Exchange collision kernel

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In the analysis of laser-spectroscopic line shapes, velocity-changing collisions are accounted for by adding to the density-matrix equations-of-motion terms involving the direct collision kernel. The direct collision kernel is the probability density per unit time that an atom has a specific velocity after a collision, as a function of its velocity before the collision. If the collision partner's velocity distribution is not thermal, however, the direct collision kernel alone does not completely characterize the effect of collisions. In such cases it is necessary to include terms involving the exchange collision kernel. The exchange kernel is the conditional probability density per unit time that the atom has a specific velocity after the collision as a function of its *collision partner's* velocity before the collision. Both the direct and the exchange collision kernels are obtained from the linearized Boltzmann equation. We derive an expression for the exchange kernel in terms of the colliding pair scattering cross section, and calculate the exchange kernel for hard-sphere collisions. Moreover, we propose a phenomenological exchange kernel similar to the Keilson-Storer direct kernel [J. Keilson and K.E. Storer, J. Appl. Math. **10**, 243 (1952)] and compare it with the hard-sphere kernel. In an earlier paper [P.R. Berman, J.E.M. Haverkort, and J.P. Woerdman, Phys. Rev. A **34**, 4647 (1986)], a connection was made between the *collision kernels* of laser spectroscopy and the *collision integrals* of classical transport theory. We expand on this earlier work by including the exchange collision kernel, and indicate how results from classical transport theory might be used in setting the parameters appearing in the phenomenological exchange kernel. We interpret an excitation-transfer experiment in terms of the exchange kernel.

I. INTRODUCTION

A. Direct and exchange collision kernels

The effect of velocity-changing collisions in the spectroscopy of atoms in a dilute gas has been studied extensively [1–4]. Laser light, because of its narrow bandwidth, interacts with narrow velocity subgroups within the wider Maxwellian profile. The collisional transfer of atoms into and out of an interacting velocity subgroup must be accounted for to adequately interpret spectroscopic line shapes. This is often done by adding terms to the density-matrix equation of motion that represent the interaction of an active atom (A) with a reservoir of perturber atoms (P). The effect of the interaction on the A atoms can be characterized by a direct collision kernel, which gives the probability density per unit time for an A atom to go from a given initial velocity to a given final velocity as a result of collisions with P atoms. Knowledge of the direct kernel allows one to construct a master equation that represents the time evolution of the active atom velocity distribution due to collisions,

$$\left(\frac{d\varrho}{dt}\right)_{\text{collision}} = -\Gamma(v)\varrho(\mathbf{v}) + \int K_d(\mathbf{v}' \rightarrow \mathbf{v})\varrho(\mathbf{v}')\, d^3v \ , \tag{1.1}$$

where $K_d(\mathbf{v}' \rightarrow \mathbf{v})$ is the direct kernel and $\Gamma(v)$ is the collision rate for A atoms with speed v given by

$$\Gamma(v) = \int K_d(\mathbf{v} \rightarrow \mathbf{v}')\, d^3v' \ . \tag{1.2}$$

The first term in Eq. (1.1) is the rate at which A atoms leave the velocity subclass and the second term is the rate that A atoms enter the velocity subclass as a result of collisions.

Equation (1.1) can be derived from the Boltzmann equation with the following approximations: (a) A-A collisions do not affect the A atom distribution, and (b) the perturber reservoir is thermalized and is not affected by A-P collisions. If one of these conditions is not satisfied, then there will be extra terms in Eq. (1.1).

A type of experiment in which the direct kernel alone adequately describes relaxation is one in which a low-density population of A atoms is immersed in a much higher density buffer gas of P atoms [4–7]. In this case the perturber population is distinct from and much larger than that of the A atoms so the A-A collisions can be neglected relative to A-P collisions. Also the effect of A-P collisions on the P distribution is negligible, so the P atoms remain in a thermal distribution. In a typical experiment of this sort a narrow velocity distribution of A atoms is produced by laser excitation and it relaxes back towards equilibrium by undergoing collisions with P atoms [8].

There are other types of experiments [9,10], however, for which the direct kernel alone cannot adequately describe the relaxation. Consider, for example, a process

involving resonant excitation exchange collisions. This process involves an initially excited atom (which we call a "P atom"), transferring its excitation to another atom (which we call an "A atom"), through a collision. In a typical experiment of this sort [9], the P atoms are not in a thermal distribution and the A atom distribution is initially Maxwellian. One is interested in the A atom distribution after an exchange collision with a P atom. In this case, the direct kernel does not contain information on the evolution of the A atom distribution. To lowest order, the right side of Eq. (1.1) vanishes. In such cases it is necessary to include terms in Eq. (1.1) involving the exchange collision kernel, which gives the probability density per unit time that an A atom will have a velocity $\mathbf{v}_1$ after colliding with a P atom having a velocity $\mathbf{v}_2'$ before the collision. The A atom velocity distribution will depend upon the initial P atom distribution and on the exchange kernel. The terms involving the exchange kernel are derived from the linearized Boltzmann equation.

B. Laser spectroscopy and kinetic theory

When analyzing spectroscopic data, one often uses phenomenological collision kernels with several adjustable parameters rather than kernels derived from the A-P cross sections. A phenomenological direct kernel that is often used is the Keilson-Storer kernel [11] with two adjustable parameters; one that characterizes the collision rate, and one that characterizes its strength. The strength parameter depends on the ratio of the masses of the colliding atoms and there are various procedures to set its value [4,12].

Recently, an article appeared [13] (hereafter referred to as I) in which a connection between the collision kernels of laser spectroscopy and the transport coefficients of classical transport theory was established. The transport coefficients characterize the bulk properties of a gas such as viscosity, diffusion, and heat conductivity [14]. They are derived from the interactions between molecules of the gas and are related to the effective transport cross sections [15] which are the matrix elements of a linearized collision operator. The effective transport cross sections can be expressed as linear combinations of the collision integrals, which are weighted integrals of the differential cross section, and thus contain information on the collisional interaction between molecules of the gas [14,16]. The relations between the effective cross sections and the collision integrals, as well as the collision integrals for different model potentials, can be found in various texts [14,16].

In I it was shown that, by writing the linearized collision operator in terms of the direct kernel, one can derive a relation between the collision integrals of transport theory and integrals of the collision kernel. Using these relations it is possible to put constraints on the parameters of the phenomenological kernels in fitting line-shape data.

The theory can be extended, in a more general treatment, to include the relation between the collision integrals and the exchange kernel. In fact it is *necessary* to include the exchange kernel when expressing the collision operator in terms of the collision kernels for a single component gas in which the A and P atoms are indistinguishable. As is done for the direct kernel, one can develop a phenomenological exchange kernel and use some of the results from transport theory to set the parameters that characterize the kernel.

This article is organized as follows: In Sec. II the linearized Boltzmann operator is expressed as a sum of two terms; one of which describes direct collisions, the other exchange collisions. We present two independent methods for calculating the collision integrals from integrals of the exchange kernel. In Sec. III, two specific exchange kernels are introduced, one based on a hard-sphere interaction and the second on a phenomenological kernel. We investigate some of the properties of these kernels and make comparisons with the direct kernels. In Sec. IV the collision integrals are calculated for these two kernels using the methods introduced in Sec. II. We discuss how the collision integrals can be used to determine the suitability of the parameters characterizing the phenomenological kernel. In Sec. V we define the longitudinal exchange kernel and compare the hard sphere and phenomenological kernels. We then use the hard-sphere longitudinal exchange kernel to discuss the results of a resonant excitation exchange collision experiment, in which the exchange kernel is effectively measured. In Sec. VI, we discuss the relation between the collision kernels and the transport coefficients for a real gas.

Throughout this article, the interacting atoms are divided into two classes labeled "A" and "P". These labels come from the first type of experiment mentioned above in which the A atoms are "active," interacting with the laser field, and the P atoms are "perturbers" which do not interact with the field, but do contribute to the relaxation of the A atoms. In the second type of experiment mentioned above, the excitation exchange collision, the A and P labels are used for convenience, they do not mean "active" or "perturber" as used above; here the P atoms interact with the field as well as with the A atoms. A more appropriate label might be "donor" and "acceptor" for the two populations; however, we use the A and P labels to maintain consistency with the usual treatment of the Boltzmann equation in laser spectroscopy [13].

In deriving the relation between the collision integrals and the collision kernel, we consider a binary gas consisting of A atoms and P atoms in which A-A and P-P collisions are ignored. Of course, for a real gas the A-A and/or the P-P collisions play an important role in determining the bulk properties of the gas. Our model, however, shows the essential relation between the collision kernels and the Boltzmann operator in a simple way. If the A and P atoms are the same, then the following discussion is correct for a one component gas. Consistent with our model in which the A-A and P-P collisions are ignored, all collision rates refer to A-P collisions, unless otherwise stated.

II. COLLISION KERNELS, THE LINEARIZED COLLISION OPERATOR, AND THE COLLISION INTEGRALS

A. Boltzmann equation

The Boltzmann equation is

$$\frac{d}{dt}f_1(\mathbf{v}_1) = \mathcal{L}f_1(\mathbf{v}_1) \ , \tag{2.1}$$

with the Boltzmann collision operator for the A atom distribution given by

$$\mathcal{L}f_1(\mathbf{v}_1) = \int [\, f_1(\mathbf{v}_1')f_2(\mathbf{v}_2') - f_1(\mathbf{v}_1)f_2(\mathbf{v}_2)]\sigma(g,\Omega)g \, d\Omega \, d^3v_2 \ , \tag{2.2}$$

where $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$ and f_1 (f_2) is the velocity distribution for the A (P) atoms, and $\sigma(g,\Omega)$ is the differential cross section in center-of-mass coordinates for A-P scattering. The primed quantities refer to those quantities before the collision and unprimed after.

The Boltzmann collision operator for a real binary gas would include another term to account for the effects on f_1 resulting from A-A collisions. This extra term is similar to Eq. (2.2) but involves the A-A rather than the A-P cross section, and is a function of f_1 alone rather than f_1 and f_2. If the A-A collision rate is negligible compared to the A-P rate, as is true in many cases of experimental interest, then Eq. (2.1) adequately describes the problem.

One can write the distribution functions as

$$f_i(\mathbf{v}_i) = n_i W_i(\mathbf{v}_i)[1 + \Phi_i(\mathbf{v}_i)] \ , \tag{2.3}$$

where n_i is the average number density of atoms of type i, and $W_i(\mathbf{v}_i)$ is the thermal distribution:

$$W_i(\mathbf{v}_i) = (\pi u_i^2)^{-\frac{3}{2}} \exp(-v_i^2/u_i^2) \ , \tag{2.4}$$

with u_i the most probable speed for atoms of type i,

$$u_i = \sqrt{2k_BT/m_i} \ ,$$

where k_B is the Boltzmann constant, T is the temperature, and m_i is the mass of an i atom. The Boltzmann operator can be linearized if either Φ_1 or Φ_2 (or both) are small such that

$$\Phi_1\Phi_2 \ll 1 \ , \tag{2.5}$$

which is the case in all situations studied here.

Using Eqs. (2.3) and (2.5) and the fact that $W_1(\mathbf{v}_1)W_2(\mathbf{v}_2) = W_1(\mathbf{v}_1')W_2(\mathbf{v}_2')$ one can write the Boltzmann operator Eq. (2.2) in terms of a direct part $\mathcal{L}_d$ and an exchange part $\mathcal{L}_e$:

$$\mathcal{L}f_1(\mathbf{v}_1) = \mathcal{L}_d f_1(\mathbf{v}_1) + \mathcal{L}_e f_1(\mathbf{v}_1) \ , \tag{2.6}$$

where

$$\mathcal{L}_d f_1(\mathbf{v}_1) = n_2 \int [f_1(\mathbf{v}_1')W_2(\mathbf{v}_2') - f_1(\mathbf{v}_1)W_2(\mathbf{v}_2)] \times g\sigma(g,\Omega)\, d\Omega \, d^3v_2 \ , \tag{2.7}$$

$$\mathcal{L}_e f_1(\mathbf{v}_1) = n_1 \int [W_1(\mathbf{v}_1')f_2(\mathbf{v}_2') - W_1(\mathbf{v}_1)f_2(\mathbf{v}_2)] \times g\sigma(g,\Omega)\, d\Omega \, d^3v_2 \ . \tag{2.8}$$

For an experiment in which the low-density nonthermal A atoms are immersed in a higher density gas of thermal P atoms, then $f_2(\mathbf{v}_2) \simeq W_2(\mathbf{v}_2)$ for all times so that $\mathcal{L}_e f_1(\mathbf{v}_1) = 0$. The direct collision operator $\mathcal{L}_d$ completely describes the (collisional) evolution of $f_1(\mathbf{v}_1)$. The exchange collision operator, on the other hand, describes the effects of collisions on an initially thermal A distribution when the P atom distribution is nonthermal.

