with conservation of momentum leads to the restriction $\mathcal{P}' = \mathcal{P}$. Hence we are left with

$$\begin{aligned} X(w) = \mathrm{tr}_3 e^{-\beta K} A_3 R_0^- R_0 \Big\{ & \left[\tau^-, B_3 \right] R_0^- R_0 \tau + \left[\tau^-, B_3 \right] R_0^- R_0 \sum_\alpha T_\alpha \\ & + \sum_\alpha \left[T_\alpha^-, B_3 \right] R_0^- R_0 \tau \Big\} \end{aligned} \tag{118}$$

Let the contour C consist of two lines above and below the real axis, with $w = E + i\epsilon$ and $w = E - i\epsilon'$. It is necessary that ϵ be less than λ and we choose $\epsilon = \frac{1}{2}\lambda = \frac{1}{2}\hbar s$. Along the lower part of the contour ϵ' can be held fixed when the limit $s \to 0$ is taken. Then $X(E - i\epsilon')$ remains finite and, as seen from Eq. (48), gives no contribution to F. Thus we may calculate F from

$$(a, Fb)_0 = -\lim_{\epsilon \to 0} \left\{ \epsilon^2 \left(2 V_0^3/3h^4\right) \int_{-e_0}^{\infty} dE\, e^{-\beta E} X(E + i\epsilon) - (\hbar/2\epsilon)\left(a, I_1^2 b\right)_0 \right\} \tag{119}$$

Here e_0 is chosen so that the path of integration extends to the left of all eigenvalues, so e_0 is greater than any of the e_i. (A minus sign occurs because the upper part of the contour is traversed from right to left.) Written out, $X(E+i\epsilon)$ is

$$
\begin{aligned}
X(E+i\epsilon) = \int d\mathbf{P}\, d\mathbf{k}\, d\mathbf{q}\, e^{-\beta K} A_3(\mathcal{P}) \int d\mathbf{k}'\, d\mathbf{q}' \left[B_3(\mathcal{P}') - B_3(\mathcal{P}) \right] \\
\times \left[(u+\kappa-E)^2+\epsilon^2 \right]^{-1} \left[(u'+\kappa'-E)^2+\epsilon^2 \right]^{-1} \\
\times \Big\{ |\tau(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q})|^2 + \tau(E-i\epsilon, \mathbf{k}\mathbf{q}, \mathbf{k}'\mathbf{q}') \\
\times \sum_\alpha T_\alpha(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) + \sum_\alpha T_\alpha(E-i\epsilon, \mathbf{k}\mathbf{q}, \mathbf{k}'\mathbf{q}') \\
\times \tau(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \Big\} \qquad (120)
\end{aligned}
$$

Now we focus on the bound-state contributions. These have a weaker singularity such that the first term in Eq. (119) gives a finite limit by itself. Hence we write F as

$$F = J + C \qquad (121)$$

where J and C are, respectively, the bound and free parts. In particular J is given by

$$(a, Jb)_0 = -(2V_0^3/3h^4) \lim_{\epsilon\to 0} \epsilon^2 \left\{ \int_{-e_0}^{\infty} dE\, e^{-\beta E} X(E+i\epsilon) \right\}_b \qquad (122)$$

and C is the remainder.

In Eq. (120) let τ and T_α be replaced by their decompositions into bound and free parts as given by Eqs. (69), (94), and (102). The result is a sum of terms containing up to four bound-state poles. Terms depending quadratically on the first term in Eq. (102) contain no poles, while the last term in (102) is a four-pole generator. A nonvanishing result is obtained only when the factor ϵ^2 in Eq. (122) is canceled by a singularity of $X(E+i\epsilon)$. Such singularities include those at $E = u + \kappa$ and $E = u' + \kappa'$ associated with free-particle motion. Of the bound-state singularities, an important case occurs when a pole, say $(E + i\epsilon - \kappa_\alpha' + e_i)^{-1}$, is paired with its conjugate, $(E - i\epsilon - \kappa_\alpha' + e_i)^{-1}$. The combination of singular factors is then

$$\left[(u+\kappa-E)^2+\epsilon^2 \right]^{-1} \left[(u'+\kappa'-E)^2+\epsilon^2 \right]^{-1} \left[(E-\kappa_\alpha'+e_i)^2+\epsilon^2 \right]^{-1} \qquad (123)$$

The three singularities cannot be realized simultaneously since

$$u' + \kappa' = u_\alpha' + \kappa_\alpha' > \kappa_\alpha' - e_i \qquad (124)$$

Thus for $E > \kappa_\alpha' - e_i$ the first two factors in (123) can become singular, while for $E < u' + \kappa'$ only the first and last can. Hence we obtain

$$\begin{aligned}\lim_{\epsilon\to 0}\epsilon^2&\left[(u+\kappa-E)^2+\epsilon^2\right]^{-1}\left[(u'+\kappa'-E)^2+\epsilon^2\right]^{-1}\\&\times\left[(E-\kappa'_\alpha+e_i)^2+\epsilon^2\right]^{-1}\\&=\pi^2(u'_\alpha+e_i)^{-2}\delta(u+\kappa-E)\left[\delta(u'+\kappa'-E)+\delta(E-\kappa'_\alpha+e_i)\right]\end{aligned}\tag{125}$$

