Collision kernels and transport coefficients

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A connection is made between classical transport theory and the usual description of collisional processes in laser spectroscopy. In classical transport theory, collisional processes are described in terms of either transport coefficients or *collision integrals*. In analyzing the influence of collisions on laser spectroscopic line shapes, collisions are often described in terms of *collision kernels*. Two sets of equations are obtained relating the collision integrals to the collision kernels. While these two sets of equations are equivalent for any physically realistic kernel, they need not be equivalent if one carries out calculations using phenomenological kernels. If the two methods give similar collision integrals for a phenomenological collision kernel, it may serve as a justification for the use of that kernel. We show that the two methods do give very similar results for the Keilson-Storer kernel but give dramatically different results for a "difference" kernel (a kernel that is a function of the difference between the initial and final velocity). The calculations, carried out for a low-density binary gas mixture, provide a link between classical transport theory and the collision kernels commonly used in analyzing experiments in laser spectroscopy. Implications of the results to experimental situations of current interest, such as light-induced drift, are explored.

I. INTRODUCTION

In analyzing laser spectroscopic experiments one often uses *collision kernels* and rates to characterize the collisions occurring in an atomic vapor. On the other hand, it is well known from classical transport theory that the *transport coefficients* of diffusion, viscosity, and thermal conductivity can also be used to characterize the collisional processes occurring in a vapor. Since the approach and language used in the theories of laser spectroscopy and classical transport theory differ significantly, it is not surprising that there has been little cross talk between the two disciplines. It is the purpose of this paper to bridge this gap somewhat by providing a connection between the collision kernels and the transport coefficients. We conclude that transport theory can put serious constraints on the fitting procedures used in the analysis of collisionally modified line shapes. Our discussion is particularly timely in view of recent experiments on light-induced transport phenomena.[1]

To simplify the discussion, we consider an atomic vapor in which there are two types of atoms, "active" atoms (A) and perturbers (P). The atomic density is assumed to be sufficiently low such that only binary collisions need to be considered and the A-atom density is assumed to be much lower than the P-atom density. As a consequence of the latter assumption, any effects of A-A collisions can be neglected relative to those of type A-P in considering modifications of the A-atom distribution function. The main objective of this study is to define the macroscopic quantities which characterize the elastic A-P collisions occurring in the vapor.

A. Laser spectroscopy

The physical quantity related to A-P scattering that one attempts to measure is the so-called collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$, defined as the probability density in velocity space per unit time that A atoms have their velocity changed from $\mathbf{v}'$ to $\mathbf{v}$ as a result of collisions with P atoms. The rate $\Gamma(v)$ at which A atoms of speed v undergo collisions with the P atoms is related to the collision kernel by

$$\Gamma(v)=\int d\mathbf{v}'K(\mathbf{v}\rightarrow\mathbf{v}')\,. \tag{1.1}$$

The collision kernel can be related to integrals involving the differential cross section for A-P scattering.[2,3]

To experimentally determine the collision kernel and rate in a typical laser spectroscopy experiment, one uses a "pump" laser to selectively excite a velocity subclass of A atoms. As a result of collisions with P atoms, the A atoms' velocity distribution is modified in a manner that is described by the shape of the collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$. A second "probe" laser monitors the change in the A-atom velocity distribution and, in doing so, provides a measure of the collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$.[2] In analyzing such data, one has often resorted to the use of phenomenological collision kernels.

[It should be noted that the collisional processes occurring in a vapor cannot, in general, be described in terms of a *single* collision kernel. Since the collision interaction normally depends on the internal atomic states of the atoms, a complete description requires a separate kernel for each atomic state population and each coherence.[2] To focus the discussion, however, we assume that the perturbers (P) always remain in their ground state and neglect, for the moment, any state dependence of the collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$ characterizing the A-P collisions.]

B. Transport theory

Transport phenomena such as diffusion, viscosity, and heat conductivity are described by the corresponding transport coefficients or, equivalently, by the effective

transport cross sections. These cross sections are matrix elements of a linearized collision operator, but may also be related to the so-called *collision integrals* of transport theory which are integrals of the differential scattering cross section, suitably weighted with respect to scattering angle and relative velocity. Linear relations between these collision integrals and the effective cross sections can be found in various textbooks.[3] The collision integrals have been calculated for different model potentials and are tabulated, for instance, in the book of Hirschfelder *et al.*[3]

C. Collision kernels — transport theory

The collision integrals and collision kernels share a common language at the level of the differential scattering cross section. Using this fact, it is possible to relate the collision integrals of classical transport theory to integrals of the collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$ over $\mathbf{v}'$ and $\mathbf{v}$ with various weighting functions of $\mathbf{v}$ and $\mathbf{v}'$. This integral relationship between the collision integrals and the collision kernel provides the bridge between the two disciplines. We shall give two different integral relationships between the collision kernel and the collision integrals, the first which we derive from well-known expressions of transport theory and a second which we formulate in this work. Although these two different sets of equations are formally equivalent for any physically acceptable collision kernel, they need not be equivalent for phenomenological collision kernels. The equality or near equality of transport coefficients calculated by the two different methods for a phenomenological collision kernel may provide some justification for use of that kernel.

The relationship between the collision integrals of transport theory and the collision kernel can also be used to place constraints on the "free" parameters that are used to fit laser spectroscopic line shapes in which collisions play a role. Since there exists a wealth of data on transport properties and theoretical methods for calculating transport coefficients from a given interatomic potential,[3] the incorporation of transport data in fitting laser spectroscopic line shapes represents an important component of a consistent analysis of the line shapes and leads to a more sensitive measure of the collision kernels.

In Sec. II, formal definitions for the collision kernels, rates, integrals, and transport coefficients are given. The connection between the collision integrals and the collision kernel is established in Sec. III, where two sets of integral relationships connecting these quantities are found. In Sec. IV, the two methods of calculating the collision integrals from the collision kernel are applied to a physically acceptable (hard-sphere) kernel and two phenomenological kernels (Keilson-Störer[4] and "difference" kernels). It is found that the difference kernel leads to drastically different results for the collision integrals calculated by the two methods, but that results obtained with the Keilson-Störer kernel are nearly identical, perhaps justifying its use as a model kernel. As anticipated, the two methods yield identical results for the hard-sphere kernel. The results of a recent article by Snider[5] on the eigenvalue expansion of the Keilson-Störer kernel simplify some of the calculations needed in this section. In Sec. V, some experimental implications of the results are discussed and various extensions of the theory are explored.

II. COLLISION KERNELS, RATES, CROSS SECTIONS, INTEGRALS, AND TRANSPORT COEFFICIENTS

This section is organized as follows. Section II A gives the definitions of Boltzmann collision operator, collision kernel, and collision rate; Sec. II B the definition of collision integrals of transport theory; Sec. II C the definition of effective transport cross sections in terms of matrix elements of a linearized collision operator; Sec. II D the definition of transport coefficients; and Sec. II E the relationship between the collision integrals and the effective cross sections.

