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Kinetic Theory of Excess Electrons in Polyatomic Gases, Liquids, and Solids

H. Ted Davis*†
Departments of Chemical Engineering and Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

and

L. D. Schmidt and R. M. Minday
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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The Cohen-Lekner kinetic theory of electron transport in simple systems is extended to polyatomic systems. The single-scatterer approximation is used to construct differential scattering cross sections for electron-molecule scattering in which the dependence on certain internal parameters such as molecular orientations and conformations, which vary with periods short compared to the duration of an electron-molecule collision, is accounted for by a fixed-internal-coordinates approximation. The resulting differential cross section, unlike the case treated by Cohen and Lekner, does not factor into a product of the electron-single-scatterer cross section and the Van Hove spectral function. The most important consequence of the internal parameters of the scattering molecules is the appearance of an incoherent scattering effect. Such an effect can be very important in liquids and solids where, because of intermolecular order, the coherent part of the cross section may be very small. Boltzmann's equation for electrons moving in a constant electric field is derived, solved formally for arbitrary field strength, and solved explicitly for a low-field limit.

I. INTRODUCTION

During the past few years, purification techniques have been developed to the point that stable free or "quasifree" electrons have been observed in the inert gases, liquids,[1,2] and solids[3] and in several hydrocarbon liquids.[4,5] Most of the studies have been of drift velocities in which the time of flight of excess electrons subject to an external electric field is measured between two electrodes of known separation.

Electron mobilities (defined as the ratio of the drift velocity to the electric field strength) in argon and krypton liquids and solids range from 400 to 1500 $\text{cm}^2/\text{V sec}$, more than 10^5 times ionic mobilities in the same systems. These electron mobilities are 50–100 times what one would have expected from dimensional analysis based on simple kinetic theory, in which it is assumed that the only differences between diffusing electrons and ions are their different masses and cross sections. In such a dimensional analysis, however, diffraction (i.e., coherent-scattering) effects due to the wave nature of low-energy electrons have been ignored. Cohen and Lekner,[6,7] on the basis of a Boltzmann equation they derived, showed that condensed-phases diffraction effects, arising from the molecular order of the systems, lead to a cross section per scatterer equal to the product of the electron-single-atom cross section and the quantity $S(0)$, where $S(\vec{K})$ is the structure factor related to the intermolecular pair correlation function $g(\vec{R})$ by the expression

$$S(\vec{K}) = 1 + n \int e^{i\vec{K}\cdot\vec{R}} [g(\vec{R}) - 1]\, d^3R . \qquad (1.1)$$

Here n denotes the molecular-number density of the system. For the inert gases, liquids, and solids, $S(0)$ is about 10^{-2}, thus accounting for the factor of 50–100 lost in dimensional analysis. Lekner[7] has shown that the Cohen-Lekner theory accounts quantitatively for the magnitude and the $T^{-3/2}$ temperature dependence of the mobility of electrons in argon below about 115 °K, and for the increase in the mobilities in argon and krypton in going from the liquid to solid phase at the melting point. Moreover, by including contributions to the cross section from fluctuations of the effective potential energy, Lekner[8] has shown that the theory provides a semiquantitative (or at least a qualitative) description of the mobilities in argon above 115 °K and in krypton where mobility maxima are observed. Thus, on the basis of the Cohen-Lekner theory one has a fairly good picture of the nature of excess electron transport in the inert gas systems.

Excess electron mobilities in the hydrocarbon liquids are much less understood than in the inert gas liquids. There is evidence in both gases and liquids that there is significant inelastic scattering of slow electrons even in the saturated hydrocarbons.[9] Moreover, the mobilities are extremely sensitive to the structure of the hydrocarbons. For example, electron mobilities of 0.16, 1.1, and 55 $\text{cm}^2/\text{V sec}$ were observed[5] in n-pentane, cyclopentane, and neopentane, respectively. It is felt intuitively[4,5] that this strong dependence on structure is connected with the electric moments, such as the dipole moments, of the C-H bonds in these molecules, the more symmetric neopentane attaining fewer conformations of nonzero dipole moment than the less symmetric cyclopentane and *n*-pentane. Just what this connection may be has not been clarified.

This paper represents what we feel is a first step toward obtaining a quantitative theory of the role of electric moments and internal degrees of freedom in excess electron transport in hydrocarbons.

In the following sections we shall present a generalization of Cohen and Lekner's theory which allows for the effect of the electric moments (or any other noncentrally symmetric forces) and internal degrees of freedom on excess electron transport in polyatomic systems. The most interesting feature of our generalization is the appearance of an incoherent scattering contribution not present in Cohen and Lekner's theory. This incoherence effect is brought out very clearly in Sec. II wherein we treat a model dipole fluid in which there is only incoherent electron scattering.

Since we shall parallel their work rather closely, it is useful at this point to review briefly Cohen and Lekner's theory. The first step is the construction of the differential cross section for electron scattering in a system of N scattering centers. To this end, Cohen and Lekner made the following two assumptions: (i) The total amplitude F_T of the scattered electron at a point in the system is the coherent sum of amplitudes scattered singly from the individual scattering centers, and (ii) the scattering centers are identical atoms having no internal states which give rise to incoherent scattering.

Under these two assumptions the total scattering amplitude may be written in the form

$$F_T = \sum_{\nu=1}^{N} F e^{i\vec{K}\cdot\vec{r}_\nu} , \tag{1.2}$$

where F is the electron-single-atom scattering length, $\vec{r}_\nu$ the position coordinate of the νth atom, and $\hbar\vec{K} = \vec{p} - \vec{p}\,'$ the momentum change for an electron scattered through the solid angle $d\Omega$ with an electron energy change $\hbar\omega = \epsilon - \epsilon'$. Equation (1.2), in turn, leads to the following expression for the ensemble-averaged differential cross section per scatterer[10]:

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)} = \frac{p'}{\hbar p} |F|^2 S(\vec{K}, \omega)$$

$$\equiv \frac{p'}{\hbar p} \tilde{\sigma}\left(\epsilon - \frac{\hbar\omega}{2}, \theta\right) S(\vec{K}, \omega), \tag{1.3}$$

where $\tilde{\sigma}$ is the electron-single-atom differential cross section and $S(\vec{K}, \omega)$ (known as the spectral function) is the four-dimensional Fourier transform of the van Hove[11,12] space-time correlation function $G(\vec{r}, t)$ of the atoms of the system. It is through this function that diffraction effects, arising from intermolecular correlations, appear in the Cohen-Lekner theory. Classically, $G(\vec{r}, t)\, d^3r$ may be thought of as the probability that, if a particle was in the volume element d^3r centered on position $\vec{r} = 0$ at time $t = 0$, there will be a particle at $\vec{r}$ in d^3r at time t. Thus, at time $t = 0$, $G(\vec{r}, t)$ obeys the condition

$$G(\vec{r}, 0) = \delta(\vec{r}) + ng(\vec{r}), \tag{1.4}$$

where the Dirac δ function represents the "self" part of G and ensures the existence of a particle at $\vec{r} = 0$ initially; the term $ng(\vec{r})$, a product of the atomic-number density and the pair correlation function, gives the contribution of correlated neighbors to G. The next step in the Cohen-Lekner theory is to construct a steady-state balance equation for the momentum distribution function $f(\vec{p})$ of electrons, not interacting with one another, moving through the system under the influence of a constant electric field $\vec{\mathcal{E}}$. They assume the balance equation is a linear Boltzmann equation of form