The pairing of $(E+i\epsilon-\kappa_\beta+e_j)^{-1}$ with $(E-i\epsilon-\kappa_\beta+e_j)^{-1}$ is covered by the formula

$$\begin{aligned}\lim_{\epsilon\to 0}\epsilon^2&\left[(u+\kappa-E)^2+\epsilon^2\right]^{-1}\left[(u'+\kappa'-E)^2+\epsilon^2\right]^{-1}\\&\times\left[(E-\kappa_\beta+e_j)^2+\epsilon^2\right]^{-1}\\&=\pi^2(u_\beta+e_j)^{-2}\delta(u'+\kappa'-E)\left[\delta(u+\kappa-E)+\delta(E-\kappa_\beta+e_j)\right]\end{aligned}\tag{126}$$

while the four-pole case is handled by

$$\begin{aligned}\lim_{\epsilon\to 0}\epsilon^2&\left[(u+\kappa-E)^2+\epsilon^2\right]^{-1}\left[(u'+\kappa'-E)^2+\epsilon^2\right]^{-1}\\&\times\left[(E-\kappa'_\alpha+e_i)^2+\epsilon^2\right]^{-1}\left[(E-\kappa_\beta+e_j)^2+\epsilon^2\right]^{-1}\\&=\pi^2(u'_\alpha+e_i)^{-2}(u_\beta+e_j)^{-2}\left[\delta(u+\kappa-E)\delta(u'+\kappa'-E)\right.\\&\qquad\left.+\delta(E-\kappa'_\alpha+e_i)\delta(E-\kappa_\beta+e_j)\right]\end{aligned}\tag{127}$$

The terms above containing the product $\delta(u+\kappa-E)\delta(u'+\kappa'-E)$ do not yield bound-state contributions, and so are to be included in C rather than J.

Actually it can be shown that the only bound-state contributions are those which arise from the above-mentioned pairing. A combination of two different poles, such as $(E+i\epsilon-\kappa'_\alpha+e_i)^{-1}(E-i\epsilon-\kappa_\beta+e_j)^{-1}$, is not singular enough to give a nonvanishing result. Roughly speaking, the point is that $\epsilon(x^2+\epsilon^2)^{-1}$ approaches a delta function, but $\epsilon(x+i\epsilon)^{-1}(y-i\epsilon)^{-1}$ approaches zero if $x\neq y$.

The last two terms in Eq. (120) can be neglected insofar as J is concerned. The operators T_α contain a factor $\delta(\mathbf{k}_\alpha-\mathbf{k}'_\alpha)$ which implies $\kappa_\alpha=\kappa'_\alpha$. Inequalities like (124) then prevent the bound-state singularity from coinciding with either of the free-particle singularities. In other words, these terms would correspond to the transition of a pair between free and bound states without interaction with the third particle, and this is prohibited by conservation of energy and momentum. Hence for the present purposes we may replace X by

$$\begin{aligned} X'(E+i\epsilon) = \int d\mathbf{P}\, d\mathbf{k}\, d\mathbf{q}\, e^{-\beta K} A_3(\mathcal{P}) \int d\mathbf{k}'\, d\mathbf{q}' \left[B_3(\mathcal{P}') - B_3(\mathcal{P}) \right] \\ \times \left[(u+\kappa-E)^2 + \epsilon^2 \right]^{-1} \left[(u'+\kappa'-E)^2 + \epsilon^2 \right]^{-1} \\ \times \left| \tau(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \right|^2 \qquad (128) \end{aligned}$$

We now substitute Eqs. (99) and (102) into the above expression for X', retaining only those terms in which bound-state poles pair off in the manner just described. The result for J can be written as a sum of three terms

$$J = J^D + J^F + J^C \qquad (129)$$

The first of these arises from a bound-state pole at $E = \kappa_\beta - e_j$ combined with the free-particle singularity at $E = u' + \kappa'$ and corresponds to dissociation of a molecule. The second is due to a free-particle singularity at $E = u' + \kappa'$ combined with $E = \kappa'_\alpha - e_i$ and describes molecular formation. The last one occurs when the bound-state singularities in initial and final states coincide at $E = \kappa_\beta - e_j = \kappa'_\alpha - e_i$; this operator describes atom–molecule collisions (including rearrangement collisions if $\alpha \neq \beta$ and inelastic collisions if $e_i \neq e_j$).