A. Laser spectroscopy: Collision operator, kernel, and rate

The time evolution of the A-atom velocity distribution $\rho_A(\mathbf{v},t)$ as a result of collisions with perturbers (P) is determined by

$$\left[\frac{\partial\rho_A(\mathbf{v},t)}{\partial t}\right]_{\text{coll}}=\mathscr{L}_{AP}\rho_A(\mathbf{v},t)\ , \tag{2.1}$$

with $\mathscr{L}_{AP}$ the Boltzmann collision operator for A-P collisions. The Boltzmann collision operator can be expressed as[3]

$$\mathscr{L}_{AP}\rho_A(\mathbf{v},t)=\int\int[\rho_A(\mathbf{v}',t)\rho_P(\mathbf{v}_p',t)-\rho_A(\mathbf{v},t)\rho_P(\mathbf{v}_p,t)]\times v_r\frac{d\sigma}{d\Omega}d\Omega\,\mathbf{v}_p\ , \tag{2.2}$$

in which $v_r=|\mathbf{v}-\mathbf{v}_p|$ is the A-P relative speed, $d\sigma/d\Omega$ is the A-P differential scattering cross section in the center-of-mass frame, $\mathbf{v}$ and $\mathbf{v}_p$ are the A- and P-atom velocities, respectively, before a collision, and $\mathbf{v}'$ and $\mathbf{v}_p'$ are the corresponding quantities after the collision. Implicit in Eq. (2.2) is the fact that $\mathbf{v}$, $\mathbf{v}'$, $\mathbf{v}_p$, and $\mathbf{v}_p'$ satisfy the conditions for conservation of energy and momentum. Although the label has been suppressed on $d\sigma/d\Omega$, *it is to be assumed that all cross sections refer to A-P scattering.* Owing to the assumption that the A-atom density is much less than the P-atom density, one can neglect the effect of A collisions on the P-atom distribution function. It is now assumed that $\rho_P(\mathbf{v},t)$ is a time-independent equilibrium distribution of the form

$$\rho_P(\mathbf{v}_p,t)=N_pW_p(\mathbf{v}_p)=N_p(\pi u_p^2)^{-3/2}\exp(-v_p^2/u_p^2)\ , \tag{2.3}$$

with N_p and u_p, respectively, the P-atom density and most probable speed.

The collision operator can be recast in terms of a collision rate $\Gamma(v)$ and a collision kernel $K(\mathbf{v}'\rightarrow\mathbf{v})$ as[2]

$$\left[\frac{\partial \rho_A}{\partial t}\right]_{\text{coll}} = \mathscr{L}_{AP}\rho_A = -\Gamma(v)\rho_A(\mathbf{v},t) + \int d\mathbf{v}' K(\mathbf{v}'\to\mathbf{v})\rho_A(\mathbf{v}',t) . \tag{2.4}$$

The kernel $K(\mathbf{v}'\to\mathbf{v})$, which gives the probability density per unit time that A atoms have their velocity changed from $\mathbf{v}'$ to $\mathbf{v}$ as a result of collisions with P atoms, is of the form

$$K(\mathbf{v}'\to\mathbf{v}) = N_p\left[\frac{m}{\mu}\right]^3 \int d\mathbf{v}_r' d\mathbf{v}_r W_p(\mathbf{v}'-\mathbf{v}_r')v_r^{-1}\delta\left[(\mathbf{v}_r-\mathbf{v}_r') - \frac{m}{\mu}(\mathbf{v}-\mathbf{v}')\right]\delta(v_r-v_r')\frac{d\sigma}{d\Omega_{v_r}}(v_r', |\mathbf{v}_r'-\mathbf{v}_r|) , \tag{2.5}$$

where m is the A-atom mass and μ is the A-P reduced mass. The collision kernel is the differential scattering cross section for A-P collisions transformed back to the laboratory frame and averaged over the P-atom velocity distribution consistent with conservation of momentum and energy (as expressed by the δ functions). Note that the second term of the right-hand side (rhs) of Eq. (2.4) with the kernel (2.5) corresponds to the first term of the rhs of Eq. (2.2), the only difference is that conservation of momentum and energy is implicit in (2.2) and explicit in (2.5).

The speed-dependent collision rate calculated from Eqs. (1.1) and (2.5) or, equivalently, from (2.2) and (2.4) is

$$\Gamma(v) = N_p \int d\mathbf{v}_p\, W_p(\mathbf{v}_p)\,|\mathbf{v}-\mathbf{v}_p|\,\sigma(|\mathbf{v}-\mathbf{v}_p|) , \tag{2.6a}$$

where

$$\sigma(v_r) = \int d\Omega_{v_r'}\frac{d\sigma}{d\Omega_{v_r'}}(v_r', |\mathbf{v}_r'-\mathbf{v}_r|) \tag{2.6b}$$

is the total A-P scattering cross section. Note that $\Gamma(v)$ is just the collision rate in the center-of-mass system averaged over the P-atom velocity distribution. It will also prove useful to define a velocity-averaged collision rate

$$\Gamma \equiv \int d\mathbf{v}\, W(\mathbf{v})\Gamma(v) = \int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}')K(\mathbf{v}'\to\mathbf{v}) \tag{2.7}$$

[the second equality following from Eq. (1.1)] in which $W(\mathbf{v})$ is the A-atom equilibrium distribution assumed to be of the form

$$W(\mathbf{v}) = (\pi u^2)^{-3/2}\exp(-v^2/u^2) \tag{2.8}$$

and u is the most probable A-atom speed. Using Eqs. (2.3), and (2.6)–(2.8), one can easily show that

$$\Gamma = N_p \int d\mathbf{v}_r\, W_r(\mathbf{v}_r)v_r\sigma(v_r) , \tag{2.9}$$

where $W_r(\mathbf{v}_r)$ is the A-P relative velocity distribution

$$W_r(\mathbf{v}_r) = (\pi u_r^2)^{-3/2}\exp(-v_r^2/u_r^2) \tag{2.10}$$

and u_r is the most probable A-P atom relative speed, i.e.,

$$u_r^2 = u_p^2 + u^2 = \frac{2k_BT}{\mu} , \tag{2.11}$$

where k_B is Boltzmann's constant and T is the absolute temperature.

B. Classical transport theory: Collision integrals

In transport theory the collision integrals for spherically symmetric interaction potentials are defined by[3]

$$\Omega^{(l,s)} = \left[\frac{k_BT}{2\pi\mu}\right]^{1/2} \times \int_0^\infty dy \int_0^\infty 2\pi b\, db\, e^{-y^2}y^{2s+3}[1-\cos^l\chi(b,y)] , \tag{2.12}$$

where l and s are integers, $\chi(b,y)$ is the scattering angle in the center-of-mass frame, b is the impact parameter, and

$$y = \frac{v_r}{u_r} . \tag{2.13}$$

Equation (2.12) can be recast in a form that will make the connection with the collision kernel somewhat more apparent. Equations (2.10) and (2.11) are used to rewrite it as

$$\Omega^{(l,s)} = \tfrac{1}{8}\int W_r(\mathbf{v}_r)v_r\left[\frac{v_r}{u_r}\right]^{2s} Q^{(l)}(v_r)d\mathbf{v}_r , \tag{2.14}$$

where

$$Q^{(l)}(v_r) = 2\pi\int_0^\infty b\, db\,[1-\cos^l\chi(b,v_r)] . \tag{2.15}$$

The fact that

$$\frac{d\sigma}{d\Omega} = \frac{b}{\sin\chi}\frac{db}{d\chi} \tag{2.16}$$

is used to rewrite (2.15) as

$$Q^{(l)} = \int d\Omega\left[\frac{d\sigma}{d\Omega}\right](1-\cos^l\chi) , \tag{2.17}$$

where $d\Omega = 2\pi(\sin\chi)d\chi$. It then follows from (2.9), (2.14), and (2.17) that

$$N_p\Omega^{(\infty,0)} = \tfrac{1}{8}\Gamma = \tfrac{1}{8}\int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}')K(\mathbf{v}'\to\mathbf{v}) , \tag{2.18}$$

where Γ is the velocity-averaged collision rate given by (2.7) and (2.9). This establishes a first integral relation between a collision integral and the collision kernel. A general relationship between the $\Omega^{(l,s)}$ and the collision kernel is established in Sec. III.