$$e\vec{\mathcal{E}} \cdot \frac{\partial f}{\partial \vec{p}} = n \iint d\Omega\, d(\hbar\omega) \frac{p'}{m} \tilde{\sigma}\left(\epsilon - \frac{\hbar\omega}{2}, \theta\right) S(\vec{K}, \omega)$$

$$\times [e^{-\beta\hbar\omega} f(\vec{p}\,') - f(\vec{p})] . \tag{1.5}$$

e is the electronic charge and $\beta = 1/kT$, where k is Boltzmann's constant and T the temperature. The left-hand side of Eq. (1.5) represents the acceleration of the electrons by the field which is balanced by the right-hand side representing the deceleration of the electrons by collision with the atoms of the system. The second term on the right-hand side of Eq. (1.5) represents the loss of electrons with momentum $\vec{p}$ by collisions. It is built up by multiplying the scattering probability $[d^2\sigma/d\Omega\, d(\hbar\omega)]\, d\Omega\, d(\hbar\omega)$ times the probable flux of scattering events $(p/m)\, nf(\vec{p})\, d^3p$ and integrating over solid scattering angle Ω and energy transfer $\hbar\omega$. The first term on the right-hand side of Eq. (1.5) represents the gain of electrons in momentum state $\vec{p}$ by collisional transition of electrons initially in momentum state $\vec{p}\,'$. This term is built up similarly to the term just considered, but with a simplification arising from the detailed balancing condition

$$S(-\vec{K}, -\omega) = e^{\beta\omega\hbar} S(\vec{K}, \omega) . \tag{1.6}$$

It is difficult, in general, to assess the validity of the single-scatterer approximation and of the Boltzmann equation. As pointed out by Cohen and Lekner,[6] a necessary condition for single scattering, and a sufficient condition for the validity of the Boltzmann equation, is that the de Broglie wavelength of the electron be short compared to its mean free path. Lekner has found for argon that even in the electron energy range for which multiple scattering occurs, its effect is largely self-canceling. It remains to be seen if such cancellation occurs in polyatomic systems. In any case, in this paper we shall continue to treat the scattering process by the single-scattering approximation and to assume the validity of the linear Boltzmann equation. Multiple-scattering effects will be studied in a future publication.

The theory presented in this paper may be divided into two parts. The first part is the derivation of an appropriate thermal-averaged differential-scattering cross section describing the scattering of electrons by the polyatomic molecules of the system. The second is the derivation and solution of the kinetic equation of electron transport. The derivation of cross sections is the subject of Secs. II–IV. In Secs. II and III, the first Born approximation is used to derive explicit cross sections for electron-multipole scattering. Several investigators[13–15] have advanced arguments in favor of using the first Born approximation for treating slow-electron–multipole scattering. In Sec. IV, a more general expression for the differential cross section is derived for the single-scatterer approximation under the assumption that a certain set of internal coordinates I, positions of nuclei for example, are fixed during a scattering event. This assumption of fixed I is sometimes[14,16–18] called the adiabatic approximation. Because of confusion that arises from the use of the word "adiabatic" for other unrelated situations, we prefer to refer to the approximation as a "fixed-internal-coordinates" approximation. To this approximation, one first calculates the differential cross section for the electron-molecule interactions characteristic of fixed I and then averages over the distribution of I characteristic of the system. The opposite of the fixed-internal-coordinates approximation would be to approximate the electron-molecule interactions by averaging over the distribution of I. The latter approximation is appropriate when the internal parameters I vary with periods short compared to the duration of the collision, while the fixed-internal-coordinates approximation is appropriate when the duration of the collision is short compared to the periods of I. To the single-scatterer approximation, both possibilities are included in our theory; the structure-independent part of the interaction potential will contain the contributions from averaging over the I's of short periods. As an example, in considering thermal electrons in a hydrocarbon, we might expect that electron interaction with rotation of the molecule, rotation of CH_2 groups about their bonds, and skeletal vibrations could be treated by the fixed-internal-coordinates approximation, while interaction with the C-H stretching and bending modes could be treated as the average potential of interaction.

Section V is devoted to the derivation and formal solution of the Boltzmann equation. An explicit solution is given only for the low-field limit and for the case of small average electron energy change per collision event. The theory developed here is presently being applied to particular molecular models. The results of these calculations will be published in the near future.

II. ELECTRON-DIPOLE-SCATTERING CROSS SECTION : BORN APPROXIMATION

In this section, we study a particular model to illustrate the ideas behind the more general theory to be presented in the next sections. Let us consider a system of N identical rotators, described by the Hamiltonian operator H_0, interacting with an electron according to the dipole potential-energy function

$$V=\sum_{\nu=1}^{N} -e\vec{D}_\nu\cdot\frac{(\vec{r}-\vec{r}_\nu)}{|\vec{r}-\vec{r}_\nu|^3}=\sum_{\nu=1}^{N} V_\nu, \qquad (2.1)$$

where e is the electronic charge, $|\vec{D}_\nu|=D$ the dipole moment of the νth rotator, $\vec{r}$ the position of the electron, and $\vec{r}_\nu$ the position of the νth rotator.

We wish to calculate the differential cross section for the scattering process in which the system of rotators goes from quantum state i to state l, and the electron with initial momentum $\hbar\vec{k}_0=\vec{p}$ is scattered into an element of solid angle $d\Omega=\sin\theta\, d\theta\, d\phi$ and has a resulting momentum $\hbar\vec{k}=\vec{p}'$. Using the Born approximation, we can express the desired cross section per scatterer per unit solid angle in the form[19]

$$\left(\frac{d\sigma}{d\Omega}\right)_{l|i}=\frac{k}{k_0N}\,|F_{l|i}|^2, \qquad (2.2)$$

where

$$F_{l|i}=-\frac{m}{2\pi\hbar^2}\left\langle l\left|\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\left(\sum_{\nu=1}^{N} V_\nu\right) e^{i\vec{k}_0\cdot\vec{r}}\right|i\right\rangle. \qquad (2.3)$$

The last expression can be simplified somewhat by interchanging the summation over ν and the integration over $\vec{r}$ and introducing the coordinate transformation $\vec{R}=\vec{r}-\vec{r}_\nu$ to obtain

$$F_{l|i}=-\sum_{\nu=1}^{N}\langle l|\, a(\gamma_\nu)e^{i\vec{K}\cdot\vec{r}_\nu}|\, i\rangle, \qquad (2.4)$$

where

$$\vec{K}=\vec{k}_0-\vec{k} \qquad (2.5)$$

and

$$a(\gamma_\nu)=+\frac{m}{2\pi\hbar^2}\int d^3\vec{R}\, e^{i\vec{K}\cdot\vec{R}}\, V_\nu$$

$$=-\frac{me}{2\pi\hbar^2}\int d^3\vec{R}\, e^{i\vec{K}\cdot\vec{R}}\,\frac{\vec{R}\cdot\vec{D}_\nu}{R^3}\quad . \qquad (2.6)$$