In detail, J^D is given by

$$\begin{aligned} (a, J^D b)_0 = -(2V_0^3/3h^4) \lim_{\epsilon\to 0} \epsilon^2 \int d\mathbf{P}\, d\mathbf{k}\, d\mathbf{q}\, e^{-\beta K} A_3(\mathcal{P}) \\ \times \int d\mathbf{k}'\, d\mathbf{q}' \left[B_3(\mathcal{P}') - B_3(\mathcal{P}) \right] \int dE\, e^{-\beta E} \left[(u+\kappa-E)^2 + \epsilon^2 \right]^{-1} \\ \times \left[(u'+\kappa'-E)^2 + \epsilon^2 \right]^{-1} \\ \times \Bigg| \sum_{\alpha,\beta} \sum_j (E+i\epsilon-\kappa_\beta+e_j)^{-1} \Bigg[W^2_{\alpha,\beta j}(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \\ + \sum_i (E+i\epsilon-\kappa'_\alpha+e_i)^{-1} W^3_{\alpha i,\beta j}(E+i\epsilon, \mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \Bigg] \Bigg|^2 \\ (130) \end{aligned}$$

Here the integration over E is restricted to the range $\kappa'_\alpha - e_i < E < u' + \kappa'$ in order to pick out the dissociation process of interest. (If the range of E covers $u' + \kappa'$ a contribution to C is obtained, while if it covers $\kappa'_\alpha - e_i$ a contribution to J^C, to be discussed below, is obtained.) As discussed above, we need retain only those terms in which the pole $(E + i\epsilon - \kappa_\beta + e_j)^{-1}$ is paired with its conjugate. Using Eq. (126) we get

$$(a, J^D b)_0 = \frac{1}{3} \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{p}_3 \varphi(p_1)\varphi(p_2)\varphi(p_3) A_3(\mathcal{P}) \sum_{\beta j} e^{\beta(u_\beta + e_j)} \\ \times \int d\mathbf{k}' d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] \delta(u' + \kappa' - \kappa_\beta + e_j) R^D_{\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \tag{131}$$

where

$$R^D_{\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) = 2\pi^2 h^5 (u_\beta + e_j)^{-2} \\ \times \left| \sum_{k/j} \sum_{\alpha} \left[W^2_{\alpha,\beta k}(\kappa_\beta - e_j + i0, \mathbf{k}'\mathbf{q}', \mathbf{kq}) \right.\right. \\ \left.\left. + \sum_i (u'_\alpha + e_i)^{-1} W^3_{\alpha i,\beta k}(\kappa_\beta - e_j + i0, \mathbf{k}'\mathbf{q}', \mathbf{kq}) \right] \right|^2 \tag{132}$$

(We have again used the notation k/j to indicate a sum over values of k for which $e_k = e_j$.)

Use of Eqs. (103) and (108) yields

$$R^D_{\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) = 2\pi^2 h^5 \left| \sum_{k/j} \bar{\psi}_k(\mathbf{q}_\beta) T^D_k(\mathbf{k}'\mathbf{q}', \mathbf{k}_\beta) \right|^2 \tag{133}$$

The operator J^D can be extracted from Eq. (131) with the result

$$(J^D b)(\mathbf{p}_1) = \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(p_2)\varphi(p_3) \sum_{\beta, j} e^{\beta(u_\beta + e_j)} \int d\mathbf{k}' d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] \\ \times \delta(u' + \kappa' - \kappa_\beta + e_j) R^D_{\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \tag{134}$$

In a similar way J^F is found to be

$$(J^F b)(\mathbf{p}_1) = \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(p_2)\varphi(p_3) \int d\mathbf{k}' d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] \\ \times \sum_{\alpha i} \delta(u + \kappa - \kappa'_\alpha + e_i) R^F_{\alpha i}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \tag{135}$$

Here $R^F_{\alpha i}$ is given by

$$\begin{aligned} R^F_{\alpha i}(\mathbf{k}'\mathbf{q}',\mathbf{kq}) &= 2\pi^2 h^5 (u'_\alpha + e_i)^{-2} \\ &\quad \times \left| \sum_{k/i} \sum_{\beta} \left[W^1_{\alpha k,\beta}(\kappa'_\alpha - e_i + i0, \mathbf{k}'\mathbf{q}', \mathbf{kq}) \right.\right. \\ &\qquad \left.\left. + \sum_j (u_\beta + e_j)^{-1} W^3_{\alpha k,\beta j}(\kappa'_\alpha - e_i + i0, \mathbf{k}'\mathbf{q}', \mathbf{kq}) \right] \right|^2 \\ &= 2\pi^2 h^5 \left| \sum_{k/i} \psi_k(\mathbf{q}'_\alpha) T^F_k(\mathbf{k}'_\alpha, \mathbf{kq}) \right|^2 \end{aligned} \tag{136}$$

Finally, J^C is found to be

$$\begin{aligned} (J^C b)(\mathbf{p}_1) &= \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(p_2)\varphi(p_3) \int d\mathbf{k}' d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] \sum_{\alpha i} \sum_{\beta j} e^{\beta(u_\beta + e_j)} \\ &\quad \times \delta(\kappa'_\alpha - e_i - \kappa_\beta + e_j) R^C_{\alpha i,\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \end{aligned} \tag{137}$$

where

$$\begin{aligned} R^C_{\alpha i,\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) &= 2\pi^2 h^5 (u'_\alpha + e_i)^{-2} (u_\beta + e_j)^{-2} \\ &\quad \times \left| \sum_{k/i} \sum_{l/j} W^3_{\alpha k,\beta l}(\kappa'_\alpha - e_i + i0, \mathbf{k}'\mathbf{q}', \mathbf{kq}) \right|^2 \end{aligned} \tag{138}$$