C. Classical transport theory: Matrix elements of the collision operator

In Sec. II D, the collision integrals will be related to transport coefficients which can, in turn, be related to matrix elements of a linearized collision operator. In this subsection, these matrix elements are defined.

In first-order Chapman-Enskog theory,[3] the Boltzmann equation is linearized with respect to the deviation of the distribution function from a Maxwellian. A linearized collision operator $\mathscr{R}_{AP}$ can be defined by

$$-N_p\mathscr{R}_{AP}=\frac{1}{W}\mathscr{L}_{AP}W\ , \tag{2.19}$$

where $W(\mathbf{v})$ is the A-atom equilibrium distribution (2.8) and $\mathscr{L}_{AP}$ is the operator (2.2). Although $\mathscr{L}_{AP}$ is nonlinear in transport theory, it becomes linear when evaluated for an equilibrium perturber distribution (2.3). The transport equation (2.4) is in effect, just the operator (2.19) acting on the distribution function $\rho_A(\mathbf{v},t)$. It then becomes convenient to expand the distribution function in terms of some complete set of orthonormal basis functions.[6] A choice of basis functions which proves particularly useful (see the following) is

$$\Phi_q^{ln}(\mathbf{v})=B_{ln}\sqrt{4\pi}\left[\frac{v}{u}\right]^l L_n^{l+1/2}\left[\frac{v^2}{u^2}\right]Y_{lq}(\theta_{\hat{\mathbf{v}}},\phi_{\hat{\mathbf{v}}})\ , \tag{2.20}$$

where $L_n^{l+1/2}$ are the associated Laguerre polynomials, Y_{lq} are the spherical harmonics, and B_{ln} is a normalized factor

$$B_{ln}=\left[\frac{n!\sqrt{\pi}}{2\Gamma(l+n+3/2)}\right]^{1/2}\ , \tag{2.21}$$

where Γ is the gamma function. The Φ_q^{ln} satisfy the normalization

$$\langle\Phi_q^{ln}(\mathbf{v})\,|\,\Phi_{q'}^{l'n'}(\mathbf{v})\rangle=\delta_{ll'}\delta_{nn'}\delta_{qq'}\ , \tag{2.22}$$

where the $\langle\ \rangle$ imply an integration over $\mathbf{v}$ with $W(\mathbf{v})$, i.e.,

$$\langle f(\mathbf{v})\,|\,g(\mathbf{v})\rangle=\int f^*(\mathbf{v})g(\mathbf{v})W(\mathbf{v})d\mathbf{v} \tag{2.23}$$

for any functions $f(\mathbf{v})$ and $g(\mathbf{v})$.

The Φ_q^{ln} are exact eigenfunctions of the operator $\mathscr{R}_{AP}$, evaluated for a repulsive A-P interaction potential varying as r^{-4} (Maxwell molecule interaction). Denoting by $\mathscr{R}_{AP}^M$ the linearized operator for the Maxwell molecule interaction, one can write the eigenvalue equation

$$\mathscr{R}_{AP}^M\Phi_q^{ln}(\mathbf{v})=\beta_{ln}\Phi_q^{ln}(\mathbf{v}) \tag{2.24}$$

in which β_{ln} are the eigenvalues given by

$$\beta_{ln}\delta_{ll'}\delta_{nn'}\delta_{qq'}=\langle\Phi_{q'}^{l'n'}\,|\,\mathscr{R}_{AP}^M\Phi_q^{ln}\rangle\ . \tag{2.25}$$

From Eqs. (2.1), (2.19), and (2.24), it follows that a distribution function $\rho_A(\mathbf{v},t)\propto\Phi_q^{ln}(\mathbf{v})$ would undergo a simple decay with rate $N_p\beta_{ln}$.

For a realistic interaction potential, the exact eigenfunctions are not known, but the Φ_q^{ln} may still serve as a good set of basis functions.[3,6] Clearly, the matrix elements in Eq. (2.25) have units of (velocity$\times$cross section) and it becomes convenient to define effective transport cross sections $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$ describing the influence of A-P collisions on the A-atom velocity distribution. For isotropic scattering, the effective cross sections are m independent and may be defined as[6]

$$\bar{v}_r\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})=\langle\Phi_q^{ln}\,|\,\mathscr{R}_{AP}\Phi_q^{l'n'}\rangle\delta_{qq'}\ , \tag{2.26}$$

where

$$\bar{v}_r=\left[\frac{8kT}{\pi\mu}\right]^{1/2}=\int v_rW_r(\mathbf{v}_r)d\mathbf{v}_r=\frac{2}{\sqrt{\pi}}u_r\ . \tag{2.27}$$

In Sec. II E, the $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$ are related to the collision integrals.

D. Classical transport theory: Transport coefficients

Both the $\Omega^{(l,s)}$ integrals and the $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$ cross sections can be related to the transport coefficients of a mixture. For diffusion, these relations are[3,6]

$$D^{[0]}=\frac{k_BT}{m}\frac{1}{N_p\bar{v}_r\mathscr{S}(\begin{smallmatrix}1 & 0\\ 1 & 0\end{smallmatrix})} \tag{2.28}$$

and

$$D^{[0]}=\frac{3}{16}\frac{k_BT}{\mu N_p\Omega^{(1,1)}}\ , \tag{2.29}$$

with $D^{[0]}$ the first-order approximation to the diffusion coefficient. This first-order approximation is implicitly dependent on the assumption that Φ_q^{10} is an exact eigenfunction of the collision operator. The viscosity and heat conductivity of a mixture are not only determined by the A-P potential in which we are interested, but also by A-A and P-P collisions. Therefore the expressions for the heat conductivity $\lambda^{[0]}$ and the viscosity $\eta^{[0]}$ of a mixture[6] are rather complicated and will not be given here. Instead, we will give an expression for $\lambda^{[0]},\eta^{[0]}$ in a hypothetical one-component gas in which the interaction potential is identical to the A-P interaction potential. Again in first-order approximation and neglecting internal degrees of freedom one obtains[3,6]

$$\eta^{[0]}=\frac{k_BT}{\bar{v}_r}\frac{1}{\mathscr{S}(\begin{smallmatrix}2 & 0\\ 2 & 0\end{smallmatrix})}=\frac{5k_BT}{8\Omega^{(2,2)}}\ , \tag{2.30a}$$

$$\lambda^{[0]}=\frac{5k_B^2T}{2m\bar{v}_r}\frac{1}{\mathscr{S}(\begin{smallmatrix}1 & 1\\ 1 & 1\end{smallmatrix})}=\frac{75k_B^2T}{32m\Omega^{(2,2)}}\ . \tag{2.30b}$$