B. Collision kernels

The direct Boltzmann operator describes the change in a nonthermal A atom distribution resulting from A-P collisions when the P atoms are in a thermal distribution. It can be written as

$$\mathcal{L}_d f_1(\mathbf{v}_1) = \int K_d(\mathbf{v}_1' \to \mathbf{v}_1)f_1(\mathbf{v}_1')\, d^3v_1' - \Gamma_1'(v_1)f_1(\mathbf{v}_1) \ , \tag{2.9}$$

where Γ_1' is the collision rate for active atoms with speed v_1, and $K_d(\mathbf{v}_1' \to \mathbf{v}_1)$ is the direct collision kernel. The A atom collision rate is obtained by integrating the direct kernel over the final A atom velocities:

$$\Gamma_1'(v_1') = \int K_d(\mathbf{v}_1' \to \mathbf{v}_1)\, d^3v_1 \ . \tag{2.10}$$

In the case that the P distribution is nonthermal, this is not the total A collision rate, but only a first approximation as is shown below, Eq. (2.15).

The exchange Boltzmann operator describes the change in an initially thermal A distribution when the P distribution is nonthermal. It can be written

$$\mathcal{L}_e f_1(\mathbf{v}_1) = \int K_e(\mathbf{v}_2' \to \mathbf{v}_1)f_2(\mathbf{v}_2')\, d^3v_2' - \int J(\mathbf{v}_2,\mathbf{v}_1)f_2(\mathbf{v}_2)\, d^3v_2 \ , \tag{2.11}$$

where $K_e(\mathbf{v}_2' \to \mathbf{v}_1)$ is the exchange kernel which is the probability density per unit time that type-1 (A) atoms have a velocity $\mathbf{v}_1$ after colliding with a type-2 (P) atom that had a velocity $\mathbf{v}_2'$ before the collision. Using Eq. (2.8) one can write the exchange kernel as

$$K_e(\mathbf{v}_2' \to \mathbf{v}_1) = n_1 \left(\frac{m_1}{\mu}\right)^3 \int W_1(\mathbf{g}' - \mathbf{v}_2')\frac{1}{g'}\sigma(g',\Omega)\delta(g-g')\delta\left(\mathbf{g} + \frac{m_1}{m_2}\mathbf{g}' - \frac{m_1}{\mu}(\mathbf{v}_2' - \mathbf{v}_1)\right) d^3g \, d^3g' \ , \tag{2.12}$$

where $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$, $\mathbf{g}' = \mathbf{v}_2' - \mathbf{v}_1'$, and $\mu = (m_1 m_2)/(m_1 + m_2)$ is the reduced mass.

The collisional flux density $J(\mathbf{v}_2, \mathbf{v}_1)$ is defined as

$$J(\mathbf{v}_2, \mathbf{v}_1) = n_1 W_1(\mathbf{v}_1) g \sigma(g) \ , \tag{2.13}$$

where $\sigma(g) = \int \sigma(g, \Omega)\, d\Omega$. The quantity $J(\mathbf{v}_2, \mathbf{v}_1) d^3 v_1$ is the number of collisions per unit time undergone by a type-2 atom having a velocity $\mathbf{v}_2'$ with thermal type-1 atoms with velocity $\mathbf{v}_1$ (within the volume $d^3 v_1$) . The total collision rate for a thermal A atom colliding with P atoms is given by the expression

$$\Gamma_1(v_1) = \frac{1}{n_1 W_1(\mathbf{v}_1)} \int J(\mathbf{v}_2, \mathbf{v}_1) f_2(\mathbf{v}_2)\, d^3 v_2 \ . \tag{2.14}$$

If $f_2(\mathbf{v}_2)$ is a Maxwellian with a correction as in Eq. (2.3), then

$$\Gamma_1(v_1) = \Gamma_1'(v_1) + \gamma(v_1) \ , \tag{2.15}$$

where Γ_1' is given by Eq. (2.10) and γ is a correction to the direct collision rate due to the non-Maxwellian part of $f_2(\mathbf{v}_2)$ given by

$$\gamma(v_1) = \frac{1}{n_1 W_1(\mathbf{v}_1)} \int J(\mathbf{v}_2, \mathbf{v}_1)[f_2(\mathbf{v}_2) - n_2 W_2(\mathbf{v}_2)]\, d^3 v_2 \ . \tag{2.16}$$

The collision rate of the perturber atoms $\Gamma_2(v_2)$ is obtained by integrating the exchange kernel over A atom velocities:

$$\Gamma_2(v_2') = \int K_e(\mathbf{v}_2' \to \mathbf{v}_1)\, d^3 v_1 \ . \tag{2.17}$$

This expression is a statement of the conservation of probability. In general, Γ_2 is not equal to Γ_1. The average collision rates are related by

$$\frac{1}{n_1}\langle \Gamma_2 \rangle = \frac{1}{n_2}\langle \Gamma_1 \rangle \ . \tag{2.18}$$

For later use, we note several easily established relations between the collision rates, the exchange kernel, and the collisional flux density:

$$n_2 \int W_2(\mathbf{v}_2) J(\mathbf{v}_2, \mathbf{v}_1)\, d^3 v_2 = n_1 W_1(\mathbf{v}_1) \Gamma_1'(\mathbf{v}_1) \ , \tag{2.19}$$

$$\int J(\mathbf{v}_2, \mathbf{v}_1)\, d^3 v_1 = \Gamma_2(v_2) \ , \tag{2.20}$$

$$\int [K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2, \mathbf{v}_1)]\, d^3 v_1 = 0 \ , \tag{2.21}$$

$$\int W_2(\mathbf{v}_2)[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2, \mathbf{v}_1)]\, d^3 v_2 = 0 \ , \tag{2.22}$$

$$n_2 W_2(\mathbf{v}_2) J(\mathbf{v}_2, \mathbf{v}_1) = n_1 W_1(\mathbf{v}_1) J(\mathbf{v}_1, \mathbf{v}_2) \ . \tag{2.23}$$

When the masses of the A atoms and P atoms are the same, the exchange kernel can be obtained from the direct kernel by the substitution in the first term of Eq. (2.7) of

$$\sigma(g, \chi) \to \sigma(g, \pi - \chi) \ , \tag{2.24}$$

where $\sigma(g, \chi)$ is the differential scattering cross section and χ is the center-of-mass scattering angle.

The significance of the two terms in $\mathcal{L}_e f_1(\mathbf{v}_1)$ is more clearly seen if we consider a specific physical situation. We calculate the velocity distribution of an A atom immediately after one collision with a P atom in a resonance exchange collision. The A atoms are initially in a Maxwellian distribution and the P atoms are in an arbitrary nonequilibrium distribution. In this case, $f_2(\mathbf{v}_2')$ is the distribution of the excited-state perturber atoms and n_2 is the density of excited state P atoms. Since the A atoms are initially in equilibrium, $\mathcal{L}_d f_1(\mathbf{v}_1) = 0$ to lowest order, and

$$\frac{d}{dt} f_1(\mathbf{v}_1) = \int K_e(\mathbf{v}_2' \to \mathbf{v}_1) f_2(\mathbf{v}_2')\, d^3 v_2' - \int J(\mathbf{v}_2, \mathbf{v}_1) f_2(\mathbf{v}_2)\, d^3 v_2 \ . \tag{2.25}$$

We can write the A atom distribution after the collision as the sum of two parts

$$f_1(\mathbf{v}_1) = n_1 W_1(\mathbf{v}_1) + \Delta f_1(\mathbf{v}_1) \ , \tag{2.26}$$

where Δf_1 is the change in the A atom distribution due to the collision, and is approximately given by

$$\Delta f_1 \simeq \frac{1}{\Gamma_1} \left(\frac{d f_1}{dt} \right)_{\text{collision}} \tag{2.27}$$

or

$$\Delta f_1(\mathbf{v}_1) = \frac{1}{\Gamma_1(v_1)} \left(\int K_e(\mathbf{v}_2' \to \mathbf{v}_1) f_2(\mathbf{v}_2')\, d^3 v_2' - \int J(\mathbf{v}_2, \mathbf{v}_1) f_2(\mathbf{v}_2)\, d^3 v_2 \right) \ . \tag{2.28}$$

We see that the expression $K_e - J$ is related to the change in the A distribution. The second term on the right is equal to $n_1 W_1(\mathbf{v}_1)$ by Eq. (2.14). Using Eq. (2.26) one finds

$$f_1(\mathbf{v}_1) = \frac{1}{\Gamma_1(v_1)} \int K_e(\mathbf{v}_2' \to \mathbf{v}_1) f_2(\mathbf{v}_2')\, d^3 v_2' \ . \tag{2.29}$$

The distribution of A atoms after an excitation exchange collision with P atoms is proportional to the integral of the exchange kernel with the P distribution. If a specific P atom velocity class has been excited, then $f_2(\mathbf{v}_2') = n_2 \delta(\mathbf{v}_2' - \mathbf{v}_2)$ and

$$f_1(\mathbf{v}_1) = \frac{n_2}{\Gamma_1(v_1)} K_e(\mathbf{v}_2 \to \mathbf{v}_1) \ . \tag{2.30}$$

C. Detailed balance

The exchange kernel must satisfy a form of the law of detailed balance, an "exchange balance." This is expressed as

$$n_2 W_2(\mathbf{v}_2') K_{21}(\mathbf{v}_2' \to \mathbf{v}_1) = n_1 W_1(\mathbf{v}_1) K_{12}(\mathbf{v}_1 \to \mathbf{v}_2') , \tag{2.31}$$

where K_{21} (K_{12}) is the probability density per unit time that type 1 (2) atoms have velocity $\mathbf{v}_1$ ($\mathbf{v}_2'$) after a collision with with type 2 (1) atoms having a velocity $\mathbf{v}_2'$ ($\mathbf{v}_1$) before the collision. The relation Eq. (2.31) is easily verified using Eq. (2.12). The kernel K_{12} is not equal to K_{21} if the type-1 and type-2 masses differ.

A kernel of the form of Eq. (2.12) derived from an interaction potential automatically satisfies this condition. A criterion for the suitability of a phenomenological kernel is that it satisfy this condition as well.