If $\alpha = \beta$ this reduces to

$$R^C_{\alpha i,\alpha j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) = 2\pi^2 h^5 \left| \sum_{k/i} \sum_{l/j} \psi_k(\mathbf{q}'_\alpha) \bar{\psi}_l(\mathbf{q}_\alpha) T^S_{kl}(\mathbf{k}'_\alpha, \mathbf{k}_\alpha) \right|^2 \tag{139}$$

while for $\alpha \neq \beta$ we have

$$R^C_{\alpha i,\beta j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) = 2\pi^2 h^5 \left| \sum_{k/i} \sum_{l/j} \psi_k(\mathbf{q}'_\alpha) \bar{\psi}_l(\mathbf{q}_\beta) T^R_{kl}(\mathbf{k}'_\alpha, \mathbf{k}_\beta) \right|^2 \tag{140}$$

6. ATOM-MOLECULE COLLISION OPERATOR

The form for J obtained in the previous section involves all three-particle momenta. However, the integration over the internal variables $\mathbf{q}$ for a bound pair can be carried out. The result is a binary atom–molecule collision operator in which the molecule is characterized by its total momentum and internal state (actually by a density matrix for its internal state). This form also displays the connection with the reaction and scattering amplitudes defined by the S matrix.

Let J^C be written as the sum of two terms

$$J^C = J^S + J^R \tag{141}$$

where J^S and J^R are obtained from the terms in Eq. (137) with $\alpha = \beta$ and $\alpha \neq \beta$, respectively. Thus J^S corresponds to ordinary scattering and J^R to rearrangement collisions. Consider first the term with $\alpha = \beta = 2,3$ and i, j held fixed. Let this operator be denoted by J_{ij}^1:

$$\begin{aligned}(J_{ij}^1 b)(\mathbf{p}_1) = &\int d\mathbf{p}_2\, d\mathbf{p}_3\, \varphi(p_2)\varphi(p_3) \int d\mathbf{k}'_{23}\, d\mathbf{q}'_{23} [B_3(\mathcal{P}) - B_3(\mathcal{P}')] \\ &\times e^{\beta(u_{23}+e_j)} \delta(\kappa'_{23} - e_i - \kappa_{23} + e_j) R^C_{23i,23j}(\mathbf{k}'\mathbf{q}', \mathbf{kq})\end{aligned} \tag{142}$$

Clearly J_{ij}^1 describes collisions between a particle, labeled 1, and a bound pair, labeled 2, 3, with the bound pair changing its energy from e_j to e_i. The dependence of $R^C_{23i,23j}$ on $\mathbf{q}_{23}$ and $\mathbf{q}'_{23}$ is given explicitly in Eq. (139). To carry out the integration over $\mathbf{q}_{23}$ we make the change of variables $\mathbf{p}_2, \mathbf{p}_3 \to \mathbf{P}_{23}, \mathbf{q}_{23}$, where $\mathbf{P}_{23} = \mathbf{p}_2 + \mathbf{p}_3$ is the total momentum of the molecule. We have

$$\varphi(p_2)\varphi(p_3) e^{\beta u_{23}} = 2^{3/2} V_0 h^{-3} \varphi_m(P_{23}) \tag{143}$$

where φ_m is the distribution function (74). This gives

$$\begin{aligned}(J_{ij}^1 b)(\mathbf{p}_1) = &\, 2K_j h^{-3} \int d\mathbf{P}_{23}\, \varphi_m(P_{23}) \int d\mathbf{k}'_{23}\, \delta(\kappa'_{23} - e_i - \kappa_{23} + e_j) \\ &\times \int d\mathbf{q}_{23}\, d\mathbf{q}'_{23} [B_3(\mathcal{P}) - B_3(\mathcal{P}')] R^C_{23i,23j}(\mathbf{k}'\mathbf{q}', \mathbf{kq})\end{aligned} \tag{144}$$

where K_j is the reaction constant (76). Let f_{ij}^s be the scattering amplitude,

$$f_{ij}^s(\mathbf{g}'_{23}, \mathbf{g}_{23}) = 2\pi\mu h T_{ij}^s(\mathbf{k}'_{23}, \mathbf{k}_{23}) \tag{145}$$

Here $\mu = 2m/3$ is the reduced mass for the atom–molecule system, and $\mathbf{g}_{23}, \mathbf{g}'_{23}$ denote the relative velocities before and after the collision,

$$\mathbf{g}_{23} = \mathbf{k}_{23}/\mu, \qquad \mathbf{g}'_{23} = \mathbf{k}'_{23}/\mu \tag{146}$$

The scattering amplitude has been normalized so that the cross section is given by

$$\sigma(\mathbf{g}, j \to \mathbf{g}', i) = (g'/g) |f_{ij}^s(\mathbf{g}', \mathbf{g})|^2 \tag{147}$$

Using Eq. (139) we get

$$\begin{aligned}R^C_{23i,23j}(\mathbf{k}'\mathbf{q}', \mathbf{kq}) = &\, (h^3/2\mu^2) \sum_{kl/i} \sum_{mn/j} \bar{\psi}_l(\mathbf{q}'_{23}) \psi_k(\mathbf{q}'_{23}) \bar{\psi}_m(\mathbf{q}_{23}) \psi_n(\mathbf{q}_{23}) \\ &\times f_{km}^s(\mathbf{g}'_{23}, \mathbf{g}_{23}) \bar{f}_{ln}^s(\mathbf{g}'_{23}, \mathbf{g}_{23})\end{aligned} \tag{148}$$