Taking a fixed-coordinate frame in which the z axis lies along the unit vector $\hat{K}=\vec{K}/K$, we may write

$$\vec{R}=R[\cos\theta_\nu\hat{K}+\sin\theta_\nu\cos\phi_\nu\hat{i}+\sin\theta_\nu\sin\phi_\nu\hat{j}],$$

$$\vec{D}_\nu=D[\cos\gamma_\nu\hat{K}+\sin\gamma_\nu\cos\eta_\nu\hat{i}+\sin\gamma_\nu\sin\eta_\nu\hat{j}],$$

and the integral of Eq. (2.6) can be performed as follows:

$$\begin{aligned}a(\gamma_\nu)&=-\frac{me}{2\pi\hbar^2}D\int_0^\infty dR\int_{-1}^{1}d(\cos\theta_\nu)\int_0^{2\pi}d\phi_\nu\,e^{-iKR\cos\theta_\nu}\\&\quad\times[\cos\theta_\nu\cos\gamma_\nu+\sin\theta_\nu\cos\phi_\nu\sin\gamma_\nu\cos\eta_\nu\\&\quad+\sin\theta_\nu\sin\phi_\nu\sin\gamma_\nu\sin\eta_\nu]\\&=-\frac{2ieDm}{\hbar^2}\frac{\cos\gamma_\nu}{K},\end{aligned}\qquad(2.7)$$

where

$$\cos\gamma_\nu=\vec{D}_\nu\cdot\vec{K}/DK.\qquad(2.8)$$

Expression (2.4) differs from that obtained for scattering by a centrally symmetric potential in that the scattering length $a(\gamma_\nu)$ cannot be taken out of the inner product $\langle l|\cdots|i\rangle$ because of the orientation dependence, i.e., the dependence on γ_ν.

The cross section per unit angle for scattering by N dipoles initially in state i, and such that the total electron energy change is $\hbar\omega$, is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_i=\sum_l\int d(\hbar\omega)\delta(E_i-E_l-\hbar\omega)\left(\frac{d\sigma}{d\Omega}\right)_{l|i}.\qquad(2.9)$$

We have summed over all final states consistent with conservation of energy by introducing the Dirac δ function in Eq. (2.9). From Eq. (2.9) it follows that the differential cross section corresponding to the ith quantum state of the system is

$$\begin{aligned}\left(\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}\right)_i&=\sum_l\delta(E_i-E_l-\hbar\omega)\left(\frac{d\sigma}{d\Omega}\right)_{l|i}\\&=(2\pi\hbar)^{-1}\sum_l\int_{-\infty}^{\infty}dt\,e^{-i(\hbar\omega-E_i+E_l)t/\hbar}\left(\frac{d\sigma}{d\Omega}\right)_{l|i}.\end{aligned}\qquad(2.10)$$

The second equality of Eq. (2.10) follows from the integral representation of the Dirac δ function

$$\delta(x)=(2\pi)^{-1}\int_{-\infty}^{\infty}dy\,e^{ixy}.\qquad(2.11)$$

The quantity t in Eq. (2.10) has the dimensions of time. Combining Eqs. (2.4) and (2.2) and using the fact that

$$e^{iH_0t/\hbar}|j\rangle=e^{iE_jt/\hbar}|j\rangle,$$

we obtain the result

$$\left(\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}\right)_i=\frac{k}{2\pi\hbar k_0N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle i|e^{iH_0t/\hbar}a(\gamma_\nu)e^{i\vec{K}\cdot\vec{r}_\nu}e^{-iH_0t/\hbar}\bar{a}(\gamma_{\nu'})e^{-i\vec{K}\cdot\vec{r}_{\nu'}}|i\rangle.\qquad(2.12)$$

Equation (2.12) gives the differential-scattering cross section corresponding to the quantum state i of the system. If the system is assumed to be in thermodynamic equilibrium at a temperature T, then the differential cross section for electron scatter by the system is obtained by thermal averaging Eq. (2.12). Thus, the desired differential cross section is

$$\begin{aligned}\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}&=\sum_i e^{-E_i/kT}\left(\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}\right)_i\Big/\sum_i e^{-E_i/kT}\\&=\frac{k}{2\pi\hbar k_0N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\\&\quad\times\langle a(\gamma_\nu(t))e^{i\vec{K}\cdot\vec{r}_\nu(t)}\bar{a}(\gamma_{\nu'}(0))e^{-i\vec{K}\cdot\vec{r}_{\nu'}(0)}\rangle_T,\end{aligned}\qquad(2.13)$$

where $\langle\cdots\rangle_T$ denotes the thermal average

$$\langle a\rangle_T=\frac{\sum_i e^{-E_i/kT}\langle i|\alpha|i\rangle}{\sum_i e^{-E_i/kT}}\equiv\frac{\mathrm{Tr}\{e^{-H_0/kT}\alpha\}}{\mathrm{Tr}\{e^{-H_0/kT}\}},\qquad(2.14)$$

and where we have used the Heisenberg operator notation

$$\begin{aligned}&A(r_1(t),r_N(t),\gamma_1(t),\ldots,\gamma_N(t))\\&\quad=e^{iH_0t/\hbar}A(r_1,\ldots,r_N,\gamma_1,\ldots,\gamma_N)e^{-iH_0t/\hbar}.\end{aligned}\qquad(2.15)$$

Equation (2.13) reduces to the well-known result for neutron scattering[19] if it is assumed that $a(\gamma_\nu)$ is independent of orientation γ_ν. The dependence of $a(\gamma_\nu)$ on γ_ν gives rise to an "incoherent" scattering term which is not present in the neutron scattering cross section. To see this more clearly, let us assume that the dipoles may be represented by freely rotating rigid rotors, i.e., the Hamiltonian H_0 is the sum of the commuting terms H_0^R and H_0^{CM}, where H_0^R denotes the rotational part of H_0, and where H_0^{CM} contains the kinetic energy of the centers of mass of the rotators and the part of the intermolecular potential energy of interaction of the rotators which we assume to be centrally symmetric. Under the assumption that H_0^R and H_0^{CM} commute, Eq. (2.13) reduces to the expression

$$\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}=\frac{k}{2\pi\hbar k_0N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}$$

$$\times \langle a(\gamma_\nu(t))\bar{a}(\gamma_{\nu'}(0))\rangle_T^R$$

$$\times \langle e^{i\vec{K}\cdot\vec{r}_\nu(t)} e^{-i\vec{K}\cdot\vec{r}_{\nu'}(0)}\rangle_T^{CM}, \qquad (2.16)$$

where the first thermal average in Eq. (2.16) is taken with respect to the Hamiltonian operator H_0^R, and the second average is taken with respect to H_0^{CM}. In the summations over ν and ν', two possibilities arise. First, there are N identical terms for which $\nu = \nu'$, and $N(N-1)$ identical terms for which $\nu \neq \nu'$. Choosing $\nu = 1$ and $\nu' = 1$ and 2, respectively, as representative contributions to Eq. (2.16), we may reduce Eq. (2.16) to the form

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\int d^3r\, e^{i\vec{K}\cdot\vec{r}}$$

$$\times [\tilde{\sigma}_{\rm inc}(t) G_s^{CM}(\vec{r}, t) + \tilde{\sigma}_{\rm coh}(t) G^{CM}(\vec{r}, t)], \qquad (2.17)$$

where we have introduced the notations

$$\tilde{\sigma}_{\rm inc} \equiv [\langle a(\gamma_1(t))\bar{a}(\gamma_1(0))\rangle_T^R - \langle a(\gamma_1(t))\bar{a}(\gamma_2(0))\rangle_T^R], \qquad (2.18)$$

$$\tilde{\sigma}_{\rm coh} \equiv \langle a(\gamma_1(t))\bar{a}(\gamma_2(0))\rangle_T^R, \qquad (2.19)$$

and the definitions

$$\int d^3r\, e^{i\vec{K}\cdot\vec{r}} G_s^{CM}(\vec{r}, t) \equiv \langle e^{i\vec{K}\cdot\vec{r}_1(t)} e^{-\vec{K}\cdot\vec{r}_1(0)}\rangle_T^{CM}, \qquad (2.20)$$

$$\int d^3r\, e^{i\vec{K}\cdot\vec{r}} G^{CM}(\vec{r}, t) = \langle e^{i\vec{K}\cdot\vec{r}_1(t)} e^{-i\vec{K}\cdot\vec{r}_1(0)}\rangle_T^{CM}$$

$$+ (N-1)\langle e^{i\vec{K}\cdot\vec{r}_2(t)} e^{-i\vec{K}\cdot\vec{r}_1(0)}\rangle_T^{CM}$$

$$= \sum_{\nu=1}^{N} \langle e^{i\vec{K}\cdot\vec{r}_\nu(t)} e^{-\vec{K}\cdot\vec{r}_1(0)}\rangle_T^{CM}. \qquad (2.21)$$