D. Linearized collision operator and the collision kernels

It is convenient to define a linearized collision operator in terms of the linearized Boltzmann operator[13,15]:

$$-n_1 n_2 \mathcal{R}\Phi_1(\mathbf{v}_1) = \frac{1}{W_1(\mathbf{v}_1)} \mathcal{L} W_1(\mathbf{v}_1)\Phi_1(\mathbf{v}_1) . \tag{2.32}$$

The collision operator $\mathcal{R}$ can be expanded into a direct part and an exchange part:

$$\mathcal{R}\Phi_1(\mathbf{v}_1) = \mathcal{R}_d\Phi_1(\mathbf{v}_1) + \mathcal{R}_e\Phi_1(\mathbf{v}_1) , \tag{2.33}$$

where

$$-n_1 n_2 \mathcal{R}_{d,e}\Phi_1(\mathbf{v}_1) = \frac{1}{W_1(\mathbf{v}_1)} \mathcal{L}_{d,e} W_1(\mathbf{v}_1)\Phi_1(\mathbf{v}_1) . \tag{2.34}$$

The effective transport cross sections are defined in terms of the matrix elements of the operators $\mathcal{R}_{d,e}$ in an eigenfunction basis $\psi_{iq}^{lm}(\mathbf{v}_i)$, where

$$\psi_{iq}^{lm}(\mathbf{v}_i) = B_{lm}\sqrt{4\pi} \left(\frac{v_i}{u_i}\right)^l L_m^{l+\frac{1}{2}}\left(\frac{v_i^2}{u_i^2}\right) Y_{lq}(\hat{\mathbf{v}}_i) . \tag{2.35}$$

The $L_m^{l+\frac{1}{2}}$ are Laguerre polynomials, and the Y_{lq} are spherical harmonics. The normalization constant B_{lm} is given by

$$B_{lm} = [\tfrac{1}{2}\sqrt{\pi}\, m!/\Gamma(l+m+\tfrac{3}{2})]^{\frac{1}{2}} ,$$

where Γ is the gamma function. The ψ^{lm} form a complete orthonormal set, and are used to expand the correction Φ_i [14–17]:

$$\Phi_i(\mathbf{v}_i) = \sum_{l,m,q} a_{ilmq}^* \psi_{iq}^{lm}(\mathbf{v}_i) .$$

The orthonormality condition is

$$\langle \psi_q^{lm} | \psi_{q'}^{l'm'} \rangle = \delta_{ll'}\,\delta_{mm'}\,\delta_{qq'} , \tag{2.36}$$

where $\langle\ \rangle$ indicates an integration over $\mathbf{v}_1$ with $W_1(\mathbf{v}_1)$,

$$\langle f(\mathbf{v}) | g(\mathbf{v}) \rangle = \int W_1(\mathbf{v}) f^*(\mathbf{v}) g(\mathbf{v})\, d^3v . \tag{2.37}$$

The direct and the exchange effective cross sections are defined by [13,15]:

$$\bar{v}_r \sigma_{d,e}\binom{ln}{ln'} = \langle \psi_{1q}^{ln} | \mathcal{R}_{d,e} \psi_{1q}^{ln'} \rangle , \tag{2.38}$$

where $\bar{v}_r = (8k_BT/\pi\mu)^{\frac{1}{2}}$ is the average relative speed.

The two parts of the collision operator are related to the collision kernels using Eqs. (2.9), (2.10), (2.11), and (2.34) as

$$n_2 \mathcal{R}_d\Phi_1(\mathbf{v}_1) = -\frac{1}{W_1(\mathbf{v}_1)} \int W_1(\mathbf{v}_1') K_d(\mathbf{v}_1' \to \mathbf{v}_1)[\Phi_1(\mathbf{v}_1') - \Phi_1(\mathbf{v}_1)]\, d^3v_1' , \tag{2.39}$$

$$n_1 \mathcal{R}_e\Phi_1(\mathbf{v}_1) = -\frac{1}{W_1(\mathbf{v}_1)} \int W_2(\mathbf{v}_2)[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2, \mathbf{v}_1)]\Phi_2(\mathbf{v}_2)\, d^3v_2 . \tag{2.40}$$

Equations (2.40) and (2.38) give the relation between the exchange kernel and the exchange effective cross section. The relation between the direct kernel and the direct effective cross section is treated in I.

It is convenient to use a quantity $\mathrm{U}_{nn'}^l$ instead of $\sigma_e\binom{ln}{ln'}$ to calculate the matrix elements of $\mathcal{R}_e$. The $\mathrm{U}_{nn'}^l$ are defined as

$$\mathrm{U}_{nn'}^l = n_1[(2l+1)\, B_{ln}\, B_{ln'}]^{-1} \sum_{q=1}^{2l+1} \langle \psi_{1q}^{ln} | \mathcal{R}_e \psi_{1q}^{ln'} \rangle . \tag{2.41}$$

Using Eqs. (2.40), (2.41), (2.37), (2.35), and the addition theorem for spherical harmonics, one finds that the $\mathrm{U}_{nn'}^l$ are given by

$$\mathrm{U}_{nn'}^l = -\int W_2(\mathbf{v}_2) \left(\frac{v_2}{u_2}\right)^l \left(\frac{v_1}{u_1}\right)^l L_n^{l+\frac{1}{2}}\left(\frac{v_2^2}{u_2^2}\right) L_{n'}^{l+\frac{1}{2}}\left(\frac{v_1^2}{u_1^2}\right) P_l(\hat{\mathbf{v}}_2 \cdot \hat{\mathbf{v}}_1)\,[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2, \mathbf{v}_1)]\, d^3v_1\, d^3v_2 , \tag{2.42}$$

where $P_l(\hat{\mathbf{v}}_2 \cdot \hat{\mathbf{v}}_1)$ is a Legendre polynomial. The first few $U^l_{nn'}$ are

$$U^1_{00} = -\int W_2(\mathbf{v}_2)\frac{\mathbf{v}_2\cdot\mathbf{v}_1}{u_2u_1}[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2,\mathbf{v}_1)]\, d^3v_1\, d^3v_2 \,, \tag{2.43}$$

$$U^1_{10} = -\int W_2(\mathbf{v}_2)\left(\frac{5}{2} - \frac{v_2^2}{u_2^2}\right)\frac{\mathbf{v}_2\cdot\mathbf{v}_1}{u_2u_1}[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2,\mathbf{v}_1)]\, d^3v_1\, d^3v_2 \,, \tag{2.44}$$

$$U^2_{00} = -\int W_2(\mathbf{v}_2)\left[\frac{3}{2}\left(\frac{\mathbf{v}_2\cdot\mathbf{v}_1}{u_2u_1}\right)^2 - \frac{1}{2}\left(\frac{v_2v_1}{u_2u_1}\right)^2\right][K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2,\mathbf{v}_1)]\, d^3v_1\, d^3v_2 \,. \tag{2.45}$$

The relations between the first few $U^l_{nn'}$ and the first few $\sigma_e\binom{ln}{ln'}$ are

$$U^1_{10} = \frac{3}{2}\sqrt{\frac{5}{2}}\, n_1\bar{v}_r\sigma_e\binom{11}{10} \,, \tag{2.46}$$

$$U^1_{00} = \tfrac{3}{2}\, n_1\bar{v}_r\sigma_e\binom{10}{10} \,, \tag{2.47}$$

$$U^2_{00} = \tfrac{15}{4}\, n_1\bar{v}_r\sigma_e\binom{20}{20} \,. \tag{2.48}$$

The $U^l_{nn'}$ are the same (to within a numerical factor) as the bracket integrals of Chapman and Cowling [14,16]. The exact relations are given in Appendix A.

E. Collision integrals and integrals of the exchange kernel

The collision integrals are defined by [14,16]:

$$\Omega^{(k,s)} = \left(\frac{2k_BT}{\pi\mu}\right)^{\frac{1}{2}} \times \int_0^\infty dg \exp(-g^2/u_r^2)\left(\frac{g}{u_r}\right)^{2s+3} Q^{(k)}(g) \,, \tag{2.49}$$

where $u_r^2 = u_1^2 + u_2^2$ is the most probable relative speed and

$$Q^{(k)}(g) = \int d\Omega\, \sigma(g,\Omega)\,(1 - \cos^k\chi) \,. \tag{2.50}$$

The collision integrals carry information on the molecular interaction and are related to the transport properties of the gas as characterized by the transport coefficients. Our objective is to provide expressions that relate the collision integrals to integrals of the exchange kernel. We propose two methods, similar to the two methods that relate the collision integrals to the direct kernel as developed in I.

Method 1. Chapman and Cowling [16] give expressions for the bracket integrals in terms of the collision integrals, and the bracket integrals are proportional to the $U^l_{nn'}$. These relations can be inverted to express the first few collision integrals in terms of the $U^l_{nn'}$, thus establishing a relationship between the collision integrals and integrals of the exchange kernel. The relations are as follows:

$$n_1\Omega^{(1,1)} = -\frac{1}{8}\frac{(1+\beta)}{\beta^{\frac{1}{2}}}\, U^1_{00} \,, \tag{2.51}$$

$$n_1\Omega^{(1,2)} = \frac{1}{8}\frac{(1+\beta)^2}{\beta^{\frac{3}{2}}}\, U^1_{10} - \frac{5}{16}\frac{(1+\beta)}{\beta^{\frac{1}{2}}}\, U^1_{00} \,, \tag{2.52}$$

$$n_1\Omega^{(2,2)} = \frac{1}{12}\frac{(1+\beta)^2}{\beta}\, U^2_{00} - \frac{5}{12}\frac{(1+\beta)}{\beta^{\frac{1}{2}}}\, U^1_{00} \,, \tag{2.53}$$

where

$$\beta = m_1/m_2 \,. \tag{2.54}$$

These expressions, together with the expressions relating the collision integrals to the direct effective cross sections as calculated in I, can be used to express the first few $\sigma_e\binom{ln}{ln'}$ in terms of the first few $\sigma_d\binom{ln}{ln'}$ as

$$\sigma_e\binom{10}{10} = -\beta^{\frac{1}{2}}\,\sigma_d\binom{10}{10} \,,$$

$$\sigma_e\binom{11}{10} = -\beta^{\frac{3}{2}}\,\sigma_d\binom{11}{10} \,,$$

$$\sigma_e\binom{20}{20} = \beta[\sigma_d\binom{20}{20} - 2\sigma_d\binom{10}{10}] \,.$$

Method 2. Following a procedure similar to the one used in I, we can provide an alternative set of expressions relating the collision integrals to integrals of the exchange kernel through the quantity G^e_{ql} defined as

$$G^e_{ql} = -\int W_2(\mathbf{v}_2)\, c_2^{2q}\, |\mathbf{v}_2 - \mathbf{v}_1|^{2l}\,[K_e(\mathbf{v}_2 \to \mathbf{v}_1) - J(\mathbf{v}_2,\mathbf{v}_1)]\, d^3v_1\, d^3v_2 \,. \tag{2.55}$$

In Appendix B we show that G^e_{ql} can be written as

$$G^e_{ql} = n_1\int g\, W_r(\mathbf{g})\, R_q(\mathbf{g})\, F_l(g)\, d^3g \,, \tag{2.56}$$

where

$$W_r(\mathbf{g}) = (\pi u_r^2)^{-3/2}\exp(-g^2/u_r^2) \,, \tag{2.57}$$

$$R_q(\mathbf{g}) = \int \left|\mathbf{y} + \frac{\mu}{m_2}\,\mathbf{g}\right|^{2q} W_T(\mathbf{y})\, d^3y \ , \tag{2.58}$$

with

$$W_T(\mathbf{y}) = (\pi u_T^2)^{-3/2} \exp(-y^2/u_T^2) \ , \tag{2.59}$$

$$u_T = \left(\frac{2k_BT}{m_1+m_2}\right)^{1/2} \ ,$$

and

$$F_l(g) = g^{2l}\left(\frac{\beta}{1+\beta}\right)^{2l} \sum_{k=1}^{l} \binom{l}{k} (1+\beta^2)^{l-k} (2\beta)^k Q^{(k)}(g) \ . \tag{2.60}$$

Expanding Eq. (2.56) for specific l and q and integrating over $\mathbf{y}$ we can write G^e_{ql} in terms of the collision integrals [Eq. (2.49)]:

$$G^e_{01} = 16 n_1 u_2^2 \frac{1}{1+\beta}\,\Omega^{(1,1)} \ , \tag{2.61}$$

$$G^e_{02} = 32 n_1 u_2^4 \frac{1}{(1+\beta)^2}\left[(\beta + 1/\beta)\Omega^{(1,2)} + \Omega^{(2,2)}\right] \ , \tag{2.62}$$

$$G^e_{11} = 16 n_1 u_2^4 \frac{1}{(1+\beta)^2}\left(\tfrac{3}{2}\,\Omega^{(1,1)} + \beta\,\Omega^{(1,2)}\right) \ , \tag{2.63}$$

and these can be inverted to give the collision integrals in terms of the G^e_{ql}:

$$n_1\Omega^{(1,1)} = \tfrac{1}{16}\,(1+\beta) u_2^{-2}\, G^e_{01} \ , \tag{2.64}$$

$$n_1\Omega^{(1,2)} = \frac{1}{16}\,\frac{(1+\beta)^2}{\beta} u_2^{-4}\, G^e_{02} - \frac{3}{32}\,\frac{(1+\beta)}{\beta} u_2^{-2}\, G^e_{01} \ , \tag{2.65}$$

$$n_1\Omega^{(2,2)} = \frac{1}{32}\,(1+\beta)^2 u_2^{-4}\, G^e_{02} - (1+\beta^2)\left[\frac{1}{16}\left(\frac{1+\beta}{\beta}\right)^2 u_2^{-4}\, G^e_{11} - \frac{3}{32}\,\frac{(1+\beta)}{\beta}\, u_2^{-2}\, G^e_{01}\right] \ . \tag{2.66}$$

We now have two different sets of expressions for the collision integrals in terms of integrals over the exchange kernel. Using a kernel derived directly from an interaction potential, the two sets of expressions, Eqs. (2.51)–(2.53) and Eqs. (2.64)–(2.66), must be identical. However, for a phenomenological kernel, there is no guarantee that the two sets should be the same.