The earlier notation has been extended so that kl/i means to sum over those values of k and l for which $e_k = e_l = e_i$. When Eq. (148) is substituted into (144) the result can be put into the form

$$\left(J_{ij}^1 b\right)(\mathbf{p}_1) = K_j \int d\mathbf{P}_{23}\, \varphi_m(P_{23}) \int d\Omega'_{23} \sum_{kl/i} \sum_{mn/j} f^s_{km} \bar{f}^s_{ln} \times \left\{ \left[b(\mathbf{p}_1) - b(\mathbf{p}'_1) \right] \delta_{kl}\delta_{mn} + \beta_{mn}(\mathbf{P}_{23})\delta_{kl} - \beta_{lk}(\mathbf{P}'_{23})\delta_{mn} \right\} \tag{149}$$

Here β_{mn} denotes the matrix element

$$\beta_{mn}(\mathbf{P}_{23}) = \int d\mathbf{q}_{23} \left[b(\mathbf{p}_2) + b(\mathbf{p}_3) \right] \bar{\psi}_m(\mathbf{q}_{23}) \psi_n(\mathbf{q}_{23}) \tag{150}$$

and $d\Omega'_{23}$ is the element of solid angle about the directions of $\mathbf{g}'_{23}$. For simplicity the arguments $\mathbf{g}'_{23}, \mathbf{g}_{23}$ of the scattering amplitudes have not been written out. Conservation of energy is expressed by

$$g'^2_{23} = g^2_{23} - (2/\mu)(e_j - e_i) \tag{151}$$

If e_j is greater than e_i, there is a threshold condition

$$g^2_{23} \geqslant (2/\mu)(e_j - e_i) \tag{152}$$

For fixed $\mathbf{p}_1$ this is a restriction on the range of integration for $\mathbf{P}_{23}$, but for simplicity this restriction has not been indicated explicitly in Eq. (149). Similar restrictions will be left implicit below.

The result (149) is the linearized form of the Waldmann–Snider collision operator for the rate of change of the distribution function for atoms, due to their collisions with molecules. The matrix β_{mn} need not be diagonal, but only elements with equal energy, $e_m = e_n$, occur. If the energy levels are nondegenerate, or if β_{mn} is diagonal, the collision operator reduces to the form due to Wang-Chang, Uhlenbeck, and deBoer:

$$\left(J_{ij}^1 b\right)(\mathbf{p}_1) = K_j \int d\mathbf{P}_{23}\, \varphi_m(P_{23}) \int d\Omega'_{23}\, g'_{23} \sigma(\mathbf{g}_{23}, j \to \mathbf{g}'_{23}, i) \times \left[b(\mathbf{p}_1) + \beta_{jj}(\mathbf{P}_{23}) - b(\mathbf{p}'_1) - \beta_{ii}(\mathbf{P}'_{23}) \right] \tag{153}$$

Consider next the terms in Eq. (137) with $\alpha = \beta = 1, 2$, and $\alpha = \beta = 1, 3$. The manipulations leading to Eq. (153) cannot be carried out in the same way since $\mathbf{p}_1$ is not integrated over so we consider

$$\left(a, J_{ij}^2 b\right)_0 = \int d\mathbf{p}_1\, d\mathbf{p}_2\, d\mathbf{p}_3\, \varphi(p_1)\varphi(p_2)\varphi(p_3) a(p_1) \int d\mathbf{k}'\, d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] \times \sum_{\alpha \neq 2,3} e^{\beta(u_\alpha + e_j)} \delta(\kappa'_\alpha - e_i - \kappa_\alpha + e_j) R^C_{\alpha i, \alpha j}(\mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \tag{154}$$

Using Eq. (139) we can reduce this to

$$\left(a, J_{ij}^{2} b\right)_0 = K_j \int d\mathbf{p}_1 \, d\mathbf{P}_{23} \, \varphi(p_1) \varphi_m(P_{23}) \int d\Omega'_{23} \, g'_{23} \sum_{kl/i} \sum_{mn/j} f^{s}_{km} \bar{f}^{s}_{ln}$$
$$\times \left\{ \delta_{kl} \gamma_{mn}(\mathbf{P}_{23}) + \alpha_{mn}(\mathbf{P}_{23}) \left[\delta_{kl} \left(b(\mathbf{p}_1) - b(\mathbf{p}'_1) \right) - \beta_{lk}(\mathbf{P}'_{23}) \right] \right\} \tag{155}$$

Here the particles have been relabeled so that the bound pair is again 2, 3 and we have introduced the matrix elements

$$\begin{aligned} \alpha_{mn}(\mathbf{P}_{23}) &= \int d\mathbf{q}_{23} \left[a(\mathbf{p}_2) + a(\mathbf{p}_3) \right] \bar{\psi}_m(\mathbf{q}_{23}) \psi_n(\mathbf{q}_{23}) \\ \gamma_{mn}(\mathbf{P}_{23}) &= \int d\mathbf{q}_{23} \left[a(\mathbf{p}_2) + a(\mathbf{p}_3) \right] \left[b(\mathbf{p}_2) + b(\mathbf{p}_3) \right] \bar{\psi}_m(\mathbf{q}_{23}) \psi_n(\mathbf{q}_{23}) \end{aligned} \tag{156}$$