The quantities $G_s^{CM}(\vec{r}, t)$ and $G^{CM}(\vec{r}, t)$ are, respectively, the self and total Van Hove space-time correlation functions which describe the dynamics of the motions of the centers of mass of the rotors.

If the scattering length $a(\gamma_\nu)$ were orientation independent, the "incoherent" term $\tilde{\sigma}_{\rm inc}$ would vanish, and Eq. (2.17) would reduce to

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)} = \frac{k}{\hbar k_0}|a|^2 S^{CM}(\vec{K}, \omega), \qquad (2.22)$$

where the spectral function $S^{CM}(\vec{K}, \omega)$ is the space-time Fourier transform of $G^{CM}(\vec{r}, t)$. Equation (2.22) is, to the Born approximation, the same as Eq. (1.3), the starting point in Cohen and Lekner's theory. Thus, the incoherent contributions arising from orientation-dependent interactions are not accounted for in the Cohen-Lekner theory, i.e., $\tilde{\sigma}_{\rm inc} \equiv 0$ for the case they treat. The term neglected in taking Eq. (2.22) for the differential cross section may, in some cases, dominate the coherent contribution to the scattering cross section. To illustrate this point, let us simplify our model further by assuming that the rigid rotors are freely rotating dumbbells so that H_0^R is separable into a sum of single rotor operators H_ν^R whose eigenfunctions are the spherical harmonics $Y_{lm}(\gamma_\nu, \eta_\nu)$ with eigenvalues

$$E_{lm} = E_l = (\hbar^2/2I)l(l+1),$$

$l = 0, 1, \ldots, m = -l, -l+1, \ldots, l$. It follows from the form of $a(\gamma_\nu)$ in Eq. (2.7) and the separability of H_0^R that

$$\tilde{\sigma}_{\rm coh} = \langle \bar{a}(\gamma_1(t)) a(\gamma_2(0))\rangle_T^R$$

$$= (k/k_0)\langle \bar{a}(\gamma_1(t))\rangle_T^R \langle a(\gamma_2(0))\rangle_T^R = 0. \qquad (2.23)$$

Thus, for this simplification of the model, *only* the incoherent term $\tilde{\sigma}_{\rm inc}$ contributes to scattering. To evaluate this term let us write $a(\gamma_\nu) = -ib\cos\gamma_\nu$, where according to Eq. (2.7)

$$b = 2eDm/\hbar^2 K. \qquad (2.24)$$

Then, evaluating the thermal average, we obtain

$$\tilde{\sigma}_{\rm inc} = b^2 \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{\langle lm|\, e^{-\beta H_1^R} e^{iH_1^R t/\hbar} \cos\gamma_1\, e^{-iH_1^R t/\hbar} \cos\gamma_1 \,|lm\rangle}{\mathrm{Tr}\{e^{-\beta H_1^R}\}}$$

$$= \frac{b^2}{\mathrm{Tr}\{e^{-\beta H_1^R}\}} \sum_{l=0}^{\infty}\sum_{m=-1}^{l}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l} e^{-\beta E_l + iE_l t/\hbar - iE_{l'} t/\hbar}$$

$$\times \langle lm|\cos\gamma_1|l'm'\rangle\langle l'm'|\cos\gamma_1|lm\rangle. \qquad (2.25)$$

The matrix elements in Eq. (2.25) may be evaluated using the identity

$$\cos\gamma_1 Y_{lm}(\gamma_1, \eta_1) = Y_{l+1,m}(\gamma_1, \eta_1)\left[\frac{(l+1-m)(l+1+m)}{(2l+1)(2l+3)}\right]^{1/2}$$

$$+ Y_{l-1,m}(\gamma_1, \eta_1)\left[\frac{(l-m)(l+m)}{(2l-1)(2l+1)}\right]^{1/2}. \qquad (2.26)$$

Using this identity, we find

$$\langle l'm'|\cos\gamma_1|lm\rangle = \int_0^{2\pi}\int_0^{2\pi} \bar{Y}_{l'm'}(\gamma_1, \eta_1)\cos\gamma_1\, Y_{lm}(\gamma_1, \eta_1)\sin\gamma_1\, d\gamma_1\, d\eta_1$$

$$= \delta_{mm'}^{Kr}\left\{\delta_{l',l+1}^{Kr}\left[\frac{(l+1-m)(l+1+m)}{(2l+1)(2l+3)}\right]^{1/2} + \delta_{l',l-1}^{Kr}\left(\frac{(l-m)(l+m)}{2l-1)(2l+1)}\right)^{1/2}\right\}. \qquad (2.27)$$

This result reduces Eq. (2.25) to the form

$$\tilde{\sigma}_{\text{inc}} = b^2 \sum_{l=0}^{\infty} e^{-\beta E_l} \sum_{m=-l}^{l} \left[\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} \; e^{i(E_l - E_{l+1})t/\hbar} + \frac{l^2 - m^2}{(2l-1)(2l+1)} e^{i(E_l - E_{l-1})t/\hbar} \right] \Big/ \sum_{l=0}^{\infty} (2l+1) e^{-\beta E_l} . \tag{2.28}$$

In arriving at Eq. (2.28), we have noted that

$$\operatorname{Tr}\{e^{-\beta H_1^R}\} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} e^{-\beta E_l} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta E_l} . \tag{2.29}$$

Noting that

$$\sum_{m=-l}^{l} 1 = 2l+1$$

and that

$$\sum_{m=-l}^{l} m^2 = \frac{l}{3}(l+1)(2l+1),$$

we can further simplify Eq. (2.28) to obtain

$$\tilde{\sigma}_{\text{inc}} = \frac{b^2}{3} \sum_{l=0}^{\infty} e^{-\beta E_l} \left[(l+1) e^{i(E_l - E_{l+1})t/\hbar} + l e^{i(E_l - E_{l-1})t/\hbar} \right] \Big/ \sum_{l=0}^{\infty} (2l+1) e^{-\beta E_l} . \tag{2.30}$$