Since each of the collision integrals is related to a specific type of transport process, through the transport coefficients, they are excellent candidates for setting the adjustable parameters for phenomenological kernels, (see Sec. IV). How well the parameters will work may be indicated by comparing Eqs. (2.51)–(2.53) and Eqs. (2.64)–(2.66) when evaluated using the phenomenological kernel. We use the notation $\Omega(U)$ to indicate an $\Omega^{(k,s)}$ calculated from the $U^l_{nn'}$, Eqs. (2.51)–(2.53), and $\Omega(G)$ to indicate an $\Omega^{(k,s)}$ calculated from the G^e_{ql}, Eqs. (2.64)–(2.66).

III. THE HARD-SPHERE AND PHENOMENOLOGICAL EXCHANGE KERNELS

We next consider two specific exchange kernels, one calculated using a hard-sphere interaction potential, and the other a phenomenological kernel similar to the Keilson-Storer direct kernel.

A. Hard-sphere exchange kernel

The differential cross section for hard-sphere scattering is $\sigma(g,\Omega) = \sigma/4\pi$ where $\sigma = \pi(r_1+r_2)^2$ and r_1 and r_2 are the radii of the two hard spheres undergoing a collision. Integrating Eq. (2.12) with this expression for $\sigma(g,\Omega)$ we get

$$K_e(\mathbf{v}_2' \to \mathbf{v}_1) = \frac{n_1\sigma(1+\beta)^2}{4\pi^{3/2}u_1}\,\frac{1}{P}\left[\exp\left(\frac{-(P-S)^2}{(1-\beta)^2u_1^2}\right) - \exp\left(\frac{-(P+S)^2}{(1-\beta)^2u_1^2}\right)\right] \ , \tag{3.1}$$

with $\beta = m_1/m_2$, $P = |\mathbf{v}_2' - \beta\mathbf{v}_1|$ and $S = |\mathbf{v}_2' - \mathbf{v}_1|$. Since the kernel Eq. (3.1) is derived from a specific interaction potential, it satisfies Eqs. (2.17) and (2.31).

For comparison, we write the direct hard-sphere kernel [8]:

$$K_d(\mathbf{v}_1' \to \mathbf{v}_1) = \frac{n_2\sigma(1+\beta)^2}{4\pi^{3/2}u_2}\,\frac{1}{S}\exp\left[-\frac{(1+\beta)^2}{4\beta}\left(S + \frac{2\hat{\mathbf{S}}\cdot\mathbf{v}_1'}{1+\beta}\right)^2 \Big/ u_1^2\right] \ , \tag{3.2}$$

where $\mathbf{S} = \mathbf{v}_1' - \mathbf{v}_1$, $\beta = m_1/m_2$.

It is noted that the direct and exchange kernels have the same form when $m_1 = m_2$. This is expected; when $m_1 = m_2$ the exchange kernel can be obtained from the direct kernel with the substitution $\sigma(g,\chi) \rightarrow \sigma(g,\pi-\chi)$. For hard-sphere scattering, the differential cross section is independent of scattering angle, so the exchange and direct kernels are the same if $m_1 = m_2$.

B. Phenomenological exchange kernel

A realistic exchange kernel should satisfy detailed balance Eq. (2.31) and the conservation of probability Eq. (2.17). These conditions are satisfied by a kernel of the form:

$$K_e(\mathbf{v}_2' \rightarrow \mathbf{v}_1) = \Gamma_{\mathrm{KS}}(\pi\omega^2)^{-3/2} \exp[-(\mathbf{v}_1 - \alpha_e \mathbf{v}_2')^2/\omega^2] \ , \tag{3.3}$$

where

$$\omega^2 = (1 - \beta\alpha_e^2)\, u_1^2 \ . \tag{3.4}$$

$\beta = m_1/m_2$, and α_e and Γ_{KS} are adjustable parameters. The parameter Γ_{KS} is the velocity-independent collision rate of P atoms and the parameter α_e is a measure of the strength of the collision and depends upon the ratio of the A-P masses, as will be shown later. Physical considerations impose limits on the value of α_e: for all values of β, $0 \le \beta\alpha_e^2 \le 1$.

This kernel is diagonal in the basis functions $\psi_{1q}^{ln}(\mathbf{v}_1)$ and $\psi_{2q'}^{l'n'}(\mathbf{v}_2')$ (see Appendix C), i.e.,

$$\int W_2(\mathbf{v}_2')\psi_{2q'}^{l'n'}(\mathbf{v}_2')K_e(\mathbf{v}_2' \rightarrow \mathbf{v}_1)\psi_{1q}^{ln}(\mathbf{v}_1)\, d^3v_2'\, d^3v_1$$

$$= \Gamma_{\mathrm{KS}}(\beta^{\frac{1}{2}}\alpha_e)^{2n+1}\, \delta_{ll'}\, \delta_{nn'}\, \delta_{qq'} \ . \tag{3.5}$$

This kernel is similar in form to the Keilson-Storer kernel [11] and becomes the same as the direct Keilson-Storer kernel for $\beta = 1$, with $\alpha_e = \alpha_d$. For comparison,the direct Keilson-Storer kernel is:

$$K_e(\mathbf{v}_2' \rightarrow \mathbf{v}_1) = \Gamma_{\mathrm{KS}}(\pi\omega^2)^{-3/2} \exp[-(\mathbf{v}_1 - \alpha_d \mathbf{v}_1')^2/\omega^2] \ , \tag{3.6}$$

where $\omega^2 = (1 - \alpha_d^2)\, u_1^2$.

C. Collision rate

We first calculate the collision rates for the P atoms, in the exchange collision, using Eq. (2.17), and the collision rate for the A atoms in the direct collision using Eq. (2.10), and the hard-sphere interaction potential. The collision rates for the Keilson-Storer kernels are adjustable parameters; they are not derived from the collisional dynamics.

The hard-sphere collision rates are

$$\Gamma_2(v_2) = \frac{1}{2}\frac{1}{(1+\beta)^{\frac{1}{2}}}\, \Gamma_{\mathrm{HS}}^{(2)}\, h_1(x_2) \ , \tag{3.7}$$

$$\Gamma_1(v_1) = \frac{1}{2}\left(\frac{\beta}{1+\beta}\right)^{\frac{1}{2}} \Gamma_{\mathrm{HS}}^{(1)}\, h_1(x_1) \ , \tag{3.8}$$

where $x_1 = \beta^{-\frac{1}{2}}\, v_1/u_1$, $x_2 = \beta^{\frac{1}{2}}\, v_2/u_2$,

$$h_1(x) = e^{-x^2} + (2x + 1/x)\frac{\sqrt{\pi}}{2}\mathrm{erf}(x) \ , \tag{3.9}$$

$$\Gamma_{\mathrm{HS}}^{(1,2)} = \frac{2}{\sqrt{\pi}}\, u_r\, \sigma\, n_{2,1} \ , \tag{3.10}$$

and $\mathrm{erf}(x) = (2/\sqrt{\pi})\int_0^x e^{-t^2}\, dt$. Both of these expressions, Eqs. (3.7) and (3.8), are constant as a function of β when v_1/u_1 and v_2/u_2 take their equilibrium values: $(v_1/u_1)^2 = (v_2/u_2)^2 = \frac{3}{2}$. We also note that the expressions are identical under the substitutions $\beta \rightarrow 1/\beta$ and $v_2/u_2 \rightarrow v_1/u_1$.

D. Persistence of velocity

After a collision, an atom will generally have a velocity component that lies in the direction of its velocity before the collision, a phenomenon known as the persistence of velocity. We generalize this notion to include a persistence of velocity in the exchange collision.

For direct collisions the persistence of velocity is a measure of an A atom's memory of its velocity before the collision; in exchange collisions it is a measure of the transfer of information of velocity from P atoms to A atoms. The persistence of velocity is defined as

$$\langle \mathbf{v}_1 \rangle_{d,e} = \frac{1}{\Gamma_{1,2}(v_{1,2}')} \int \mathbf{v}_1 K_{d,e}(\mathbf{v}_{1,2}' \rightarrow \mathbf{v}_1)\, d^3v_1 \ . \tag{3.11}$$

In carrying out the integration of Eq. (3.11) using the direct and exchange Keilson-Storer kernels Eqs. (3.6) and (3.3) we obtain

$$\langle \mathbf{v}_1 \rangle_d^{\mathrm{KS}} = \alpha_d\, \mathbf{v}_1' \ , \tag{3.12}$$

$$\langle \mathbf{v}_1 \rangle_e^{\mathrm{KS}} = \alpha_e\, \mathbf{v}_2' \ , \tag{3.13}$$

As is well known [12], and seen here, the parameter α_d is associated with the persistence of velocity. We also see that α_e is associated with the persistence of velocity in the exchange process. Thus one way to fix the value of α_e is to set it equal to the corresponding expression for the persistence of velocity in the hard-sphere case, as is often done for α_d [4].

Carrying out the integration for the hard sphere interaction we get

$$\langle \mathbf{v}_1 \rangle_d^{\mathrm{HS}} = \frac{\beta}{1+\beta}\left(1 - \frac{1}{\beta}\frac{h_2(x_1)}{h_1(x_1)}\right) \mathbf{v}_1' \ , \tag{3.14}$$

$$\langle \mathbf{v}_1 \rangle_e^{\mathrm{HS}} = \frac{1}{1+\beta}\left(1 - \beta\frac{h_2(x_2)}{h_1(x_2)}\right) \mathbf{v}_2' \ , \tag{3.15}$$

where $x_1 = \beta^{-\frac{1}{2}}\, v_1'/u_1$, $x_2 = \beta^{\frac{1}{2}}\, v_2'/u_2$,

$$h_2(x) = \frac{1}{2x^2}\left(e^{-x^2} + (2x - 1/x)\frac{\sqrt{\pi}}{2}\mathrm{erf}(x)\right) , \tag{3.16}$$

and $h_1(x)$ is given above, Eq. (3.9). Again, these expressions are identical under the substitutions $\beta \to 1/\beta$ and $v_2'/u_2 \to v_1'/u_1$. We consider these expressions for the limits $m_1 \ll m_2$ and $m_2 \ll m_1$.

In the following expansion of Eq. (3.14) in the limit $\beta \to 0$, we require $v_1'/u_1 \gg \sqrt{\beta}$ or $|x_1| \gg 1$. One finds

$$\langle \mathbf{v}_1 \rangle_d^{\mathrm{HS}} \simeq \beta[1 - (u_1/v_1')^2]\mathbf{v}_1' . \tag{3.17}$$

For the expansion of Eq. (3.15) in the limit $\beta \to 0$ we require $v_2'/u_2 \ll 1/\sqrt{\beta}$ or $|x_2| \ll 1$ to get

$$\langle \mathbf{v}_1 \rangle_e^{\mathrm{HS}} \simeq \left(1 - \frac{4}{3}\beta\right)\mathbf{v}_2' . \tag{3.18}$$

These are expected results; with $m_2 \gg m_1$ the collision is strong and the A atom loses nearly all memory of its velocity before the the collision. In the exchange process, however, nearly all the information about the P atom's initial velocity is transferred to the A atom distribution. The A atom distribution is offset by an amount v_2' in the direction $\hat{\mathbf{v}}_2'$.