The operator J^S is the sum

$$J^S = \sum_{ij} \left[J_{ij}^1 + J_{ij}^2 \right] \tag{157}$$

For rearrangement collisions there are again basically two different operators which are distinguished by whether particle 1 is included in the bound pair or not. Consider first the case when it is not, so $\beta = 2, 3$ and take, say, $\alpha = 1, 2$. Call this operator J_{ij}^3:

$$\left(J_{ij}^{3} b\right)(\mathbf{p}_1) = \int d\mathbf{p}_2 \, d\mathbf{p}_3 \, \varphi(p_2) \varphi(p_3) \int d\mathbf{k}' \, d\mathbf{q}' \left[B_3(\mathcal{P}) - B_3(\mathcal{P}') \right] e^{\beta(u_{23} + e_j)}$$
$$\times \delta\left(\kappa'_{12} - e_i - \kappa_{23} + e_j \right) R^{C}_{12i,23j}(\mathbf{k}'\mathbf{q}', \mathbf{k}\mathbf{q}) \tag{158}$$

A straightforward calculation along the lines given above yields

$$\left(J_{ij}^{3} b\right)(\mathbf{p}_1) = K_j \int d\mathbf{P}_{23} \, \varphi_m(P_{23}) \int d\Omega'_{12} \, g'_{12} \sum_{kl/i} \sum_{mn/j} f^{R}_{km}(\mathbf{g}'_{12}, \mathbf{g}_{23}) \bar{f}^{R}_{ln}(\mathbf{g}'_{12}, \mathbf{g}_{23})$$
$$\times \left\{ \delta_{kl} \delta_{mn} \left[b(\mathbf{p}_1) - b(\mathbf{p}'_3) \right] + \delta_{kl} \beta_{mn}(\mathbf{P}_{23}) - \delta_{mn} \beta_{lk}(\mathbf{P}'_{12}) \right\} \tag{159}$$

The rearrangement amplitude has been defined by

$$f_{ij}^{R}(\mathbf{g}'_{12}, \mathbf{g}_{23}) = 2\pi\mu h T_{ij}^{R}(\mathbf{k}'_{12}, \mathbf{k}_{23}) \tag{160}$$

The result (159) is a fairly obvious modification of (149).

The operator J_{ij}^3 counts twice since it is also obtained when $\beta = 2, 3$ and $\alpha = 1, 3$. A different operator occurs if, say, $\beta = 1, 3$; we include both

$\alpha = 1,2$ and $\alpha = 2,3$ and define J_{ij}^4 by

$$\left(a, J_{ij}^4 b\right)_0 = \int d\mathbf{p}_1 \, d\mathbf{p}_2 \, d\mathbf{p}_3 \, \varphi(p_1)\varphi(p_2)\varphi(p_3) a(\mathbf{p}_1) \int d\mathbf{k}' \, d\mathbf{q}' \left[B_3(\mathscr{P}) - B_3(\mathscr{P}') \right]$$
$$\times e^{\beta(u_{13}+e_j)} \left\{ \delta\left(\kappa_{12}' - e_i - \kappa_{13} + e_j\right) R_{12i,13j}^C(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \right.$$
$$\left. + \delta\left(\kappa_{23}' - e_i - \kappa_{13} + e_j\right) R_{23i,13j}^C(\mathbf{k}'\mathbf{q}', \mathbf{kq}) \right\} \tag{161}$$

After some manipulation this can be reduced to

$$\left(a, J_{ij}^4 b\right)_0 = K_j \int d\mathbf{p}_2 \, d\mathbf{P}_{13} \, \varphi(p_2)\varphi_m(P_{13})$$
$$\times \int d\Omega_{12}' \, g_{12}' \sum_{kl/i} \sum_{mn/j} f_{km}^R(\mathbf{g}_{12}', \mathbf{g}_{13}) \bar{f}_{ln}^R(\mathbf{g}_{12}', \mathbf{g}_{13})$$
$$\times \left\{ \alpha_{mn}(\mathbf{P}_{13}) \left[\delta_{kl}\left(b(\mathbf{p}_2) - b(\mathbf{p}_3')\right) - \beta_{lk}(\mathbf{P}_{12}') \right] + \delta_{kl}\gamma_{mn}(\mathbf{P}_{13}) \right\} \tag{162}$$

The same operator also arises from the choice $\beta = 1,2$ with $\alpha = 1,3$ and $\alpha = 2,3$. Thus the total contribution to J^R is

$$J^R = 2\sum_{ij} \left[J_{ij}^3 + J_{ij}^4 \right] \tag{163}$$

The reduction of J^D follows similar lines. It is found that

$$J^D = \sum_j \left[J_j^5 + J_j^6 \right] \tag{164}$$

where J_j^5 is defined by

$$\left(J_j^5 b\right)(\mathbf{p}_1) = 4\pi^2 h^2 K_j \int d\mathbf{P}_{23} \, \varphi_m(P_{23}) \int d\mathbf{k}' \, d\mathbf{q}' \, \delta\left(u' + \kappa' - \kappa_{23} + e_j\right)$$
$$\times \sum_{kl/j} T_k^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_{23}) \bar{T}_l^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_{23})$$
$$\times \left\{ \delta_{kl}\left[b(\mathbf{p}_1) - b(\mathbf{p}_1') - b(\mathbf{p}_2') - b(\mathbf{p}_3') \right] + \beta_{kl}(\mathbf{P}_{23}) \right\} \tag{165}$$