The important feature of the dipole model developed to this point is that the diffraction (or coherent-scattering) effect observed in electron scattering in the inert gases, liquids, and solids has been suppressed by the orientation dependence of the electron-dipole potential of interaction. For example, the diffusion cross section per scatterer predicted by the Cohen-Lekner theory, for low-energy electrons undergoing nearly elastic collisions in liquid and solid argon is[7]

$$\sigma_{\text{diff}} = \sigma_{ea} S(0), \tag{2.31}$$

where σ_{ea} is the electron-single-molecule cross section similar to the gas kinetic cross section, and $S(0)$ is the structure factor, Eq. (1.1), which accounts for the coherence (or diffraction) of scattering in condensed phases. For liquids and solids $S(0) \approx 10^{-2}$ so that the diffusion cross section in simple dense fluids and solids is much smaller than the gas kinetic-diffusion cross section. Let us compare this conclusion with the diffusion cross section predicted for the dipole model developed here. The diffusion cross section associated with the self-diffusion of an electron may be defined by the equation

$$\sigma_{\text{diff}} = \hbar^3 \iiint f \frac{d^2\sigma}{d\Omega \, d(\hbar\omega)} (1 - \cos\theta) \, d\Omega \, d(\hbar\omega) \, d^3k_0 , \tag{2.32}$$

where the initial momenta $\hbar\vec{k}_0 = \vec{p}$ are distributed according to the Maxwell distribution function

$$f = (\beta/2\pi m)^{3/2} e^{-(\beta\hbar^2/2m)k_0^2} . \tag{2.33}$$

As did Cohen and Lekner in arriving at Eq. (2.31), we shall evaluate Eq. (2.32) only in the limit that the collisions be almost elastic, i.e., $k_0 \approx k$ and $K = k_0[2(1-\cos\theta)]^{1/2}$. Then the integration over $\hbar\omega$ leads to the factor $\delta(t)$, which in turn eliminates the time integration in (2.17) by substituting $t = 0$ in $\tilde{\sigma}_{\text{inc}}(t)$ and $G_s^{\text{CM}}(\vec{r}, t)$. But, by definition,

$$G_s^{\text{CM}}(\vec{r}, 0) = \delta(\vec{r}) . \tag{2.34}$$

Thus, the $\vec{r}$ integration is eliminated in (2.17). Finally, recalling the form of b, Eq. (2.24), we obtain

$$\sigma_{\text{diff}} = \frac{1}{3}(2eDm)^2 \frac{1}{2\hbar^2} \iint \frac{f}{\hbar^2 k_0^2} \, d\Omega \, d^3k_0$$

$$= \frac{8\pi}{3} \frac{(eDm)^2}{mkT\hbar^2} = \frac{8\pi m}{3kT} \left(\frac{De}{\hbar} \right)^2 . \tag{2.35}$$

This result is the same as that predicted for the same model by Altshuler[14] for electron swarm diffusion in dipolar gases, proving our claim that the orientation dependence of the scattering potential can eliminate the diffraction effect observed in scattering in the monatomic liquids and solids. Incidentally, as partial justification for using the Born approximation to arrive at Eq. (2.34), Altshuler showed that this expression led to good agreement when compared to the measured Townsend cross sections of water and ammonia. Christodoulides[15] has found good agreement between experiment and the first Born approximation in thermal electron scattering experiments on many polar molecules.

III. ELECTRON-MULTIPOLE-SCATTERING CROSS SECTION: BORN APPROXIMATION

In this section, we shall treat, to the first Born approximation, the problem of electron scattering by the multipole potential of a system of N identical molecules. For a given nuclear configuration of the molecules of the system the electron-multipole potential function may be expressed in the form[20]

$$V = \sum_{\nu=1}^{N} V_\nu , \tag{3.1}$$

where

$$V_\nu \approx \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{C_l^m}{|\vec{r} - \vec{r}_\nu|^{l+1}} Y_l^m(\theta_\nu, \phi_\nu) \tag{3.2}$$

for large $\vec{r}-\vec{r}_\nu$. c_l^m is the constant characterizing the contribution of the lth electric moment to the electron-molecule potential. The angles θ_ν and ϕ_ν are, respectively, the polar and azimuthal angles of $\vec{r}-\vec{r}_\nu$ with respect to a coordinate frame fixed in the νth molecule.

For small $|\vec{r}-\vec{r}_\nu|$, the form of V_ν must be determined by a detailed examination of the charge distribution of the molecules. However, for the purposes of illustration we shall use Eq. (3.2) at all values of $|\vec{r}-\vec{r}_\nu|$. For numerical calculations, the detailed form of V_ν for small $|\vec{r}-\vec{r}_\nu|$ should not be omitted, although the fact that thermalized electrons have a rather long de Broglie wavelength does favor the point-multipole representation of Eq. (3.2).

As in Sec. II, the first Born approximation leads to the following amplitude for the $i\to l$ transition:

$$F_{l|i}=-\sum_{\nu=1}^{N}\langle l|\,a(\gamma_\nu,\eta_\nu)e^{i\vec{K}\cdot\vec{r}_\nu}|\,i\rangle\,, \tag{3.3}$$

where

$$a(\gamma_\nu,\eta_\nu)=(m/2\pi\hbar^2)\int d^3R\,e^{i\vec{K}\cdot\vec{R}}V_\nu\,. \tag{3.4}$$

γ_ν and η_ν denote, respectively, the polar and azimuthal angles of $\vec{K}$ with respect to a coordinate frame fixed in the νth molecule. We can evaluate $a(\gamma_\nu,\eta_\nu)$ with the aid of (a) the expansion[21]

$$e^{-i\vec{K}\cdot\vec{R}}=\sum_{l=0}^{\infty}(2l+1)(-i)^l j_l(KR)P_l(\cos(\vec{K},\vec{R})), \tag{3.5}$$

where j_l is the lth-order spherical Bessel function, and (b) the addition theorem[21]

$$P_l(\cos(\vec{K},\vec{R}))=\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_{lm}(\gamma_\nu,\eta_\nu)\,\overline{Y}_{lm}(\theta_\nu,\phi_\nu)\,. \tag{3.6}$$

Inserting the expansions of Eqs. (3.2), (3.5), and (3.6) into Eq. (3.4), letting

$$d^3R=R^2\sin\theta_\nu\,d\theta_\nu\,d\phi_\nu\,dR\,,$$

we can obtain the result

$$\begin{aligned}a(\gamma_\nu,\eta_\nu)&=+\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{l'=0}^{\infty}\sum_{m'=l'}^{l'}4\pi(-i)^{l'}c_l^m\,Y_{l'm'}(\gamma_\nu,\eta_\nu)\\&\quad\times\int_0^\infty dR\,\frac{j_l(KR)}{R^{l-1}}\int_0^\pi\int_0^{2\pi}d\theta_\nu\,d\phi_\nu\\&\quad\times\sin\theta_\nu\,\overline{Y}_{l'm'}(\theta_\nu,\phi_\nu)Y_{lm}(\theta_\nu,\phi_\nu)\\&=+\sum_{l=0}^{\infty}\sum_{m=-l}^{l}4\pi(-i)^lA_lc_l^mY_{lm}(\gamma_\nu,\eta_\nu)K^{l-2}\,,\end{aligned} \tag{3.7}$$

where

$$A_l=\int_0^\infty dx\,\frac{j_l(x)}{x^{l-1}}\quad. \tag{3.8}$$

The integral defining A_l diverges for $l=0$. However, this causes us no difficulty since we are restricting ourselves to neutral molecules, in which case $c_0^0\equiv 0$. For $l\geq 1$, A_l is definite. If the electron-induced dipole potential were included in Eq. (3.2), the term corresponding to $l=0$, i.e., the centrally symmetric term, would not vanish. A detailed calculation of the scattering cross section should include this term, although for low-energy electrons the dipole term would probably dominate the cross section.