In the limit that $\beta \to \infty$ [with $\sqrt{\beta} \gg v_1'/u_1$ or $|x_1| \ll 1$ in Eq. (3.14) and $v_2'/u_2 \gg 1/\sqrt{\beta}$ or $|x_2| \gg 1$ in Eq. (3.15)] one finds

$$\langle \mathbf{v}_1 \rangle_d^{\mathrm{HS}} \simeq \left(1 - \frac{4}{3}\frac{1}{\beta}\right)\mathbf{v}_1' , \tag{3.19}$$

$$\langle \mathbf{v}_1 \rangle_e^{\mathrm{HS}} \simeq \frac{1}{\beta}[1 - (u_2/v_2')^2]\mathbf{v}_2' . \tag{3.20}$$

Again this result is expected. With $m_1 \gg m_2$ the active atoms undergo very weak collisions. The velocity does not change much and the A atom has nearly complete memory of its velocity before the collision. Also, there is very little transfer of information from the P atom to the A atom distribution. In this limit the P atoms have little effect on the A atom distribution.

One may fix the value of Γ_{KS} by setting

$$\Gamma_{\mathrm{KS}} = \Gamma_{\mathrm{HS}} \tag{3.21}$$

and the value of α_e by setting

$$\langle \mathbf{v}_1 \rangle_e^{\mathrm{KS}} = \langle \mathbf{v}_1 \rangle_e^{\mathrm{HS}} \tag{3.22}$$

resulting in

$$\alpha_e^{\mathrm{HS}} = \frac{1}{1+\beta}\left(1 - \beta\frac{h_2(\beta^{\frac{1}{2}} v_2/u_2)}{h_1(\beta^{\frac{1}{2}} v_2/u_2)}\right) . \tag{3.23}$$

In using this expression, one must also choose a value for v_2/u_2. Often the experimental situation will determine what value is to be used. Here, we generally will choose $(v_2/u_2)^2 = \frac{3}{2}$, which is its average value for an equilibrium distribution.

IV. CALCULATION OF THE COLLISION INTEGRALS FOR HARD-SPHERE AND PHENOMENOLOGICAL KERNELS

In using the phenomenological exchange kernel, one must choose an appropriate α_e and Γ_{KS}. One way, as mentioned previously, is to use the hard-sphere persistence of velocity and average collision rate. In the following we will consider the role of the collision integrals in determining the suitability of a particular set of parameters.

The collision integrals are the link between the microscopic properties of a gas—the interaction between pairs of individual molecules—and the macroscopic properties of the gas as characterized by the transport coefficients [14,16]. Therefore a particular collision integral will be appropriate in determining the suitability of a phenomenological kernel when the process under investigation is related to a particular transport process. For example, if diffusive processes give rise to the exchange collisions, then $\Omega^{(1,1)}$ may be appropriate for determining the parameters since it is related to the coefficient of diffusion. Some justification for the manner of choosing α_e is achieved if the value of α_e gives the same value for $\Omega^{(k,s)}$ as calculated by the two methods described above [Eqs. (2.51), (2.53) and Eqs. (2.64), (2.66)]. In the following we calculate the $\Omega^{(k,s)}$ by the two methods and comparisons are made.

A. Calculation of the collision integrals

We first calculate the $\mathrm{U}_{nn'}^l$ and the G_{ql}^e for the hard-sphere and phenomenological kernels and then calculate the $\Omega^{(k,s)}$ by the two methods [Eqs. (2.51), (2.53) and Eqs. (2.64), (2.66)].

Using Eq. (2.42) for the $\mathrm{U}_{nn'}^l$ we obtain, for a hard-sphere interaction,

$$\mathrm{U}_{00}^1 = -2\frac{\beta^{\frac{1}{2}}}{1+\beta}\Gamma_{\mathrm{HS}}^{(2)} , \tag{4.1}$$

$$\mathrm{U}_{10}^1 = \frac{\beta^{\frac{3}{2}}}{(1+\beta)^2}\Gamma_{\mathrm{HS}}^{(2)} , \tag{4.2}$$

$$\mathrm{U}_{00}^2 = -4\frac{\beta}{1+\beta}\Gamma_{\mathrm{HS}}^{(2)} , \tag{4.3}$$

with

$$\Gamma_{\mathrm{HS}}^{(2)} = \frac{2}{\sqrt{\pi}} u_r \sigma n_1 , \tag{4.4}$$

the hard-sphere velocity averaged collision rate.

Using Eq. (2.55) for the G_{ql}^e we get, for a hard-sphere interaction,

$$\mathrm{G}_{01}^e = 4\frac{1}{1+\beta} u_2^2 \Gamma_{\mathrm{HS}}^{(2)} , \tag{4.5}$$

$$\mathrm{G}_{11}^e = 6\frac{1}{1+\beta}\left(1 + \frac{\beta}{1+\beta}\right) u_2^4 \Gamma_{\mathrm{HS}}^{(2)} , \tag{4.6}$$

$$G^e_{02} = 8\left[\frac{3}{\beta} - \frac{4}{(1+\beta)^2}\right] u_2^4\,\Gamma^{(2)}_{\rm HS} \ . \tag{4.7}$$

Using the $U^l_{nn'}$ and Eqs. (2.51)–(2.53) or the G^e_{ql} and Eqs. (2.64)–(2.66), we get, in both cases,

$$n_1\Omega^{(1,1)} = \tfrac{1}{4}\Gamma^{(2)}_{\rm HS} \ , \tag{4.8}$$

$$n_1\Omega^{(1,2)} = \tfrac{3}{4}\Gamma^{(2)}_{\rm HS} \ , \tag{4.9}$$

$$n_1\Omega^{(2,2)} = \tfrac{1}{2}\Gamma^{(2)}_{\rm HS} \ , \tag{4.10}$$

which agrees with the previously derived results in I for the direct kernel.

To evaluate the $U^l_{nn'}$ and the G^e_{ql} with the Keilson-Storer kernel we must also choose a phenomenological $J(\mathbf{v}_2,\mathbf{v}_1)$. A reasonable choice is

$$J(\mathbf{v}_2,\mathbf{v}_1) = \Gamma_{\rm KS}\, W_1(\mathbf{v}_1) \ . \tag{4.11}$$

Note that this satisfies Eqs. (2.19)–(2.22) and detailed balance, Eq. (2.23).

We now obtain expressions for the collision integrals in terms of the adjustable parameters. The $U^l_{nn'}$ are diagonal matrix elements of the phenomenological collision operator. Using Eqs. (3.3), (4.11), (2.42), and (3.5) we obtain

$$U^l_{nn'} = (\Gamma_{\rm KS}/B^2_{ln})\,[\delta_{n0}\,\delta_{l0} - (\beta^{\frac{1}{2}}\alpha_e)^{2n+l}]\,\delta_{nn'} \tag{4.12}$$

or

$$U^1_{00} = -\tfrac{3}{2}\beta^{\frac{1}{2}}\,\alpha_e\,\Gamma_{\rm KS} \ , \tag{4.13}$$

$$U^1_{10} = 0 \ , \tag{4.14}$$

$$U^2_{00} = -\frac{15}{4}\beta\,\alpha_e^2\,\Gamma_{\rm KS} \ . \tag{4.15}$$

One evaluates the G^e_{ql} with Eqs. (3.3), (4.11), and (2.55) to get

$$G^e_{01} = 3\alpha_e\,u_2^2\,\Gamma_{\rm KS} \ , \tag{4.16}$$

$$G^e_{11} = \frac{3}{2}(5-\alpha_e)\alpha_e\,u_2^4\,\Gamma_{\rm KS} \ , \tag{4.17}$$

$$G^e_{02} = 15(1+1/\beta-\alpha_e)\alpha_e\,u_2^4\,\Gamma_{\rm KS} \ . \tag{4.18}$$

Using the formulas Eqs. (2.51)–(2.53) we get a first set of expressions for the collision integrals:

$$n_1\Omega^{(1,1)}(U) = \tfrac{3}{16}(1+\beta)\alpha_e\,\Gamma_{\rm KS} \ , \tag{4.19}$$

$$n_1\Omega^{(1,2)}(U) = \tfrac{15}{32}(1+\beta)\alpha_e\,\Gamma_{\rm KS} \ , \tag{4.20}$$

$$n_1\Omega^{(2,2)}(U) = \tfrac{5}{16}(1+\beta)[2-(1+\beta)\alpha_e]\alpha_e\,\Gamma_{\rm KS} \ . \tag{4.21}$$

With the substitution

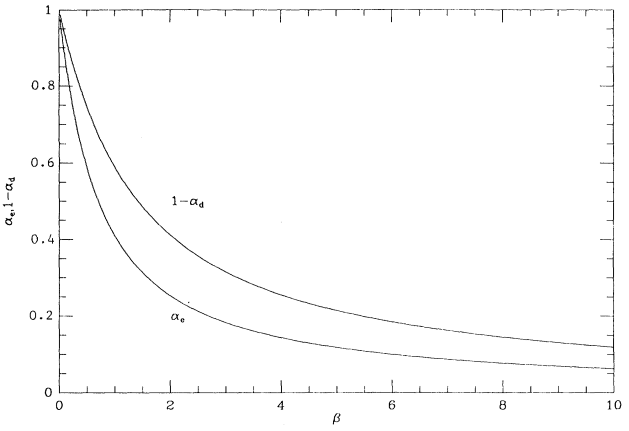

FIG. 1. α_e and $1-\alpha_d$ as obtained via the persistence of velocity as a function of $\beta = m_1/m_2$. The hard-sphere interaction is used, and $(v_1/u_1)^2 = (v_2/u_2)^2 = \frac{3}{2}$.

$$\alpha_e = 1 - \alpha_d \tag{4.22}$$

these expressions for the $\Omega(U)$ are identical to those that were calculated in I with the $\sigma_d(^{l\,n}_{l\,n'})$. Thus the expressions for the $\Omega^{(k,s)}$ give a relationship between the parameter α_d for the direct Keilson-Storer with the parameter α_e for the exchange Keilson-Storer. However, relationship Eq. (4.22) is not consistent with the values of α_e and α_d obtained from the persistence of velocity. For example, α_e and α_d calculated from Eqs. (3.19) and (3.20), in the limit $\beta \to \infty$ do not satisfy Eq. (4.22). Furthermore, substitution of $\alpha_e = \alpha_e^{\rm HS}$ (in the limit $\beta \to \infty$) into the expression for $\Omega^{(1,1)}$, Eq. (4.19), does not give the correct hard sphere result, Eq. (4.8), while substitution of $\alpha_e = 1 - \alpha_d^{\rm HS}$ does give the correct result. This indicates that the persistence of velocity may not be the best method for setting α_e. In Fig. 1 we show a plot of $\alpha_e^{\rm HS}$ and $1-\alpha_d^{\rm HS}$, with $(v_1/u_1)^2 = (v_2/u_2)^2 = \frac{3}{2}$, as a function of β. The curves show a significant difference for most values of β.