E. Relation between $\Omega^{(l,s)}$ and $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$

The relationship between the $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$ and the collision integrals can be established in the following manner. First, one can relate the $\mathscr{S}(\begin{smallmatrix}l & n\\ l' & n'\end{smallmatrix})$ to the square bracket integrals

given by Chapman and Cowling.[3] These quantities differ by a multiplicative factor only, the precise relationship given in Appendix A. Since Chapman and Cowling have already related their bracket integrals to the collision integrals,[3,7] one can use their results, along with the results of Appendix A, to show that the first few $\mathcal{S}(\begin{smallmatrix} l & n \\ l' & n' \end{smallmatrix})$ are given by

$$\bar{v}_r \mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix}) = \frac{16}{3}\frac{\mu}{m}\Omega^{(1,1)} , \tag{2.31a}$$

$$\bar{v}_r \mathcal{S}(\begin{smallmatrix} 2 & 0 \\ 2 & 0 \end{smallmatrix}) = \frac{16}{3}\frac{\mu}{m}\left[2\left[\frac{\mu}{m_p}\right]\Omega^{(1,1)} + \frac{3}{5}\left[\frac{\mu}{m}\right]\Omega^{(2,2)}\right] , \tag{2.31b}$$

$$\bar{v}_r \mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 1 \end{smallmatrix}) = \tfrac{16}{3}(\tfrac{2}{5})^{1/2}\left[\frac{\mu}{m}\right]^2 (\tfrac{5}{2}\Omega^{(1,1)} - \Omega^{(1,2)}) , \tag{2.31c}$$

where m_p is the P-atom mass.

III. RELATIONS BETWEEN COLLISION INTEGRALS AND KERNEL

The question remains as to how to relate the collision integrals $\Omega^{(l,s)}$ [or effective cross section $\mathcal{S}(\begin{smallmatrix} l & n \\ l' & n' \end{smallmatrix})$] to the collision kernel $K(\mathbf{v}' \to \mathbf{v})$. Two methods are proposed below.

Method 1. The first method consists of an explicit evaluation of the effective cross sections. Using Eqs. (2.26), (2.23), (2.19), (2.4), (1.1), (2.20), and the addition theorem for spherical harmonics, one can obtain

$$N_p \bar{v}_r \mathcal{S}(\begin{smallmatrix} l & n \\ l & n' \end{smallmatrix}) = B_{lr} B_{lr'} \int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}') K(\mathbf{v}' \to \mathbf{v}) \times \left[\left[\frac{v'}{u}\right]^{2l} L_n^{l+1/2}\left[\frac{v'^2}{u^2}\right] L_{n'}^{l+1/2}\left[\frac{v'^2}{u^2}\right] - \left[\frac{v'v}{u^2}\right]^{l} L_{n'}^{l+1/2}\left[\frac{v'^2}{u^2}\right] L_n^{l+1/2}\left[\frac{v^2}{u^2}\right] P_l(\cos\theta)\right] , \tag{3.1}$$

where P_l is a Legendre polynomial and θ is the angle between $\mathbf{v}'$ and $\mathbf{v}$, i.e.,

$$\cos\theta = \frac{\mathbf{v}\cdot\mathbf{v}'}{vv'} . \tag{3.2}$$

Although Eq. (3.1) may appear complicated, it is an easy matter to explicitly carry out the integrations to show that the first few $\mathcal{S}(\begin{smallmatrix} l & n \\ l & n' \end{smallmatrix})$ are given by the relatively simple expressions

$$N_p \mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix}) = -\frac{2}{3u^2\bar{v}_r}\int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}') K(\mathbf{v}' \to \mathbf{v})(\mathbf{v}'\cdot\mathbf{s}) , \tag{3.3a}$$

$$N_p \mathcal{S}(\begin{smallmatrix} 2 & 0 \\ 2 & 0 \end{smallmatrix}) = \frac{2}{15u^4\bar{v}_r}\int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}') K(\mathbf{v}' \to \mathbf{v}) \times [s^2 v'^2 - 4(\mathbf{s}\cdot\mathbf{v}')v'^2 - 3(\mathbf{s}\cdot\mathbf{v}')^2] , \tag{3.3b}$$

$$N_p \mathcal{S}(\begin{smallmatrix} 1 & 1 \\ 1 & 0 \end{smallmatrix}) = -\tfrac{2}{3}(\tfrac{2}{5})^{1/2}\frac{1}{u^2\bar{v}_r} \times \int d\mathbf{v}\, d\mathbf{v}'\, W(\mathbf{v}') K(\mathbf{v}' \to \mathbf{v})\left[\frac{5}{2} - \frac{v'^2}{u^2}\right]\mathbf{v}'\cdot\mathbf{s} , \tag{3.3c}$$

where

$$\mathbf{s} = \mathbf{v} - \mathbf{v}' . \tag{3.3d}$$

The relations (3.3) along with the inverse of Eqs. (2.31), i.e.,

$$\Omega^{(1,1)} = \tfrac{3}{16}\bar{v}_r\left[\frac{m}{\mu}\right]\mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix}) , \tag{3.3e}$$

$$\Omega^{(2,2)} = \tfrac{5}{16}\bar{v}_r\left[\frac{m}{\mu}\right]\left[\frac{m}{\mu}\mathcal{S}(\begin{smallmatrix} 2 & 0 \\ 2 & 0 \end{smallmatrix}) - 2\left[\frac{m}{m_p}\right]\mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix})\right] , \tag{3.3f}$$

$$\Omega^{(1,2)} = \tfrac{3}{16}\bar{v}_r\left[\frac{m}{\mu}\right]\left[\tfrac{5}{2}\mathcal{S}(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix}) - \left[\frac{5}{2}\right]^{1/2}\left[\frac{m}{\mu}\right]\mathcal{S}(\begin{smallmatrix} 1 & 1 \\ 1 & 0 \end{smallmatrix})\right] , \tag{3.3g}$$

give the explicit relationship between the collision kernel and the collision integrals for the first few $\Omega^{(l,s)}$. Similar expressions can be generated for higher order $\Omega^{(l,s)}$, but the $\Omega^{(l,s)}$ given in (3.3) are the ones which enter in the lowest-order theory of diffusion and thermal conductivity. Equations (3.3) achieve the objectives of this work—the collision integrals have been directly related to the collision kernel.

For large l one can drop the second term in the rhs of Eq. (3.1). It then follows from Eqs. (3.1), (2.20), (1.1), and (2.23) that

$$\lim_{l\to\infty} N_p \bar{v}_r \mathcal{S}(\begin{smallmatrix} l & n \\ l & n \end{smallmatrix}) = \lim_{l\to\infty} \langle \Phi_q^{ln} \,|\, \Gamma(v) \Phi_q^{ln} \rangle , \tag{3.4}$$

which implies that $N_p \bar{v}_r \mathcal{S}(\begin{smallmatrix} \infty & n \\ \infty & n \end{smallmatrix})$ is identically equal to Γ if

$\Gamma(v)$ is independent of v.

As an aside, we may note that Eqs. (3.3e)–(3.3g) can be calculated from Eqs. (3.3a)–(3.3c) when the definition (2.5) for $K(\mathbf{v}'\rightarrow\mathbf{v})$ is used. This method of deriving Eqs. (3.3e)–(3.3g) provides what appears to be a less laborious alternative to that given in standard texts[3] relating the effective cross sections to the collision integrals.