Following the steps outlined in Sec. II, we obtain the following thermal-averaged differential cross section:

$$\begin{aligned}\frac{d^2\sigma}{d\Omega\,d(\hbar\omega)}&=\frac{k}{2\pi\hbar k_0N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\\&\quad\times\langle a(I_\nu(t))e^{i\vec{K}\cdot\vec{r}_\nu(t)}\,\overline{a}(I_\nu(0))e^{-i\vec{K}\cdot\vec{r}_{\nu'}(0)}\rangle_T\,,\end{aligned} \tag{3.9}$$

where I_ν denotes the angles γ_ν and η_ν.

IV. ELECTRON-MOLECULE-SCATTERING CROSS SECTION: SINGLE-SCATTERER APPROXIMATION

In this section we consider a system of N identical molecules, described by the Hamiltonian operator H_0, interacting with an electron through a pairwise additive potential-energy function,

$$V=\sum_{\nu=1}^{N}V_\nu\,. \tag{4.1}$$

We shall assume that V_ν depends on the distance of separation of the electron and the center of mass of the νth molecule and on the internal state of the molecule, i.e., on the orientation, relative bond angles, conformation, etc. We shall denote by I_ν all the parameters describing the internal state of molecule ν and on which V_ν depends sensibly during an electron-molecule collision. Any internal coordinates which vary with a period small compared to the time it takes an electron to pass through the potential field of a molecule (i.e., compared to the electron-molecule collision time) are assumed to contribute to V_ν only in an average manner. Thus, the internal coordinates I_ν that appear explicitly in V_ν are those which vary with a period long compared to the electron-molecule time.

As we did in Secs. II and III, we consider a scattering process in which the system goes from state i to state l and the electron with initial momentum $\vec{k}_0$ is scattered into an element of solid angle $d\Omega=\sin\theta\,d\theta\,d\phi$ with a resulting momentum k. Assuming the validity of the single-scatterer approximation and assuming that I_ν is fixed during the scattering event, we may write the cross section per unit solid angle per scatterer in the form

$$\left(\frac{d\sigma}{d\Omega}\right)_{l|i}=\frac{k}{k_0N}\left|F_{l|i}\right|^2, \tag{4.2}$$

where

$$F_{l|i}=\left\langle l\left|\sum_{\nu=1}^{N}F(I_\nu)e^{i\vec{K}\cdot\vec{r}_\nu}\right|i\right\rangle. \tag{4.3}$$

$F(I_\nu)$ is the I_ν – modulated-electron–single-molecule-scattering amplitude [$F(I_\nu)$ also depends on the solid angle Ω and on $\vec{k}_0$ and $\vec{k}$, but in our notation we omit this dependence]. The fixed-internal-coordinates (fixed I_ν) approximation to the electron-single-molecule-scattering amplitude has been discussed by Chase[16] and used by Altshuler[14] and others[15,18] in treating scattering by polar molecules. The validity criterion is that the number of excited states of a target molecule which contribute to the total scattered wave function be limited and that the traversal time of the scattered particle through the interaction region of the target molecule be small compared with the period of the target motion excitable in the collision. The fixed-internal-coordinates approximation and the form of Eq. (4.3) follow directly from the Born approximation, so that the Born approximation is a special case of Eq. (4.3). How general Eq. (4.3) is we cannot determine at this point. This seems to be the weakest point in the present theory as well as in the Cohen-Lekner theory.

Starting with Eq. (4.3), the thermal-averaged differential cross section is obtained by the procedure used in Sec. II. The result is

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)}=\frac{k}{2\pi\hbar k_0N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}$$

$$\times\langle F(I_\nu(t))e^{i\vec{K}\cdot\vec{r}_\nu(t)}\bar{F}(I_{\nu'}(0))e^{-i\vec{K}\cdot\vec{r}_{\nu'}(0)}\rangle_T. \tag{4.4}$$

Equation (4.4) is the most general form we shall give for the differential cross section.

In the special case that the Hamiltonian is the sum of an operator H_0^I involving only the internal coordinates $I_1, \ldots, I_N$ and an operator H_0^{CM} involving only the center-of-mass positions $\mathrm{r}_1, \ldots, \mathrm{r}_N$, Eq. (4.4) may be written in the form

$$\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)}=\frac{1}{2\pi\hbar}\frac{k}{k_0}\int_{\infty}^{\infty}dt\, e^{-i\omega t}\int d^3r\, e^{i\vec{K}\cdot\vec{r}}$$

$$\times\{\tilde{\sigma}_{\mathrm{inc}}(t)G_s^{\mathrm{CM}}(\vec{r},t)+\tilde{\sigma}_{\mathrm{coh}}(t)G^{\mathrm{CM}}(\vec{r},t)\}, \tag{4.5}$$

where G_s^{CM} and G^{CM} are defined by Eqs. (2.20) and (2.21), respectively, and where

$$\tilde{\sigma}_{\mathrm{inc}}(t)\equiv[\langle F(I_1(t))\bar{F}(I_1(0))\rangle_T^I-\langle F(I_1(t))\bar{F}(I_2(0))\rangle_T^I], \tag{4.6}$$

$$\tilde{\sigma}_{\mathrm{coh}}(t)\equiv\langle F(I_1(t))\bar{F}(I_2(0))\rangle_T^I. \tag{4.7}$$

The ensemble averages indicated by $\langle\cdots\rangle_T^I$ are taken with respect to the Hamiltonian H_0^I.

As is illustrated by Eq. (4.5), the ensemble-averaged differential cross section involves not only the position correlation functions $G^{\mathrm{CM}}(\vec{r},t)$ and $G_s^{\mathrm{CM}}(\vec{r},t)$ but also correlation functions such as $\langle F(I_i(t))\bar{F}(I_1(0))\rangle_T^I$, $i=1, 2, \ldots,$ involving relaxation of the internal coordinates I. In general, the full correlation function $\langle F(I_\nu(t))e^{i\vec{K}\cdot\vec{r}_\nu(t)}\bar{F}(I_{\nu'}(0)) \times e^{-i\vec{K}\cdot\vec{r}_{\nu'}(0)}\rangle_T$ cannot be factored into translational and internal correlation functions as in Eq. (4.5) and, therefore, must be characterized as a coupled relaxation of translational and internal degrees of freedom.

V. KINETIC EQUATION FOR ELECTRON DISTRIBUTION FUNCTION

Consider a dilute solution of electrons (dilute enough that electron-electron interactions may be neglected) in a system of N identical neutral molecules. Assume that there is a constant external electric field $\vec{\mathcal{E}}$ applied to the system. We wish to derive a balance equation for the momentum distribution function $f(\vec{p})$ of the electrons at steady state. At steady state, the action of the field $\vec{\mathcal{E}}$ on the electrons causes the following rate of change in $f(\vec{p})\,d^3p$, the probable number density of electrons with momenta between $\vec{p}$ and $\vec{p}+d\vec{p}$ (i.e., in momentum state $\vec{p}$):

$$e\vec{\mathcal{E}}\cdot\frac{\partial f}{\partial\vec{p}}(\vec{p})\,d^3p. \tag{5.1}$$

The balance equation for $f(\vec{p})$ is obtained by equating Eq. (5.1) to the rate of change of $f(\vec{p})\,d^3p$ arising from collisions between the electrons and molecules.