Using the formulas Eqs. (2.64)–(2.66) we get a second set of expressions for the collision integrals:

$$n_1\Omega^{(1,1)}(G) = \tfrac{3}{16}(1+\beta)\alpha_e\,\Gamma_{\rm KS} \ , \tag{4.23}$$

$$n_1\Omega^{(1,2)}(G) = \tfrac{3}{32}(1+\beta)\{5+(1/\beta)[2-(1+\beta)\alpha_e]\}\alpha_e\,\Gamma_{\rm KS} \ , \tag{4.24}$$

$$n_1\Omega^{(2,2)}(G) = \tfrac{3}{32}(4-1/\beta^2)(1+\beta)[2-(1+\beta)\alpha_e]\alpha_e\,\Gamma_{\rm KS} \ . \tag{4.25}$$

B. Comparison of the $\Omega(U)$ and the $\Omega(G)$

The expressions for $\Omega^{(1,1)}$ are identical using both methods. This is expected; for any kernel that satisfies

detailed balance, it can be shown using Eqs. (2.43) and (2.55) that

$$u_2^{-2} G_{01}^e = -2\beta^{-\frac{1}{2}} U_{00}^1 .$$

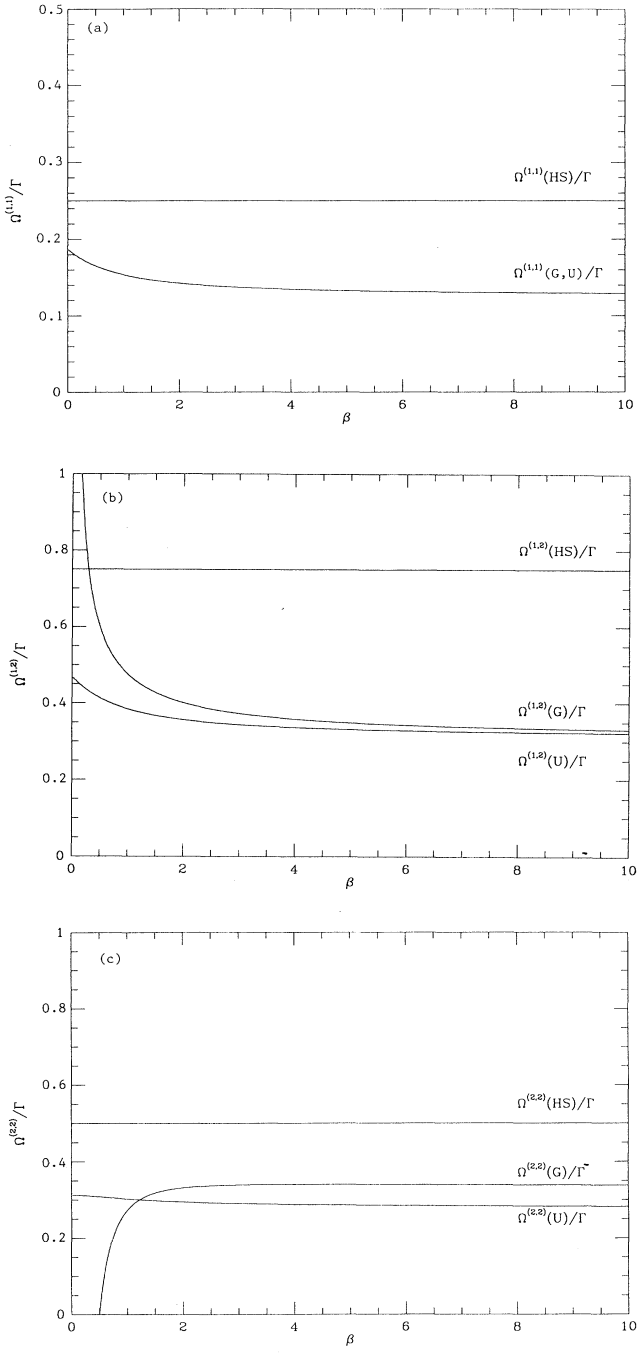

FIG. 2. The collision integrals divided by the average collision rate as a function of m_1/m_2. The $\Omega(U)$ have been calculated with the $U_{nn'}^l$ and the $\Omega(G)$ have been calculated with the G_{ql}^e. Also shown are the values for Ω(HS), the collision integrals for hard-sphere interaction. (a) is $\Omega^{(1,1)}$, (b) is $\Omega^{(1,2)}$, and (c) is $\Omega^{(2,2)}$.

Using Eqs. (2.51) and (2.61) we see that

$$\Omega^{(1,1)}(U)/\Omega^{(1,1)}(G) = -2\beta^{-\frac{1}{2}} U_{00}^1/u_2^{-2} G_{01}^e$$

so

$$\Omega^{(1,1)}(U) = \Omega^{(1,1)}(G) .$$

In addition, $\Omega^{(1,1)}$ is guaranteed to be finite for all β for a kernel that satisfies detailed balance since $\Omega^{(1,1)}(\beta) = \Omega^{(1,1)}(1/\beta)$ must hold owing to the fact that the diffusion coefficient $D_{12} = D_{21}$.

The other collision integrals have very different forms in the two cases. To compare them, then, one must choose a value for α_e . We choose the persistence of velocity to set α_e, Eq. (3.23), with $(v_2/u_2)^2 = \frac{3}{2}$. Figures 2(a), 2(b), and 2(c) are plots of $\Omega^{(1,1)}$, $\Omega^{(1,2)}$, and $\Omega^{(2,2)}$, respectively, as obtained by the two methods as a function of β . On these plots the constant value for the hard sphere $\Omega^{(k,s)}$ is also shown.

For $\beta \geq 1$, the two methods give remarkably similar values, differing at most by 10%, and showing a relatively constant value as β is increased. For $0 < \beta \leq 1$, the $\Omega^{(k,s)}(U)$ show only a slight deviation from the constant value as $\beta \to 0$. However, $\Omega^{(1,2)}(G)$ and $\Omega^{(2,2)}(G)$ diverge for $\beta \to 0$, and these divergences persist for any physically realistic α_e . The reason for the divergences has to do with the way in which the G_{ql}^e are defined and the fact that the Keilson-Storer collision rate is independent of velocity.

The $\Omega^{(k,s)}(U)$ are finite and approximately constant but their values differ from those of the hard sphere by as much as 50% when $\Gamma_{KS} = \Gamma_{HS}$. This can be adjusted by altering the phenomenological collision rate.

V. EXPERIMENTAL MEASUREMENT OF THE LONGITUDINAL EXCHANGE KERNEL

We consider here an experiment in which the exchange kernel was effectively measured [9]. To compare the results of this experiment with the preceding analysis, we first calculate the longitudinal exchange kernel for both a hard-sphere interaction and the Keilson-Storer kernel. We compare plots of the two longitudinal kernels for several mass ratios.

A. Longitudinal exchange kernel

In using collision kernels to fit experimental data, one is often interested in the one-dimensional longitudinal exchange kernel rather than the full three-dimensional kernel Eq. (2.12) because the laser picks out a velocity subclass along one dimension only. The longitudinal exchange kernel is obtained from Eq. (2.12) by averaging over an initial P atom transverse velocity distribution and summing over the A atom final transverse velocities. The initial P atom transverse distribution is assumed to be in equilibrium and is given by

$$W_{2t}(\mathbf{v}'_{2t}) = (\pi u_2^2)^{-1} \exp[-(v'_{2t}/u_2)^2] , \tag{5.1}$$

where $\mathbf{v}'_{2t} = \mathbf{v}'_2 - \hat{\mathbf{z}} v'_{2z}$ is the transverse velocity, with $\hat{\mathbf{z}}$ a unit vector in the z direction. The longitudinal exchange kernel is given by

$$\tilde{K}_e(v'_{2z} \rightarrow v_{1z}) = \int W_{2t}(\mathbf{v}'_{2t}) K_e(\mathbf{v}'_2 \rightarrow \mathbf{v}_1)\, d^2 v'_{2t}\, d^2 v_{1t} , \tag{5.2}$$

where $\mathbf{v}_{1t} = \mathbf{v}_1 - \hat{\mathbf{z}} v_{1z}$. Carrying out the integrations for the case of hard-sphere interaction we get

$$\tilde{K}_e(v'_{2z} \rightarrow v_{1z}) = \frac{n_1 \sigma}{4} \frac{1+\beta}{\beta^{\frac{1}{2}}} \times \left\{ e^{-[(v_{1z}/u_1)^2 - (v'_{2z}/u_2)^2]} \left[(1+\epsilon) + \alpha \operatorname{erf}\left(\frac{v_{1z} - \epsilon|1+\beta/1-\beta|k}{u_2} \right) - \alpha \operatorname{erf}(v'_{2z}/u_2) \right] + \beta^{\frac{1}{2}} \left[(1-\epsilon) + \alpha \operatorname{erf}(v_{1z}/u_1) - \alpha \operatorname{erf}\left(\frac{v'_{2z} - \epsilon|1+\beta/1-\beta|k}{u_1} \right) \right] \right\} , \tag{5.3}$$

where $\beta = m_1/m_2$, $\epsilon = (\beta - 1/|\beta - 1|)$, $k = v'_{2z} - v_{1z}$, and $\alpha = k/|k|$.

When $\beta = 1$, the expression Eq. (5.3) assumes the same form as the hard sphere longitudinal direct kernel as derived by Kol'chenko, Pukhov, and Shalagin [18]:

$$\tilde{K}_e(v'_{2z} \rightarrow v_{1z}) = \frac{1}{2} n_1 \sigma \{ e^{-[(v_{1z}/u_1)^2 - (v'_{2z}/u_2)^2]} [1 - \alpha \operatorname{erf}(v'_{2z}/u_2)] + [1 + \alpha \operatorname{erf}(v_{1z}/u_1)] \} . \tag{5.4}$$

The longitudinal form of the phenomenological kernel Eq. (3.3) is found using Eq. (5.2) to be

$$\tilde{K}_e(v'_{2z} \rightarrow v_{1z}) = \Gamma_{\mathrm{KS}} (\sqrt{\pi}\omega)^{-1} \exp[-(v_{1z} - \alpha_e v'_{2z})^2/\omega^2] . \tag{5.5}$$

Figures 3(a)–3(c) are plots of the hard-sphere [Eq. (5.3)] and the phenomenological [Eq. (5.5)] longitudinal exchange kernels as a function of v_{1z}. We have chosen in all cases $v'_{2z} = u_2/\sqrt{2} = \sqrt{\beta/2}\, u_1$, its most probable value in a thermal distribution. We have chosen the parameters for the Keilson-Storer kernel as follows: The collision rate $\Gamma_{\mathrm{KS}} = \Gamma_2(u_2/\sqrt{2})$ so that the curves are normalized, and α_e is its hard-sphere value given by Eq. (3.23). The three plots use mass ratios $\beta = m_1/m_2$ of 0.01, 1, and 10, respectively. The arrow indicates the velocity v'_{2z}. There is fair agreement between the two curves with greatest disagreement occurring for $m_1 \ll m_2$.

B. Excitation transfer

A situation in which the exchange kernel plays an important role is in an excitation exchange collision. This is a collision between an excited atom and a ground-state atom in which the excitation is transferred during the collision. A typical experiment might involve exciting a narrow velocity subclass of P atoms (donors) with a pump laser, then probing the A atoms (acceptors) with a weak probe beam after the excitation has been transferred from the P to the A atoms as a result of an excitation transfer collision. If an excited A atom is probed immediately after the transfer, before it has undergone another collision, its longitudinal velocity distribution will have precisely the same shape as the longitudinal exchange kernel divided by the longitudinal collision rate, with the value of $\mathbf{v}_2$ determined by the P atom subclass that is excited [see Eq. (2.30) and preceding discussion]. An excitation exchange experiment was carried out by Picqué and Vetter [9] using Kr atoms as the P atoms and Xe as the A atoms. Their experiment differed from the above description, however, in that the *hole* burned in the *lower* Kr level by interaction with a pump field is transferred to the Xe excited-state population, which is then probed. The signal is sensitive only to the perturbation in the Xe excited state due to the hole in the Kr donor state, and they found the width of the Xe perturbation to be only $\frac{2}{3}$ the inhomogeneous width.

The level scheme is shown in Fig. 4; the Kr levels a and b are coupled by the pump field χ_1, level a' of the Xe atom is populated by excitation exchange collisions with Kr atoms, and this population is monitored by the weak probe field χ_2 coupling Xe levels a' and c'. The Kr transition is between $4p^5 5s\,[3/2]_2$ and $4p^5 5p'\,[1/2]_1$ and the Xe transition between $5p^5 5d\,[1/2]_1$ and $5p^5 6p\,[1/2]_1$.