In addition, J_j^6 is determined by

$$\left(a, J_j^6 b\right)_0 = 4\pi^2 h^2 K_j \int d\mathbf{p}_1 \, d\mathbf{P}_{23} \, \varphi(p_1)\varphi_m(P_{23}) \int d\mathbf{k}' \, d\mathbf{q}' \, \delta\left(u' + \kappa' - \kappa_{23} + e_j\right)$$
$$\times \sum_{kl/j} T_k^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_{23}) \bar{T}_l^D(\mathbf{k}'\mathbf{q}', \mathbf{k}_{23})$$
$$\times \left\{ \gamma_{kl}(\mathbf{P}_{23}) + \alpha_{kl}(\mathbf{P}_{23}) \left[b(\mathbf{p}_1) - b(\mathbf{p}_1') - b(\mathbf{p}_2') - b(\mathbf{p}_3') \right] \right\} \tag{166}$$

In Eq. (135) J^F is given as a sum over pairs α, but the three terms differ only in the labeling of the primed momenta. Hence each term gives the same contribution and the result is found to be

$$J^F = 3\sum_i J_i^7 \tag{167}$$

where

$$\begin{aligned}(J_i^7 b)(\mathbf{p}_1) = 2\pi^2 h^5 \int d\mathbf{p}_2\, d\mathbf{p}_3\, \varphi(p_2)\varphi(p_3) \int d\mathbf{k}'_{23}\, \delta(u + \kappa - \kappa'_{23} + e_i) \\ \times \sum_{kl/i} T_k^F(\mathbf{k}'_{23}, \mathbf{kq})\, \overline{T}_l^F(\mathbf{k}'_{23}, \mathbf{kq}) \\ \times \left\{ \delta_{kl}\left[b(\mathbf{p}_1) + b(\mathbf{p}_2) + b(\mathbf{p}_3) - b(\mathbf{p}'_1) \right] - \beta_{lk}(\mathbf{P}'_{23}) \right\}\end{aligned} \tag{168}$$

7. DISCUSSION

The analysis given above has dealt with transport in a moderately dense gas in which the particles can bind together to form molecules. Bound-state contributions were calculated in the Enskog order, which is the next order in density beyond that of Boltzmann, and involves collisions in clusters of three particles instead of the binary collisions basic to the Boltzmann equation. The analysis was based on the correlation-function approach and so is applicable primarily to transport coefficients such as the thermal conductivity and viscosity.

The discussion has centered on the triple-collision operator I_2 defined by Eq. (40). In Eq. (43) this operator was broken down into two parts, $I_2 = I_2' + I_2''$. The part I_2'' arises because of equilibrium pair correlations, and its bound-state contribution (which is analogous to the bound-state contribution to the Beth–Uhlenbeck formula) is given by Eq. (79). The part I_2' was further broken down, $I_2' = F + G$. The operator G, which involves only the two-body problem, is seen by Eq. (50) to represent a modification of the linearized Boltzmann collision operator like the Enskog correction to the collision frequency; the bound-state contribution to G is given by Eqs. (50), (52), and (73). The operator F depends on the three-body problem. Its bound state part, denoted by J, is expressed in Eqs. (129) and (141) as the sum of terms corresponding to molecular dissociation, formation, atom–molecule scattering (including inelastic scattering), and rearrangement collisions. The detailed form of the operators comprising J were worked out in Section 6. These have roughly a Boltzmann gain–loss form but depend on the amplitudes (or S-matrix elements) for the various processes which can occur in the atom–molecule system. The operator which describes inelastic scattering is basically the linearized form of the Waldmann–Snider collision operator. However, there are also terms containing the matrix γ_{mn} of Eq. (156) which are due to a correlation over the molecular state of the fluxes in the Green–Kubo formula. These terms, which have apparently not been obtained in the context of the Waldmann–Snider equation, arise because the composite nature of a molecule allows for a flux across it; this effect can occur even with elastic collisions.

Numerical evaluation of the transport coefficients would require input regarding the various amplitudes, and this problem has not been considered here. Such evaluation should also include the collisional transfer contributions, as well as the purely scattering contributions which have been discussed by Sengers *et al.*(17) and Resibois.(18)

Some understanding of collisional transfer can be obtained by the ad hoc inclusion of potential terms in the pair functions A_2, B_2. In particular the energy flux for the pair 1, 2 is

$$\begin{aligned} S_i = (1/2m)\big\{(1/m)\big[p_{1i}p_1^2 + p_{2i}p_2^2\big] \\ + (p_{1i} + p_{2i})V_{12} - r_i(p_{1j} + p_{2j})\partial V_{12}/\partial r_j\big\} \end{aligned} \tag{169}$$

where r_i is the relative position of the two atoms. The momentum flux for the pair is(22)

$$T_{ij} = (1/m)\big[p_{1i}p_{1j} + p_{2i}p_{2j}\big] - r_j\partial V_{12}/\partial r_i \tag{170}$$