Method 2. It is seen in Eq. (2.18) that one of the collision integrals $\Omega^{(\infty,0)}$ is related to an integral of the collision kernel. Values of $\Omega^{(l,s)}$ for $l\neq\infty$ depend on integrals containing a factor $\cos^l\chi$ [see Eq. (2.12)]. We have found that alternative expressions relating the collision integrals to the collision kernel can be generated by considering expressions of the form

$$G_{ql}=\int d\mathbf{v}\,d\mathbf{v}'(v')^{2q}\,|\,\mathbf{v}-\mathbf{v}'\,|^{2l}K(\mathbf{v}'\rightarrow\mathbf{v})W(\mathbf{v}')\,, \tag{3.5}$$

where q and l are integers. One notes immediately that $G_{00}=\Gamma=8N_p\Omega^{(\infty,0)}$. By considering various values of q and l, one can show that the G_{ql} generate linear combinations of the $\Omega^{(m,n)}$. In Appendix B, an explicit calculation of the first few G_{ql} is presented which leads to the results

$$G_{01}=16(\mu/m)u^2N_p\Omega^{(1,1)}\,, \tag{3.6a}$$

$$G_{02}=32(\mu/m)^2u^4N_p(2\Omega^{(1,2)}-\Omega^{(2,2)})\,, \tag{3.6b}$$

$$G_{11}=16(\mu/m)u^4N_p\left[\frac{3}{2}\frac{\mu}{m_p}\Omega^{(1,1)}+\frac{\mu}{m}\Omega^{(1,2)}\right]. \tag{3.6c}$$

These equations may be inverted to yield

$$N_p\Omega^{(1,1)}=\frac{G_{01}}{16(\mu/m)u^2}\,, \tag{3.7a}$$

$$N_p\Omega^{(1,2)}=\frac{G_{11}-\frac{3}{2}\left[\frac{\mu}{m_p}\right]u^2G_{01}}{16\left[\frac{\mu}{m}\right]^2u^4}\,, \tag{3.7b}$$

$$N_p\Omega^{(2,2)}=\frac{-G_{02}+4G_{11}-6\left[\frac{\mu}{m_p}\right]u^2G_{01}}{32\left[\frac{\mu}{m}\right]^2u^4}\,, \tag{3.7c}$$

where, for convenience, we rewrite Eq. (3.5),

$$G_{ql}=\int d\mathbf{v}\,d\mathbf{v}'(v')^{2q}\,|\,\mathbf{v}-\mathbf{v}'\,|^{2l}K(\mathbf{v}'\rightarrow\mathbf{v})W(\mathbf{v}')\,. \tag{3.7d}$$

We now have two apparently different sets of equations relating the collision integrals to the collisions kernels [Eqs. (3.3) and (3.7), respectively]. As must be the case, however, these two sets of results are entirely equivalent *provided* one calculates the G and $\mathcal{E}$ appearing in these equations using physically correct kernels; that is, kernels which are of the form given by Eq. (2.5). If one uses some phenomenological collision kernel in calculating the G's and $\mathcal{E}$'s, there is no longer any guarantee that the two sets of expressions (3.3) and (3.7) will yield the same set of collision integrals $\Omega^{(l,s)}$. In fact, the difference in the values of $\Omega^{(l,s)}$ calculated using Eqs. (3.3) and (3.7) when a phenomenological collision kernel is used to calculate the G's and $\mathcal{E}$'s may serve as an indication as to whether or not one is justified in using such a kernel. This point is pursued in the following section.

IV. CALCULATION OF THE COLLISION INTEGRALS FOR SPECIFIC KERNELS

A calculation of the $\mathcal{E}$'s, G's, and Ω's is now given for one physically correct kernel (hard-sphere kernel) and two phenomenological kernels (Keilson-Störer and difference kernels).

A. Hard-sphere kernel

The differential cross section for hard-sphere scattering is $r_0^2/4$, where r_0 is the sum of the radii of the two hard spheres undergoing a collision. When this cross section is substituted into Eq. (2.5) one finds a collision kernel[8]

$$K_{\rm HS}(\mathbf{v}'\rightarrow\mathbf{v})=\frac{N_p\pi r_0^2u_p}{\pi^{3/2}\beta^2u^2s}\exp\left[-\left[s+\frac{2\mu\mathbf{s}\cdot\mathbf{v}'}{ms}\right]^2\frac{1}{\beta^2u^2}\right], \tag{4.1}$$

where

$$\mathbf{s}=\mathbf{v}-\mathbf{v}' \tag{4.2}$$

and

$$\beta=2\left[\frac{\mu}{m}\frac{u_p}{u}\right]. \tag{4.3}$$

Using Eqs. (3.3) and (4.1), one can obtain

$$N_p\bar{v}_r\mathcal{E}\left(\begin{smallmatrix}1&0\\1&0\end{smallmatrix}\right)=\frac{4}{3}\left[\frac{\mu}{m}\right]\Gamma_{\rm HS}\,, \tag{4.4a}$$

$$N_p\bar{v}_r\mathcal{E}\left(\begin{smallmatrix}2&0\\2&0\end{smallmatrix}\right)=\frac{8}{3}\left[\frac{\mu}{m}\right]\left[\left[\frac{\mu}{m_p}\right]+\frac{3}{5}\frac{\mu}{m}\right]\Gamma_{\rm HS}\,, \tag{4.4b}$$

$$N_p\bar{v}_r\mathcal{E}\left(\begin{smallmatrix}1&1\\1&0\end{smallmatrix}\right)=-\frac{2}{3}\left[\frac{2}{5}\right]^{1/2}\left[\frac{\mu}{m}\right]^2\Gamma_{\rm HS}\,, \tag{4.4c}$$

where the average collision rate $\Gamma_{\rm HS}$, as given by Eq. (2.9), is

$$\Gamma_{\rm HS}=N_p\bar{v}_r\sigma_{\rm HS}=N_p\left[\frac{2}{\sqrt{\pi}}u_r\right]\pi r_0^2\,. \tag{4.5}$$

Similarly, by using Eq. (3.5), one may obtain

$$G_{01}=4\left[\frac{\mu}{m}\right]u^2\Gamma_{\rm HS}\,, \tag{4.6a}$$

$$G_{02}=32\left[\frac{\mu}{m}\right]^2u^4\Gamma_{\rm HS}\,, \tag{4.6b}$$

$$G_{11}=6\left[1+\frac{\mu}{m}\right]\left[\frac{\mu}{m}\right]u^4\Gamma_{\rm HS}\,. \tag{4.6c}$$

For this physically correct kernel, one can calculate the

collision integrals from either Eqs. (3.3) or Eqs. (3.7). In each case, one finds

$$N_p\Omega^{(1,1)}=\tfrac{1}{4}\Gamma_{\rm HS}\ ;$$
$$N_p\Omega^{(2,2)}=\tfrac{1}{2}\Gamma_{\rm HS}\ ; \tag{4.7}$$
$$N_p\Omega^{(1,2)}=\tfrac{3}{4}\Gamma_{\rm HS}\ ,$$

in agreement with the results of Chapman and Cowling.[3]

B. Keilson-Störer kernel

A phenomenological kernel proposed by Keilson and Störer has the form[4]

$$K_{\rm KS}(\mathbf{v}'\to\mathbf{v})=\frac{\Gamma_{\rm KS}}{(\pi\omega^2)^{3/2}}e^{-(\mathbf{v}-\alpha\mathbf{v}')^2/\omega^2}\ , \tag{4.8a}$$

where

$$\omega^2=(1-\alpha^2)u^2 \tag{4.8b}$$

and $0\leqq\alpha<1$. This kernel has many advantages. It is easy to work with, it satisfies detailed balance, and it can simulate both "strong" collisions ($\alpha\simeq 0$) or "weak" collisions ($\alpha\simeq 1$). Yet the Keilson-Störer kernel is not a physically correct kernel since it cannot be derived from an equation of the form (2.5). Thus, there is no guarantee that the two methods for calculating the Ω integrals will yield the same results.