We can interpret their experiment in terms of the theory developed here. The donor (P atom) velocity distribution is $\rho_{aa}(\mathbf{v}'_2)$, and the acceptor (A atom) velocity distribution is $\rho_{a'a'}(\mathbf{v}_1)$. (In the following we associate the subscript 1 with the acceptor population and the subscript 2 with the donor population.) We write the density-matrix equation of motion for $\rho_{a'a'}(\mathbf{v}_1)$ as (neglecting the effect of the probe field χ_2)

$$\frac{d}{dt}\rho_{a'a'}(\mathbf{v}_1) = -[\Gamma_1^{\mathrm{tot}}(v_1) + \gamma_{\mathrm{sp}}]\rho_{a'a'}(\mathbf{v}_1) + \int K_e(\mathbf{v}'_2 \rightarrow \mathbf{v}_1)\rho_{aa}(\mathbf{v}'_2)\, d^3 v'_2 , \tag{5.6}$$

which in the steady state becomes

$$[\Gamma_1^{\rm tot}(v_1)+\gamma_{\rm sp}]\rho_{a'a'}(\mathbf{v}_1) = \int K_e(\mathbf{v}_2' \rightarrow \mathbf{v}_1)\rho_{aa}(\mathbf{v}_2')\, d^3v_2' \,, \tag{5.7}$$

where $\gamma_{\rm sp}$ is the rate of spontaneous emission from level

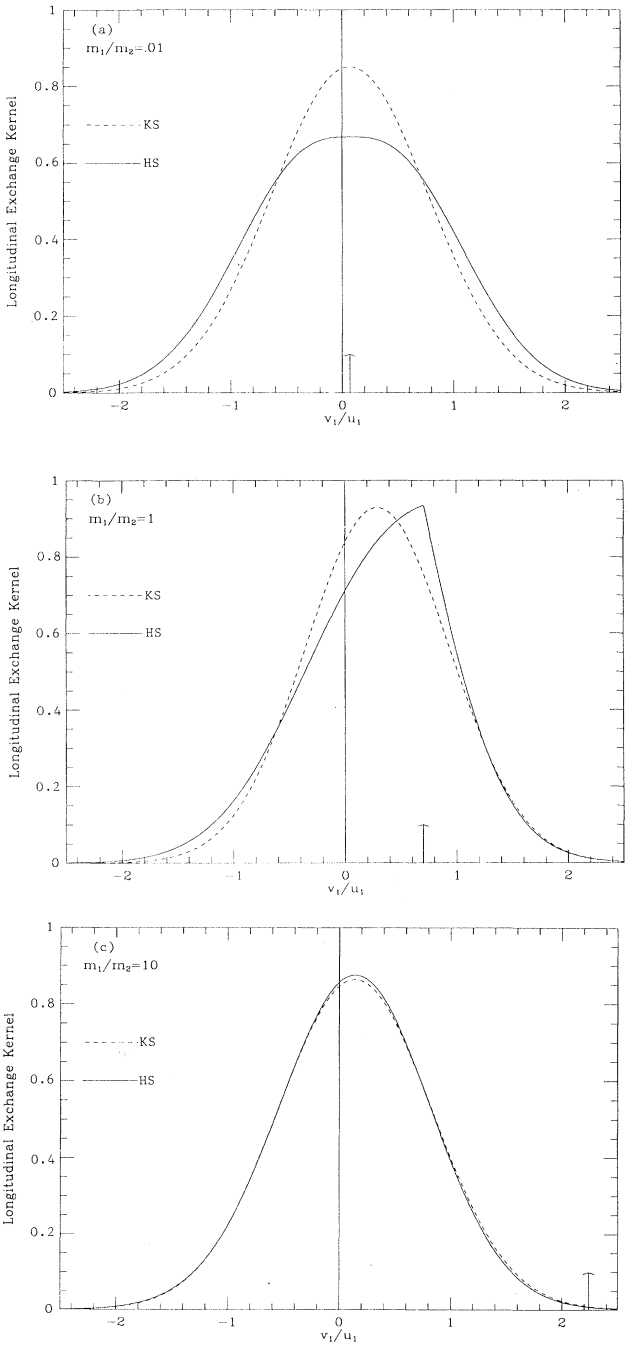

FIG. 3. The longitudinal exchange kernel as a function of the final A atom velocity. The initial P atom velocity is indicated by the arrow. Shown are both the hard-sphere and Kielson-Storer exchange kernels. (a) $m_1/m_2 = 0.01$, (b) $m_1/m_2 = 1$, and (c) $m_1/m_2 = 10$.

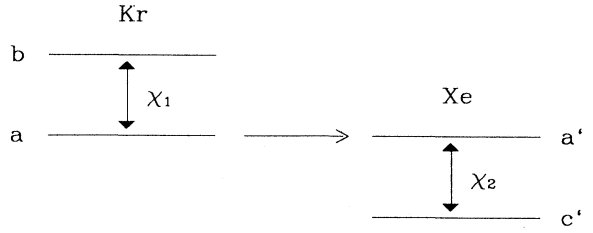

FIG. 4. The energy-level scheme for the excitation transfer experiment. Kr is the donor atom and Xe is the acceptor atom. Population is transferred from the Kr level b (not the ground state) to the Xe level a' as a result of excitation exchange collisions.

a'. This equation differs in two significant ways from Eq. (2.29): the inclusion of spontaneous emission as a relaxation mechanism, and a velocity-dependent collision rate that includes *all* collisions, so that $\Gamma_1^{\rm tot}(v_1) > \Gamma_1(v_1)$. The quantity $\Gamma_1(v_1)$ is defined by Eq. (2.14), and is the rate of excitation exchange collisions for an acceptor atom, while $\Gamma_1^{\rm tot}(v_1)$ is the *total* rate of collisions for an excited acceptor atom, and will equal the sum of the collision rates for collisions between an atom in $\rho_{a'a'}(\mathbf{v}_1)$ and atoms in each of the populated Kr levels (the density $n_2 \gg n_1$ so A-A collisions are ignored).

Under the conditions of the experiment, the spontaneous emission rate is always somewhat larger than the total collision rate [19]. This justifies the fact that we do not include the direct collision kernel in the density matrix equation of motion—the atoms in $\rho_{a'a'}(\mathbf{v}_1)$ will decay away before undergoing a collision.

The population of level a is given by

$$\rho_{aa}(\mathbf{v}_2') = n_2' W_2(\mathbf{v}_2) + \phi_2(\mathbf{v}_2') \,, \tag{5.8}$$

where the unperturbed population density of level a is $n_2' = f n_2$, where n_2 is the number density of Kr atoms and f is the fraction that are in level a. The perturbation in level a is

$$\phi_2(\mathbf{v}_2') = -n_2' W_2(\mathbf{v}_2) \frac{I\Gamma_{ab}^2}{(\Delta - k_1 v_{2z}')^2 + \Gamma_{ab}^2} \,, \tag{5.9}$$

where I is the dimensionless intensity, Γ_{ab} is the dephasing rate, Δ is the field detuning from resonance, $k_1 v_{2z}'$ is the Doppler shift for an atom with velocity $\mathbf{v}_2'$, and k_1 is the wave vector of the pump field, directed in the $\hat{\mathbf{z}}$ direction.

We first consider the acceptor population, $\rho_{a'a'}(\mathbf{v}_1)$, when the pump field χ_1 is off. In this case, $\rho_{aa}(\mathbf{v}_2') = n_2' W_2(\mathbf{v}_2)$. Using Eqs. (2.19) and (2.22) the right side of Eq. (5.7) becomes

$$\int K_e(\mathbf{v}_2' \rightarrow \mathbf{v}_1) W_2(\mathbf{v}_2)\, d^3v_2' = n_1 \Gamma_1(v_1) W_1(\mathbf{v}_1) \,. \tag{5.10}$$

The term on the right is the number of A atoms per

velocity interval entering the velocity subclass $\mathbf{v}_1$ of level a' per unit time. Using Eqs. (5.7) and (5.10) we can write the zero field a' population as

$$\rho_{a'a'}(\mathbf{v}_1) = n'_1(\mathbf{v}_1) \ , \tag{5.11}$$

with

$$n'_1(\mathbf{v}_1) = \frac{\Gamma_1(v_1)}{\Gamma_1^{\rm tot}(v_1) + \gamma_{\rm sp}} n_1 \, W_1(\mathbf{v}_1) \ , \tag{5.12}$$

where n_1 is the number density of Xe atoms. If spontaneous emission is negligible compared to the total collision rate, then the velocity dependence of $\Gamma_1(v_1)$ and $\Gamma_1^{\rm tot}(v_1)$ cancel and the distribution $n'_1(\mathbf{v}_1)$ is Maxwellian. However, if spontaneous emission is a significant relaxation mechanism, $n'_1(\mathbf{v}_1)$ will have a width *greater* than that of a thermal distribution. This can be understood by the fact that faster atoms undergo exchange collisions at a greater rate, but relaxation due to spontaneous emission is independent of speed.

When the pump field is on, we can write $\rho_{a'a'}(\mathbf{v}_1)$ as

$$\rho_{a'a'}(\mathbf{v}_1) = n'_1(\mathbf{v}_1) + \phi_1(\mathbf{v}_1) \ , \tag{5.13}$$

where $\phi_1(\mathbf{v}_1)$ is the perturbed part of the population. Due to the modulation technique used by Picqué and Vetter, the experiment measures the perturbation. We solve Eq. (5.7) for $\phi_1(\mathbf{v}_1)$ using Eqs. (5.8), (5.10), and (5.13) to get

$$[\Gamma_1^{\rm tot}(v_1)+\gamma_{\rm sp}]\phi_1(\mathbf{v}_1) = \int K_e(\mathbf{v}'_2 \rightarrow \mathbf{v}_1)\phi_2(\mathbf{v}'_2) \, d^3v'_2 \ . \tag{5.14}$$

The longitudinal form of this equation is obtained by summing over the transverse velocity of $\mathbf{v}_1$. We make the assumption that the transverse distributions remain in equilibrium so that

$$\phi_1(\mathbf{v}_1) = \phi_{1z}(v_{1z}) \, W_{1t}(\mathbf{v}_{1t}) \ , \tag{5.15}$$

$$\phi_2(\mathbf{v}'_2) = \phi_{2z}(v'_{2z}) \, W_{2t}(\mathbf{v}'_{2t}) \ , \tag{5.16}$$

where

$$W_{it}(\mathbf{v}_{it}) = (\pi u_i^2)^{-1} \exp[-(v_{it}/u_i)^2]$$

and $\mathbf{v}_{it} = \mathbf{v}_i - v_{iz}\hat{\mathbf{z}}$ with $i = 1, 2$. We want to compare the width of the perturbation $\phi_{1z}(v_{1z})$ and the width of the zero-field longitudinal distribution $n'_{1z}(v_{1z})$ to see the line narrowing effect.