Consider first the rate that electrons are lost from the state $\vec{p}=\hbar\vec{k}_0$ by the scattering process in which the electrons are scattered into the solid angle $d\Omega$, attain the momentum $\vec{p}'=\hbar\vec{k}$ and incur an energy change between $\hbar\omega$ and $\hbar\omega+d\hbar\omega$. This rate is

$$\left(\frac{d^2\sigma(\vec{p}\rightarrow\vec{p}';\omega)}{d\Omega\, d(\hbar\omega)}d\Omega\, d(\hbar\omega)\right)\frac{p}{m}f(\vec{p})\,d^3p\, n. \tag{5.2}$$

Equation (5.2) is built up by multiplying $[d^2\sigma/d\Omega\, d(\hbar\omega)]d\Omega\, d(\hbar\omega)$, the scattering probability per scatterer, by $(p/m)f(\vec{p})d^3p$, the flux of electrons in state $\vec{p}$, to obtain the rate of loss of electrons from state $\vec{p}$ per scattering molecule. Multiplication by n, the number density of scatterers, yields Eq. (5.2). This equation is then integrated over all Ω and $\hbar\omega$ to obtain the following total rate of change in $f(\vec{p})$ due to "loss" collisions:

$$d^3p\, n\int\!\!\int d\Omega\, d(\hbar\omega)\frac{p}{m}\frac{d^2\sigma(\vec{p}\rightarrow\vec{p}';\omega)}{d\Omega\, d(\hbar\omega)}f(\vec{p}). \tag{5.3}$$

Next consider the rate that electrons are gained in the state $\vec{p}$ by the scattering process in which electrons initially in the momentum state $\vec{p}'$ are scattered through the solid angle $d\Omega_0$ and attain the momentum state $\vec{p}$. This process is accompanied by the electron energy change $-\hbar\omega$. Integrating the expression analogous to Eq. (5.2) but for the transition $\vec{p}' \to \vec{p}$, we obtain the following total rate of change in $f(\vec{p})$ due to "gain" collisions:

$$d^3p'\, n \int\int d\Omega_0\, d(\hbar\omega) \frac{p'}{m} \frac{d^2\sigma(\vec{p}' \to \vec{p};\, -\omega)}{d\Omega\, d(\hbar\omega)} f(\vec{p}') . \tag{5.4}$$

The conservation of momentum and energy imply that

$$p\, d\Omega_0\, d^3p' = p'\, d\Omega\, d^3p , \tag{5.5}$$

and time reversal and isotropy imply the condition of detailed balancing in the form

$$\frac{p}{p'} \frac{d^2\sigma(\vec{p} \to \vec{p}';\, \omega)}{d\Omega\, d(\hbar\omega)} = e^{\beta\hbar\omega} \frac{p'}{p} \frac{d^2\sigma(\vec{p}' \to \vec{p};\, -\omega)}{d\Omega\, d(\hbar\omega)} . \tag{5.6}$$

Combining Eqs. (5.4)–(5.6), forming the difference between the resulting form of Eq. (5.4) and Eq. (5.3), and equating this difference to Eq. (5.1), we obtain the following for the Boltzmann equation:

$$e\vec{\mathcal{E}} \cdot \frac{\partial f}{\partial \vec{p}} = n \int\int d\Omega\, d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega)$$

$$\times [e^{-\beta\hbar\omega} f(\vec{p}') - f(\vec{p})] , \tag{5.7}$$

where we have introduced the notation

$$\Theta(\vec{K}, \omega) = \frac{p}{p'} \frac{d^2\sigma(\vec{p} - \vec{p}';\, \omega)}{d\Omega\, d(\hbar\omega)} . \tag{5.8}$$

Equation (5.7) reduces to Cohen and Lekner's result, Eq. (1.5), in the special case for which the differential cross section has the form given by Eq. (1.3).

Equation (5.7) can be solved formally by expanding $f(\vec{p})$ in Legendre polynomials:

$$f(\vec{p}) = \sum_{l=0}^{\infty} f_l(\epsilon) P_l(\cos\zeta) , \tag{5.9}$$

where ζ is the angle between the momentum $\vec{p}$ and the field $\vec{\mathcal{E}}$ and $\epsilon = \hbar^2 k_0^2/2m = p^2/2m$. Inserting (5.9) into the right- and left-hand sides of Eq. (5.7), we obtain

$$e\mathcal{E}\frac{p}{m} \left\{ P_0 \frac{1}{3}\left(f_1' + \frac{f_1}{\epsilon}\right) + P_1(\cos\zeta)\left(f_0' + \frac{2}{5} f_2' + \frac{3}{5}\frac{f_2}{\epsilon}\right) + P_2(\cos\zeta)\frac{1}{3}\left(2f_1' - \frac{f_1}{\epsilon}\right) + \cdots \right\}$$

$$= n \int d\Omega \int d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega) \sum_{l=0}^{\infty} [e^{-\beta\hbar\omega} f_l(\epsilon') P_l(\cos\zeta') - f_l(\epsilon) P_l(\cos\zeta)] . \tag{5.10}$$

The prime on f_l' denotes the derivative with respect to ϵ. Since the quantities in the integrand of Eq. (5.10) do not depend on the azimuthal angle φ of Ω, the addition theorem, Eq. (3.6), leads – after integration over φ – to the following form for the right-hand side of Eq. (5.10):

$$2\pi \int d\theta \sin\theta \int d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega) \sum_{l=0}^{\infty} P_l(\cos\zeta)$$

$$\times [e^{-\beta\hbar\omega} f_l(\epsilon') P_l(\cos\theta) - f_l(\epsilon)] . \tag{5.11}$$

Inserting this result in Eq. (5.10) and equating factors of $P_l(\cos\zeta)$ on each side of the equation, we find the first three members of the set of equations for $f_l(\epsilon)$:

$$\frac{e\mathcal{E}p}{3m}\left(f_1' + \frac{f_1}{\epsilon}\right) = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega)$$

$$\times [e^{-\beta\hbar\omega} f_0(\epsilon') - f_0(\epsilon)] . \tag{5.12a}$$

$$\frac{e\mathcal{E}p}{m}\left(f_0' + \tfrac{2}{5} f_2' + \frac{3}{5}\frac{f_2}{\epsilon}\right) = 2\pi n \int d\theta \sin\theta$$

$$\times \int d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega) \times \{e^{-\beta\hbar\omega} f_1(\epsilon') P_1(\cos\theta) - f_1(\epsilon)\} , \tag{5.12b}$$

$$\frac{e\mathcal{E}p}{3m}\left(2f_1' - \frac{f_1}{\epsilon}\right) = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega) \frac{p'}{m} \Theta(\vec{K}, \omega)$$

$$\times \{e^{-\beta\hbar\omega} f_2(\epsilon') P_2(\cos\theta) - f_2(\epsilon)\} . \tag{5.12c}$$

Following arguments first advanced by Shockley,[22] Cohen and Lekner claim that terms of order $l \geq 2$ in (5.9) may be neglected for both low and high fields. Though Shockley's conclusion will be seen below to remain true for the low-field limit, his arguments in the high-field limit depend on the assumption that for electron energies much less than the electronic excitation energies of the molecules an electron colliding with a molecule loses an average energy of about $(2m/M)\langle\epsilon\rangle$ per collision. M is the mass of the molecule and $\langle\epsilon\rangle$ is the average energy of the electron. Since an electron scattered by polyatomic molecules can involve substantially larger energy transfer than Shockley's estimate, his conclusion that terms of order f_l for $l \geq 2$ can be neglected in the high-field limit, must be treated with some reservation. The high-field limit will be investigated for some specific polyatomic models in a future publication. In the present paper, we shall restrict our attention to the low-field limit and to the special case in which the average electron energy loss per collision is small compared to the average energy $\langle\epsilon\rangle$ ($\langle\epsilon\rangle \sim kT$ in the low-field limit) even though it may be substantially larger than the "elastic" value of $(2m/M)\langle\epsilon\rangle$. The scattering of slow electrons by nitrogen provides an example of such a case.[13] The average electron energy loss per collision is of the order of $100(m/M)\langle\epsilon\rangle$.