The $\mathfrak{S}$'s may be calculated directly from Eqs. (3.3) and (4.8). Although such a calculation is not very difficult, an even simpler method is available. Snider[5] has shown that the Φ_q^{ln} are eigenfunctions of the Keilson-Störer kernel with eigenvalues $\Gamma_{\rm KS}\alpha^{l+2n}$, i.e.,

$$\frac{1}{W(\mathbf{v})}\int W(\mathbf{v}')K_{\rm KS}(\mathbf{v}'\to\mathbf{v})\Phi_q^{ln}(\mathbf{v}')d\mathbf{v}'=\Gamma_{\rm KS}\alpha^{l+2n}\Phi_q^{ln}(\mathbf{v})\ . \tag{4.9}$$

Combining this result with Eqs. (2.26), (2.19), (2.4), (2.23), and (2.22) immediately yields

$$N_p\bar{v}_r\mathfrak{S}\left(\begin{smallmatrix}1&0\\0&\end{smallmatrix}\right)=\Gamma_{\rm KS}(1-\alpha)\ , \tag{4.10a}$$

$$N_p\bar{v}_r\mathfrak{S}\left(\begin{smallmatrix}2&0\\0&\end{smallmatrix}\right)=\Gamma_{\rm KS}(1-\alpha^2)\ , \tag{4.10b}$$

$$N_p\bar{v}_r\mathfrak{S}\left(\begin{smallmatrix}1&1\\0&\end{smallmatrix}\right)=0\ . \tag{4.10c}$$

The G's may be calculated from Eqs. (3.5) and (4.8) as

$$G_{01}=3\Gamma_{\rm KS}(1-\alpha)u^2\ , \tag{4.11a}$$

$$G_{02}=15\Gamma_{\rm KS}(1-\alpha)^2u^4\ , \tag{4.11b}$$

$$G_{11}=\tfrac{3}{2}\Gamma_{\rm KS}(4-\alpha)(1-\alpha)u^4\ . \tag{4.11c}$$

We now obtain the collision integrals using both Eqs. (3.3) and (3.7). We use an argument "$\mathfrak{S}$" to indicate an Ω calculated from Eqs. (3.3) and an argument "G" to indicate an Ω calculated from Eqs. (3.7). It is an easy matter to obtain

$$N_p\Omega^{(1,1)}(\mathfrak{S})=N_p\Omega^{(1,1)}(G)=\frac{3}{16}\left[\frac{m}{\mu}\right](1-\alpha)\Gamma_{\rm KS}\ , \tag{4.12}$$

$$N_p\Omega^{(2,2)}(\mathfrak{S})=\frac{5}{16}\left[\frac{m}{\mu}\right](1-\alpha)\left[(1+\alpha)-\frac{m}{m_p}(1-\alpha)\right]\Gamma_{\rm KS}\ , \tag{4.13}$$

$$N_p\Omega^{(2,2)}(G)=\frac{9}{32}\left[\frac{m}{\mu}\right](1-\alpha)\left[(1+\alpha)-\frac{m}{m_p}(1-\alpha)\right]\Gamma_{\rm KS}\ , \tag{4.14}$$

$$N_p\Omega^{(1,2)}(\mathfrak{S})=\frac{15}{32}\left[\frac{m}{\mu}\right](1-\alpha)\Gamma_{\rm KS}\ , \tag{4.15}$$

$$N_p\Omega^{(1,2)}(G)=\frac{3}{32}\left[\frac{m}{\mu}\right]\left[(4-\alpha)+\frac{m}{m_p}(1-\alpha)\right](1-\alpha)\Gamma_{\rm KS}\ . \tag{4.16}$$

Quite incredibly, the two methods give identical results for $\Omega^{(1,1)}$ and the same functional form for $\Omega^{(2,2)}$ [$\Omega^{(2,2)}(\mathfrak{S})/\Omega^{(2,2)}(G)\simeq 1.11$]. This might suggest that the Keilson-Störer kernel can be used with some justification to describe diffusion, viscosity, and thermal conductivity in vapors. The collision integrals $\Omega^{(1,2)}(\mathfrak{S})$ and $\Omega^{1,2}(G)$ differ in functional form, but if one correlates the value of α with the ratio of m/m_p,[9] Eqs. (4.15) and (4.16) will not differ greatly (between 6 and 20%).

C. Difference kernel

To describe small-angle scattering in laser spectroscopy, one often uses a difference kernel that is a kernel which is a function of $|\mathbf{v}-\mathbf{v}'|$ only. All the features of such a kernel can be illustrated by choosing a specific difference kernel of the form

$$K_d(\mathbf{v}'\to\mathbf{v})=\Gamma_d[\pi(\delta u)^2]^{-3/2}e^{-|\mathbf{v}-\mathbf{v}'|^2/(\delta u)^2}\ , \tag{4.17}$$

with $(\delta u)\ll u$. Although a difference kernel does not satisfy detailed balance, it has been used successfully in experimental situations in which the atoms cannot achieve thermal equilibrium during the coherence time of the experiment. As such, the detailed balance violation is not important on the time scale of the experiment.

For a kernel of the form (4.17), it follows immediately from Eqs. (3.3) that

$$\mathfrak{S}\left(\begin{smallmatrix}1&0\\1&\end{smallmatrix}\right)=\mathfrak{S}\left(\begin{smallmatrix}2&0\\2&\end{smallmatrix}\right)=\mathfrak{S}\left(\begin{smallmatrix}1&1\\1&\end{smallmatrix}\right)=0 \tag{4.18}$$

while the various G's can be obtained from Eqs. (3.5) and (4.17) as

$$G_{01}=\tfrac{3}{2}\Gamma_d(\delta u)^2\ , \tag{4.19a}$$

$$G_{02}=\tfrac{15}{4}\Gamma_d(\delta u)^4\ , \tag{4.19b}$$

$$G_{11}=\tfrac{9}{4}\Gamma_d(\delta u)^2u^2\ . \tag{4.19c}$$

The corresponding collision integrals are

$$N_p\Omega^{(1,1)}(G)=\frac{3}{32}\left[\frac{m}{\mu}\right]\left[\frac{\delta u}{u}\right]^2\Gamma_d\ , \tag{4.20}$$

$$N_p\Omega^{(2,2)}(G)=\frac{3}{32}\frac{m}{\mu}\left[3\left[\frac{\delta u}{u}\right]^2-\frac{5}{4}\frac{m}{\mu}\left[\frac{\delta u}{u}\right]^4\right]\Gamma_d\ , \tag{4.21}$$

$$N_p\Omega^{(1,2)}(G)=\frac{9}{64}\left[\frac{m}{\mu}\right]\left[\frac{\delta u}{u}\right]^2\Gamma_d\ , \tag{4.22}$$

$$N_p\Omega^{(1,1)}(\mathcal{S})=N_p\Omega^{(2,2)}(\mathcal{S})=N_p\Omega^{(1,2)}(\mathcal{S})=0\ . \tag{4.23}$$