Integrating both sides of Eq. (5.14) with respect to $\mathbf{v}_{1t}$ we get

$$\left(\int [\Gamma_1^{\rm tot}(v_1) + \gamma_{\rm sp}] W_{1t}(\mathbf{v}_{1t}) \, d^2v_{1t}\right) \phi_{1z}(v_{1z}) = \int \left(\int K_e(\mathbf{v}'_2 \rightarrow \mathbf{v}_1) W_{2t}(\mathbf{v}'_{2t}) \, d^2v'_{2t} \, d^2v_{1t}\right) \phi_{2z}(v'_{2z}) \, dv'_{2z} \ . \tag{5.17}$$

The term in large parentheses on the right is $\tilde{K}_e(v'_{2z} \rightarrow v_{1z})$, the longitudinal exchange kernel [Eq. (5.3)], and the first term in large parentheses on the left is the longitudinal collision rate, $\tilde{\Gamma}_1^{\rm tot}(v_{1z})$. The a' level perturbation can be written

$$\phi_{1z}(v_{1z}) = \frac{1}{\tilde{\Gamma}_1^{\rm tot}(v_{1z}) + \gamma_{\rm sp}} \times \int \tilde{K}_e(v'_{2z} \rightarrow v_{1z}) \, \phi_{2z}(v'_{2z}) \, dv'_{2z} \ . \tag{5.18}$$

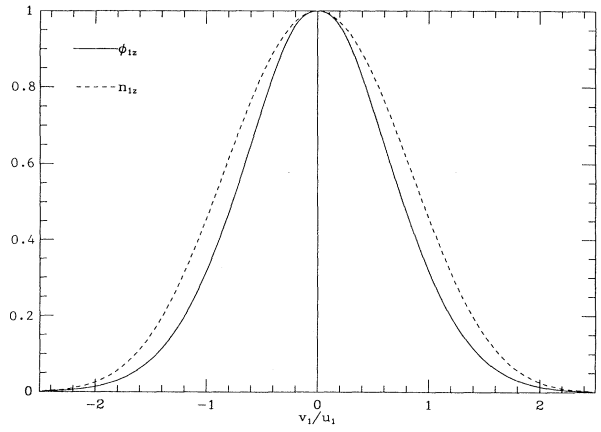

FIG. 5. A comparison of the hole in the a' population distribution, ϕ_{1z}, with the a' equilibrium distribution, n'_{1z}.

We obtain the zero-field longitudinal distribution $n'_{1z}(v_{1z})$ by summing over the transverse velocity of the zero-field distribution $n'_1(\mathbf{v}_1)$, to get

$$n'_{1z}(v_{1z}) = \frac{\tilde{\Gamma}_1(v_{1z})}{\tilde{\Gamma}_1^{\rm tot}(v_{1z}) + \gamma_{\rm sp}} n_1 \, W_{1z}(v_{1z}) \ . \tag{5.19}$$

We approximate the interaction between the Kr and Xe atoms as that of hard spheres and use the hard-sphere exchange kernel. In making this approximation, we expect that the calculated width of $\phi_{1z}(v_{1z})$ will be somewhat narrower than the actual width since the long-range part of the interaction is being ignored. A collision with a large impact parameter will change the velocities of the colliding atoms very little; when these large impact parameter collisions are significant and included in the expression for the exchange kernel (by including a long-range part in the interaction potential) the final A atom velocity distribution will tend towards a Maxwellian, and less of the donor perturbation will be transferred to the acceptor population.

Figure 5 is a plot of $\phi_{1z}(v_{1z})$ and of $n'_{1z}(v_{1z})$. We use $m_{\rm Xe}/m_{\rm Kr} = \beta = \frac{86}{136} = 0.63$. The width of $\phi_{1z}(v_{1z})$ is approximately $\frac{3}{4}$ that of $n'_{1z}(v_{1z})$, showing a slight narrowing. The degree of narrowing, however, differs with the results of Picqué and Vetter, who observed a width for $\phi_{1z}(v_{1z})$ equal to $\frac{2}{3}$ that of a *thermal* distribution. As yet, we can offer no explanation for this discrepancy.

VI. TRANSPORT COEFFICIENTS AND THE COLLISION KERNELS

To relate the transport coefficients to the collision kernels in a real binary gas we must include several other kernels in addition to the direct and exchange kernels discussed here. As already mentioned the correct Boltzmann operator for a binary gas includes a term involving A-A collisions. In addition, to fully characterize the gas, another equation describing the time evolution of the P atoms is needed. This equation involves two terms also: the effect of P-P collisions and the effect of P-A collisions on the P distribution. Each term can be analyzed as we have done in Sec. II, yielding a direct kernel and an exchange kernel for each term. There is a different set of collision integrals corresponding to each of the types of collision: A-P, A-A, and P-P, and the transport coefficients are related to sums of the collision integrals over the sets [14]. In certain limits, the contributions due to one of the types of collision will be negligible, but always there will be more kernels with non-negligible contributions to the bulk properties of the gas than the simplified treatment in Sec. II gives.

The usefulness in relating the collision integrals to transport coefficients comes from the fact that the transport coefficients are related to specific processes occurring in the gas. There are various techniques for calculating the transport coefficients from the collisional cross section; these techniques can be employed in setting the phenomenological parameters [14].

VII. CONCLUSION

We have shown that the direct and the exchange kernels can be obtained from the Boltzmann equation, and have given a physical interpretation of the exchange Boltzmann operator in terms of an excitation exchange collision.

Two independent methods of obtaining the collision integrals from integrals of the exchange kernel were developed.

The exchange kernel for a hard-sphere interaction potential was obtained and a phenomenological exchange kernel similar to the Keilson-Storer direct kernel was proposed. The collision rates and the persistence of velocity for these exchange kernels and the corresponding direct kernels were calculated.

A method for setting the adjustable parameters using the collision integrals was proposed, and a comparison of the collision integrals as calculated with a hard-sphere potential and a phenomenological kernel was made.

ACKNOWLEDGMENTS

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APPENDIX A

The relations between the $\mathrm{U}^l_{nn'}$ and the Chapman and Cowling square bracket integrals are

$$\mathrm{U}^1_{nn'} = \left[L_n^{\frac{3}{2}}(\mathcal{C}_1^2)\,\mathcal{C}_1\,,\, L_{n'}^{\frac{3}{2}}(\mathcal{C}_2^2)\,\mathcal{C}_2\right]_{12}\,,$$

$$\mathrm{U}^2_{nn'} = \frac{3}{2}\left[L_n^{\frac{5}{2}}(\mathcal{C}_1^2)\,\mathcal{C}_1\mathcal{C}_1\,,\, L_{n'}^{\frac{5}{2}}(\mathcal{C}_2^2)\,\mathcal{C}_2\mathcal{C}_2\right]_{12}\,,$$

where L_n^x are Laguerre polynomials, $\mathcal{C}_i = \mathbf{v}_i/u_i$ and $\mathcal{C}_i\mathcal{C}_i$ is a symmetric, traceless tensor.

APPENDIX B

In the following we show how the G^e_{ql} can be put into the form of Eq. (2.56) from which they can be easily expanded into linear combinations of collision integrals. We start with the definition of G^e_{ql}, Eq. (2.55), and express $K_e(\mathbf{v}_2' \to \mathbf{v}_1)$ and $J(\mathbf{v}_2, \mathbf{v}_1)$ using Eqs. (2.12) and (2.13), respectively. Writing $g\sigma(g) = \int (1/g')\,\sigma(g', \Omega)\delta(g' - g)\,d^3g'$ in the expression for $J(\mathbf{v}_2, \mathbf{v}_1)$, we get

$$\begin{aligned}\mathrm{G}^e_{ql} = &-n_1 \int v_2'^{2q}\,|\mathbf{v}_2' - \mathbf{v}_1|^{2l}\,W_2(\mathbf{v}_2')W_1(\mathbf{g}' - \mathbf{v}_2')\frac{1}{g'}\,\sigma(g', \Omega)\delta(g' - g)\\ &\times\delta\left(\frac{\mu}{m_1}\mathbf{g} + \frac{\mu}{m_2}\mathbf{g}' - (\mathbf{v}_2' - \mathbf{v}_1)\right)\,d^3g\,d^3g'\,d^3v_1\,d^3v_2'\\ &+n_1 \int v_2^{2q}\,|\mathbf{v}_2 - \mathbf{v}_1|^{2l}\,W_2(\mathbf{v}_2)W_1(\mathbf{v}_1)\frac{1}{g'}\,\sigma(g', \Omega)\delta(g' - g)\,d^3g'\,d^3v_1\,d^3v_2\,.\end{aligned}$$

Integrating over $\mathbf{v}_1$ in the first term, and substituting $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$ so $d^3v_1 = d^3g$ in the second term, one can obtain

$$\mathrm{G}^e_{ql} = n_1 \int v_2^{2q}\,W_2(\mathbf{v}_2)W_1(\mathbf{g} - \mathbf{v}_2)\frac{1}{g'}\,\sigma(g', \Omega)\delta(g' - g)\left(g^{2l} - \left|\frac{\mu}{m_2}\mathbf{g} + \frac{\mu}{m_1}\mathbf{g}'\right|^{2l}\right)\,d^3g\,d^3g'\,d^3v_2\,.$$

Integrating over g' and noting that the angle between $\mathbf{g}$ and $\mathbf{g}'$ is the scattering angle χ, one finds for the term in large parentheses:

$$\frac{g^{2l}}{(1+\beta)^{2l}}\sum_{k=1}^{l}\binom{l}{k}(1+\beta^2)^{l-k}(2\beta)^k(1-\cos^k\chi)\,,$$

where we have used $\beta = m_1/m_2$.

Using the fact that

$$W_2(\mathbf{v}_2)W_1(\mathbf{g} - \mathbf{v}_2) = W_r(\mathbf{g})W_T(\mathbf{y})\,,$$

where $\mathbf{y}$ is the velocity of the two particle center of mass given by $\mathbf{y} = \mathbf{v}_2 - \mu/m_2\,\mathbf{g}$ and W_r and W_T are given by Eqs. (2.57) and (2.59), and using the definition of $Q^{(k)}(g)$, Eq. (2.50), we obtain

$$G^e_{ql} = n_1 \int d^3g \left(\int d^3y \left| \mathbf{y} + \frac{\mu}{m_2}\mathbf{g} \right|^{2q} W_T(\mathbf{y}) \right) W_r(\mathbf{g}) \frac{g^{2l+1}}{(1+\beta)^{2l}} \sum_{k=1}^{l} \binom{l}{k} (1+\beta^2)^{l-k} (2\beta)^k Q^{(k)}(g) ,$$

which is the same as Eq. (2.56).

APPENDIX C

In determining the eigenvalues of the exchange Keilson-Storer kernel, we follow the procedure developed by Snider [20] to determine the eigenvalues of the direct Keilson-Storer kernel.

The generating function of Kumar [21]

$$G(\mathbf{a}, \mathbf{t}) = \exp(-a^2 + 2\mathbf{a}\cdot\mathbf{t})$$

can be expanded into a series of the eigenfunctions ψ^{ln} [Eq. (2.35)]:

$$G(\mathbf{a}, \mathbf{v}_i/u_i) = \sum_{n,l,q} b_{ln}\, a^{2n+l}\, Y^*_{lq}(\hat{\mathbf{a}})\, \psi^{ln}_{iq}(\mathbf{v}_i) ,$$

where Y_{lq} is a spherical harmonic, and $b_{ln} = (-1)^n / [4\, B_{ln}\, \Gamma(n + l + \frac{1}{2})]$.

Using

$$K^{\mathrm{KS}}_e(\mathbf{v}'_2 \to \mathbf{v}_1) = \Gamma_{\mathrm{KS}} (\pi\omega^2)^{-\frac{3}{2}} \exp[-(\mathbf{v}_1 - \alpha\mathbf{v}'_2)^2/\omega^2]$$

one finds that

$$\int W_2(\mathbf{v}'_2)\, K^{\mathrm{KS}}_e(\mathbf{v}'_2 \to \mathbf{v}_1)\, G(\mathbf{a}, \mathbf{v}'_2/u_2)\, d^3v'_2$$

$$= \Gamma_{\mathrm{KS}}\, W_1(\mathbf{v}_1)\, G(\alpha\sqrt{\beta}\,\mathbf{a}, \mathbf{v}_1/u_1)$$

provided that $\alpha^2 u_2^2 + \omega^2 = u_1^2$, which agrees with our previous definition of ω, Eq. (3.4). Expanding G on both sides of the above equation, and setting equal the coefficients of like functions of $\mathbf{a}$, we obtain

$$\int W_2(\mathbf{v}'_2)\, K^{\mathrm{KS}}_e(\mathbf{v}'_2 \to \mathbf{v}_1)\, \psi^{ln}_{2q}(\mathbf{v}'_2)\, d^3v'_2$$

$$= \Gamma_{\mathrm{KS}}\, (\sqrt{\beta}\,\alpha)^{2n+l}\, W_1(\mathbf{v}_1)\, \psi^{ln}_{1q}(\mathbf{v}_1) ,$$

which is the eigenvalue equation for the Keilson-Storer exchange kernel.

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