(In a mixture the particle fluxes do not depend on the potential energy and so there are no collisional-transfer contributions to the coefficients of diffusion.) Matrix elements such as (150) and (156) should then be replaced by matrix elements of the above operators, such as

$$(S_i)_{mn} = \int d\mathbf{q}_{12}\,\bar{\psi}_m(\mathbf{q}_{12})S_i\psi_n(\mathbf{q}_{12}) \tag{171}$$

The transformation to relative and total momenta gives

$$\begin{aligned} S_i &= (P_i/2m)\big[(P^2/4m) + h\big] + (P_j/2m)T_{ij}^{\text{int}} \\ T_{ij} &= P_iP_j/2m + T_{ij}^{\text{int}} \end{aligned} \tag{172}$$

where

$$T_{ij}^{\text{int}} = 2q_iq_j/m - r_j\partial V/\partial r_i \tag{173}$$

Here the particle labels have been dropped; **P** denotes the total momentum of the pair and **q** the relative momentum. In addition h is the Hamiltonian for the pair, in the center-of-mass frame.

The internal stress (173) can be expressed as

$$\begin{aligned} T_{ij}^{\text{int}} &= \frac{1}{2}\,\frac{d}{dt}\left[q_i r_j + q_j r_i\right] \\ &= \frac{1}{4}\,m\,\frac{d^2}{dt^2}\,r_i r_j \end{aligned} \tag{174}$$

This shows that matrix elements of T_{ij}^{int} vanish between states of equal energy. Consequently, the matrices β_{mn} and α_{mn} defined in Eqs. (150) and (156) (but with potential terms included) can be calculated with the energy and momentum fluxes replaced by

$$\begin{aligned} S_i^{\text{con}} &= (P_i/2m)\left[(P^2/4m) + h\right] \\ T_{ij}^{\text{con}} &= P_i P_j/2m \end{aligned} \tag{175}$$

These describe a convective flow of energy and momentum due to motion of the molecule with velocity $P_i/2m$. The convective fluxes are just the ones normally used when the Chapman–Enskog procedure is applied to solve the kinetic equations for a molecular gas. However, the matrix elements γ_{mn} defined in Eq. (156) will involve an autocorrelation of the internal stress, and in general this will not vanish. It may nevertheless be small; indeed Eq. (174) shows that there is no internal stress for a model, such as the rigid dumbbell, which has a fixed moment of inertia.

APPENDIX

Here we show how the formula (40) can be reduced to the linearized Boltzmann collision operator with the quantum-mechanical cross section.

As in Section 5 we choose the contour C in Eq. (67) to consist of lines at $w = E + i\epsilon$ and $w = E - i\epsilon'$ with $\epsilon = \frac{1}{2}\lambda$. The lower part of the contour gives no contribution to I_1, and so Eqs. (40), (67) yield

$$\begin{aligned} (a, I_1 b)_0 = &-\left(2V_0^2/h^4\right)\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dE\, e^{-\beta E}\int dP\, dq\, dq'\, e^{-\beta K} A_2(\mathcal{P}) \\ &\times\left[B_2(\mathcal{P}') - B_2(\mathcal{P})\right]\left[(E-u)^2 + \epsilon^2\right]^{-1}\left[(E-u')^2+\epsilon^2\right]^{-1} \\ &\times\left|t(E + i\epsilon, \mathbf{q}', \mathbf{q})\right|^2 \\ = &\left(2\pi^2 V_0^2/h^4\right)\int_{-\infty}^{\infty} dE\, e^{-\beta E}\int dP\, dq\, dq'\, e^{-\beta K} A_2(\mathcal{P}) \\ &\times\left[B_2(\mathcal{P}) - B_2(\mathcal{P}')\right]\delta(E-u)\delta(E-u')\left|t(E + i0, \mathbf{q}', \mathbf{q})\right|^2 \\ = &\left(2\pi^2 V_0^2/h^4\right)\int dP\, dq\, dq'\, e^{-\beta(K+u)}\delta(u-u') \\ &\times A_2(\mathcal{P})\left[B_2(\mathcal{P}) - B_2(\mathcal{P}')\right]\left|t(E + i0, \mathbf{q}', \mathbf{q})\right|^2 \end{aligned}$$

The scattering amplitude is given by

$$f = \pi m h t(E + i0, \mathbf{q}', \mathbf{q})$$

and the cross section is $\sigma = |f|^2$. Using Eq. (42) for the Maxwellian we get

$$(a, I_1 b)_0 = (2/m)^2 \int dp_1\, dp_2\, dq'\, \varphi(p_1)\varphi(p_2)\delta(u - u')\sigma(\mathbf{q}, \mathbf{q}')$$

$$\times a(\mathbf{p}_1)\left[b(\mathbf{p}_1) + b(\mathbf{p}_2) - b(\mathbf{p}_1') - b(\mathbf{p}_2')\right]$$

The delta function allows for the integration over the magnitude of q', and the result (41) is then obtained.

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