At first glance, one might say that these results are an indication that one should not use a difference kernel to model collisions in a vapor. This conclusion is certainly true if the time scales are such that thermal equilibrium can be established—in that case a difference kernel leads to incorrect results. On the other hand, the difference kernel can be obtained as a limit of the Keilson-Störer kernel in which

$$\alpha\approx 1;\quad \omega^2=(1-\alpha^2)u^2\approx 2(1-\alpha)u^2\rightarrow(\delta u)^2\ . \tag{4.24}$$

Since we have already shown the Keilson-Störer kernel to be a "reasonable" one, one might also expect that the difference kernel can adequately describe diffusion, viscosity, or thermal conductivity, provided the time scale of an experiment is such that thermal equilibrium cannot be reestablished. In this case, however, the G's must be used to obtain the collision integrals, since the $\Omega^{(l,s)}(\mathcal{S})$'s are identically zero.

V. DISCUSSION

In analyzing collisional processes in atomic vapors, one quickly appreciates the fact that the collision kernel, rather than the differential scattering cross section, is the quantity of practical interest. One also quickly appreciates that it is much easier to adopt a phenomenological kernel rather than attempt to calculate the collision kernel from first principles.[10,11] One is then faced with the problem of how to make an intelligent choice for the kernel.

In this paper, we have shown that transport theory can be used as a building block in constructing an acceptable kernel. Basically, two steps are involved. First one has to choose a specific kernel and second one needs to specify the adjustable parameters.

(1) One must decide whether or not a given phenomenological collision kernel represents a "reasonable" choice. By having derived two sets of equations relating the collision integrals of transport theory to the collision kernels [Eqs. (3.3) and (3.7), respectively], we have a means of testing whether or not a phenomenological kernel gives rise to identical or nearly identical collision integrals by the two methods. Whereas identical results are guaranteed for any physically correct kernel, there is no such guarantee for a phenomenological one. The degree to which a phenomenological kernel produces identical collision integrals by the two methods can serve as some justification for its use. We have shown that a Keilson-Störer kernel produces nearly identical collision integrals while a "difference" kernel produces very different ones.

(2) Having decided that a given kernel is reasonable, it is then possible to reduce the number of free parameters appearing in the kernel by making use of available transport data. For example, suppose that we have an independent value for the diffusion coefficient

$$\mathcal{S}_D=\mathcal{S}\begin{pmatrix}1 & 0\\ 1 & 0\end{pmatrix} \tag{5.1}$$

and wish to fit some line-shape data using a Keilson-Störer kernel. The cross section $\mathcal{S}_{KS}=\Gamma_{KS}/N_p\bar{v}_r$ is no longer a free parameter since it is related to $\mathcal{S}_D$ [see Eq. (4.10a)] by

$$\mathcal{S}_{KS}=\mathcal{S}_D/(1-\alpha)\ , \tag{5.2}$$

where α is the strength parameter [see Eq. (4.8)]. Moreover, if α is chosen to its equivalent hard-sphere value,[9] the second free parameter in the Keilson-Störer kernel is also eliminated.

In order to make use of transport data, one must have values for the transport coefficients. Experimental values for the coefficients can be found for many ground-state–ground-state A-P interactions, but are rarely available for excited-state–ground-state A-P interactions. The latter enter into systems of practical interest in laser spectroscopy and light-induced drift. If such experimental values are not available, it is possible to calculate the transport coefficients[12] whenever the A-P interatomic potentials are known from other sources (e.g., *ab initio* calculations or beam-scattering experiments). Fitting a Keilson-Störer kernel without any adjustable parameters to experimental data provides a rather severe test of the validity of the kernel. Presently, we are using this method to fit collision data relevant to the light-induced drift effect.[1,13]

We can apply these ideas to an experiment of Aminoff *et al.*[14] who studied collisions between ground-state sodium atoms (A) and ground-state neon perturbers (P). They fit their data using the sum of two collision kernels, a Keilson-Störer kernel with parameters[14]

$$\mathcal{S}_{KS}=55\ \text{Å}^2,\quad \alpha=0.37 \tag{5.3a}$$

added to a difference kernel [see Eq. (4.17)] with parameters[14]

$$\mathcal{S}_d=58\ \text{Å}^2,\quad \frac{\delta u}{u}=0.39 \tag{5.3b}$$

with uncertainties of 10–20%. Using Eqs. (4.10a), (4.20), (2.31a), and the definitions

$$\mathcal{S}_d=\frac{\Gamma_d}{N_p\bar{v}_r},\quad \mathcal{S}_{KS}=\frac{\Gamma_{KS}}{N_p\bar{v}_r} \tag{5.4}$$

one obtains a total diffusion cross section

$$\mathcal{S}_D=(1-\alpha)\mathcal{S}_{KS}+\frac{1}{2}\left[\frac{\delta u}{u}\right]^2\mathcal{S}_d=39\ \text{Å}^2 \tag{5.5}$$

again with an uncertainty of about 20%. On the other hand, one can use available curves for the interatomic potentials[15] to calculate a diffusion cross section of ground-state sodium atoms in neon[12]

$$\mathcal{S}_D = 16\ \text{Å}^2 .$$

The large difference between these two values of $\mathcal{S}_D$ indicates that the fit of Aminoff *et al.* does not seem to be consistent with available transport data, this despite the fact that the agreement between theoretical and experimental line shapes was excellent.

Finally, we should like to discuss some possible extensions of the theory. We first note that the collision kernel is an inherently richer quantity than the transport coefficients. The transport coefficients are related to *integrals* over the collision kernels and, as such, are related to various moments of the collision kernel. The transport coefficients cannot give detailed information on the collision kernel unless some specific form for the kernel is assumed. On the other hand, the collision kernel completely determines all the transport coefficients.

The theory can be extended to derive transport coefficients for quantities other than ground-state elastic scattering. In laser spectroscopy, one often measures collision kernels relating to inelastic scattering, Zeeman coherence, and optical coherence for atoms in both excited and ground states. Using techniques similar to the ones employed in Sec. III, one could define collision integrals and transport coefficients for these quantities and relate them to the collision kernels.

The theory can also be extended to account for a collisional process in which atom A enters the collision with velocity $\mathbf{v}'$ and atom P leaves the collision with velocity $\mathbf{v}$. This type of process leads to an *exchange kernel* involving an average over the initial velocity distribution of the P atoms and a sum (integration) over all the final velocities of the A atoms. In a single-component gas where one cannot distinguish the A and P atoms, this exchange kernel contributes to the transport phenomena and must be included in the analysis—a fact well known in classical transport theory. It might be noted that there have been experimental measurements of such exchange kernels in Kr-Xe and ^{20}Ne-^{22}Ne collisions.[10,16]

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APPENDIX A: RELATING THE $\mathcal{S}(\begin{smallmatrix} l & n \\ l' & n' \end{smallmatrix})$ TO SQUARE BRACKET INTEGRALS

Chapman and Cowling[2] use the notation

$$\Omega^{l}_{12}(s) = \Omega^{(l,s)} . \tag{A1}$$

They also give square bracket integrals in their Table 9.6 which are related to the $\mathcal{S}(\begin{smallmatrix} l & n \\ l' & n' \end{smallmatrix})$ as follows:

$$[\mathbf{C}_1, \mathbf{C}_1]_{12} = \tfrac{3}{2}\bar{v}_r \mathcal{S}\left(\begin{smallmatrix} 1 & 0 \\ 1 & 0 \end{smallmatrix}\right) , \tag{A2}$$

$$[\mathbf{C}_1^0\mathbf{C}_1, \mathbf{C}_1^0\mathbf{C}_1] = \tfrac{5}{2}\bar{v}_r \mathcal{S}\left(\begin{smallmatrix} 2 & 0 \\ 2 & 0 \end{smallmatrix}\right) , \tag{A3}$$

$$[\mathbf{C}_1, S^{(1)}_{3/2}(C_1^2)\mathbf{C}_1] = \frac{3}{2}\left[\frac{5}{2}\right]^{1/2} \bar{v}_r \mathcal{S}\left(\begin{smallmatrix} 1 & 1 \\ 1 & 0 \end{smallmatrix}\right) . \tag{A4}$$

APPENDIX B: RELATING THE G_{ql}'s TO THE $\Omega^{(m,n)}$'s

The starting point for the calculation is Eq. (3.5),

$$G_{ql} = \int d\mathbf{v}\, d\mathbf{v}' (v')^{2q} |\mathbf{v}-\mathbf{v}'|^{2l} K(\mathbf{v}'\to\mathbf{v}) W(\mathbf{v}') . \tag{B1}$$

One then substitutes Eq. (2.5) for $K(\mathbf{v}'\to\mathbf{v})$ in Eq. (B1), uses the fact that

$$W_p(\mathbf{v}'-\mathbf{v}_r') W(\mathbf{v}') = W_r(\mathbf{v}_r') W_T(\mathbf{y}) , \tag{B2}$$

where W_a, W_p, and W_r are defined by (2.8), (2.3), and (2.10), respectively,

$$W_T(\mathbf{y}) = (\pi u_T^2)^{-3/2} e^{-y^2/u_T^2} , \tag{B3}$$

$$u_T^2 = \frac{2k_B T}{M}; \quad M = m + m_p \tag{B4}$$

(u_T is the most probable speed associated with the A-P center-of-mass distribution),

$$\mathbf{y} = \left[\mathbf{v}' - \frac{\mu}{m}\mathbf{v}_r\right] , \tag{B5}$$

and performs the integration over $\mathbf{v}$ and $\mathbf{v}_r$ to obtain

$$G_{ql} = N_p \int W_r(\mathbf{v}_r') v_r' R_q(\mathbf{v}_r') F_l(v_r')\, d\mathbf{v}_r' , \tag{B6}$$

where

$$R_q(\mathbf{v}_r') = \int \left|\mathbf{y} + \frac{\mu}{m}\mathbf{v}_r'\right|^{2q} W_T(\mathbf{y})\, d\mathbf{y} \tag{B7}$$

and

$$F_l(v_r') = \int \left|\frac{\mu}{m}(v_r'\hat{\mathbf{v}}_r - \mathbf{v}_r')\right|^{2l} \times \frac{d\sigma}{d\Omega_{v_r}}(v_r', |v_r'\hat{\mathbf{v}}_r - \mathbf{v}_r'|)\, d\Omega_{v_r} . \tag{B8}$$

For spherically symmetric interaction potentials, one can use the relationships $d\sigma/d\Omega = (b/\sin\chi)db/d\chi$ and

$|\mathbf{v}_r-\mathbf{v}_r'|=2v_r\sin(\chi/2)$ to rewrite Eq. (B8) as

$$F_l(v_r')=2\pi\left[2v_r'\left[\frac{\mu}{m}\right]\right]^{2l}\int_0^\infty b\,db\,\sin^{2l}\left[\frac{\chi}{2}\right], \quad \text{(B9)}$$

where b is the impact parameter of the collision and χ is the scattering angle in the center-of-mass frame (χ is a function of b and v_r).

By choosing different values for q and l one finds that the G_{ql} given by Eqs. (B6), (B7), and (B9) are linear combinations of the $\Omega^{(l,s)}$ defined by Eqs. (2.14) and (2.15). As an example, we calculate G_{01}, G_{02}, and G_{11}.

$q=0$, $l=1$. Using the relationship $\sin^2(\chi/2)=(1-\cos\chi)/2$, it immediately follows from Eqs. (B6), (B7), (B9), (2.14), and (2.15) that

$$R_0(v_r')=1;\quad F_1(v_r')=2\left[\frac{\mu}{m}\right]^2(v_r')^2Q^{(1)} \quad \text{(B10)}$$

and

$$G_{01}=16\left[\frac{\mu}{m}\right]u^2N_p\Omega^{(1,1)}. \quad \text{(B11)}$$

$q=0$, $l=2$. By writing

$$\sin^4(\chi/2)=\tfrac{1}{4}[-(1-\cos^2\chi)+2(1-\cos\chi)]$$

it is again an easy matter to derive

$$R_0(v_r)=1;\qquad F_2(v_r')=4\left[\frac{\mu}{m}\right]^4(v_r')^4(-Q^{(2)}+2Q^{(1)}) \quad \text{(B12)}$$

and

$$G_{02}=32\left[\frac{\mu}{m}\right]^2u^4N_p(2\Omega^{(1,2)}-\Omega^{(2,2)}). \quad \text{(B13)}$$

$q=1$, $l=1$. The quantity $F_1(v_r')$ is still given by Eq. (B10), but now we need

$$R_1(v_r')=\tfrac{3}{2}u_T^2+\left[\frac{\mu}{m}\right]^2(v_r')^2. \quad \text{(B14)}$$

Inserting $R_1(v_r')$ and $F_1(v_r')$ into Eq. (B6) and comparing with Eq. (2.14), one finds

$$G_{11}=16\left[\frac{\mu}{m}\right]u^4N_p\left[\frac{3}{2}\left[\frac{\mu}{m_p}\right]\Omega^{(1,1)}+\left[\frac{\mu}{m}\right]\Omega^{(1,2)}\right]. \quad \text{(B15)}$$

Other collision integrals can be generated in a similar fashion. This method for generating the $\Omega^{(l,s)}$ integrals seems less cumbersome than those in classical texts[3] on this subject matter.

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[7]The collision integrals relevant to the present discussion are those in which the $\Omega^{(l,s)}$ also contain the subscript 12, i.e., $\Omega_{12}^{(l,s)}$, which indicates that the integrals are appropriate to collisions between different species of atoms.

[8]For a calculation of the collision kernel and rate for hard-sphere scattering, see the Appendix of the article by Liao *et al.* [P. F. Liao, J. E. Bjorkholm, and P. R. Berman, Phys. Rev. A **21**, 1927 (1980)]. Note that a factor of 2 is missing in the second term of Eq. (A4) and $\sqrt{2}$ should be replaced by $\sqrt{\pi}$ in Eq. (A8) in that paper.

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