The simplification of the low-field limit lies in the fact that the set of equations for f_l implies

$$f_l \propto \mathcal{E}^l + \text{terms of higher order in } \mathcal{E}. \tag{5.13}$$

Thus, to terms linear in $\mathcal{E}$, the expansion for $f(\vec{p})$ is

$$f(\vec{p}) = f_0(\epsilon) + f_1(\epsilon)\cos\zeta, \tag{5.14}$$

where f_0 and f_1 are, respectively, solutions to the equations

$$0 = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega)\,(p'/m)\,\Theta(\vec{K},\omega) \times \{e^{-\beta\hbar\omega} f_0(\epsilon') - f_0(\epsilon)\} \tag{5.15}$$

and

$$(e\mathcal{E}p/m)\,f_0' = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega)\,(p'/m)\,\Theta(\vec{K},\omega) \times [e^{-\beta\hbar\omega} f_1(\epsilon')P_1(\cos\theta) - f_1(\epsilon)]. \tag{5.16}$$

The solution to Eq. (5.15) is the Maxwellian equilibrium distribution

$$f_0(\epsilon) = c\,e^{-\epsilon/kT}, \tag{5.17}$$

where c is a normalization constant. Equation (5.16) may be put in a more convenient form with the aid of the definition

$$f_1(\epsilon) \equiv f_0(\epsilon)\psi_1(\epsilon) \tag{5.18}$$

and the fact that $f_0(\epsilon')\,e^{-\beta\hbar\omega} = f_0(\epsilon)$, because of the conservation of energy. In terms of $\psi_1(\epsilon)$, Eq. (5.16) becomes

$$-\frac{e\mathcal{E}p}{mkT} = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega)\,(p'/m)\,\Theta(\vec{K},\omega) \times \{\psi_1(\epsilon')P_1(\cos\theta) - \psi_1(\epsilon)\}. \tag{5.19}$$

Equation (5.19) is exact to first order in the field $\vec{\mathcal{E}}$. To proceed further without approximation, we would have to know $\Theta(\vec{K},\omega)$ and, in general, would have to solve for ψ numerically. However, we shall simplify the problem greatly by using the assumption that the average energy transferred per collision by the electron is small compared to the average energy of the electron. In particular, we (i) expand p' and $\psi_1(\epsilon')$ in a power series in ϵ, (ii) expand $\Theta(\vec{K},\omega)$ with respect to $\vec{K}$ in a series about the elastic scattering momentum $K_0 = k_0 \times [2(1-\cos\theta)]^{1/2}$, and (iii) neglect all but the lowest-order terms of the expansions (i) and (ii) in the integrand of Eq. (5.18). The result is

$$-e\mathcal{E}p/mkT = 2\pi n \int d\theta \sin\theta \int d(\hbar\omega)\,(p/m)\,\Theta(\vec{K}_0,\omega) \times \{\psi_1(\epsilon)[P_1(\cos\theta) - 1]\}, \tag{5.20}$$

which yields for $f_1(\epsilon)$ the expression

$$f_1(\epsilon) = e\mathcal{E}\Lambda_1 f_0/kT, \tag{5.21}$$

with the definition

$$\Lambda_1^{-1} = 2\pi n \int d\theta \sin\theta [1 - P_1(\cos\theta)] \times \{\int d(\hbar\omega)\,\Theta(\vec{K}_0,\omega)\}. \tag{5.22}$$

The quantity $\Theta(\vec{K}_0,\omega)$ is obtained by setting $\vec{K} = \vec{K}_0$ in the scattering lengths and the exponential factors appearing in $\Theta(\vec{K},\omega)$. Λ_1 has the physical significance of a mean free path of drift of electrons of energy ϵ.

Assuming that $\Theta(\vec{K}_0,\omega)$ has the form determined by Eq. (4.4), we can perform the integrations over ω and t explicitly to obtain the rather simple result

$$\int d(\hbar\omega)\,\Theta(\vec{K}_0,\omega) = \frac{1}{N}\sum_{\nu=1}^{N}\sum_{\nu'=1}^{N}\langle F(I_\nu(0))F(I_{\nu'}(0)) \times e^{i\mathrm{K}_0\cdot[\vec{r}_\nu(0)-\vec{r}_{\nu'}(0)]}\rangle_T. \tag{5.23}$$

In the special case that the Hamiltonian H_0 is the sum of an operator H_0^I involving only the internal coordinates $I_1, \ldots, I_N$ and an operator H_0^{CM} involving only the center-of-mass positions $\vec{r}_1, \ldots, \vec{r}_N$, Eq. (5.23) becomes

$$\int d(\hbar\omega)\,\Theta(\vec{K}_0,\omega) = \{\tilde{\sigma}_{\mathrm{inc}}(0) + \tilde{\sigma}_{\mathrm{coh}}(0)S^{\mathrm{CM}}(\vec{K}_0)\}, \tag{5.24}$$

where $\tilde{\sigma}_{\mathrm{inc}}(0)$ and $\tilde{\sigma}_{\mathrm{coh}}(0)$ are defined by Eqs. (4.6) and (4.7) and $S^{\mathrm{CM}}(\vec{K}_0)$ is of the form given by Eq. (1.1) with the condition that $g(\vec{R})$ denote the pair correlation function of the centers of mass of the molecules of the system. In the limit that $\tilde{\sigma}_{\mathrm{inc}}(0) \equiv 0$, the expression for Λ_1 reduces to Cohen and Lekner's low-field result.

The low-field mobility, defined as the ratio of the magnitude of the drift velocity, given by the relation

$$\vec{v}_d = \int\left(\frac{\vec{p}}{m}\right) f(\vec{p})\,d^3p \Big/ \int f(\vec{p})\,d^3p, \tag{5.25}$$

to the magnitude of the field $\vec{\mathcal{E}}$, may be computed in terms of f_0 and f_1 as follows:

$$\mu = \frac{1}{2}\left(\frac{2}{3}\right)^{1/2} \frac{e}{mkT} \int \left(\frac{p}{m}\right) \Lambda_1 f_0 d^3p \bigg/ \int f_0 d^3p \ . \quad (5.26)$$

This result, along with Eq. (5.24), demonstrates that in solids and liquids, where $S^{\mathrm{CM}}(\vec{\mathrm{K}}_0)$ is small ($\sim 10^{-2}$), the incoherent scattering cross section $\bar{\sigma}_{\mathrm{inc}}$ may give an appreciable contribution even when in the gas phase, where $S^{\mathrm{CM}}(\vec{\mathrm{K}}_0) \approx 1$, $\bar{\sigma}_{\mathrm{coh}}$ gives the major contribution.

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[*] Sloan Foundation Fellow (1968–70).

[†] Guggenheim Fellow (1969–70).

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Three-Body Interactions in Liquid and Solid Helium

R. D. Murphy[*] and J. A. Barker

IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California 95114

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We have calculated the contribution of the triple-dipole three-body interactions to the ground-state energy of liquid He^4 and solid He. The liquid calculation was done by a Monte Carlo method using a variationally determined product wave function, and the solid calculation by evaluating the triple-dipole sum in the static lattice for several crystal lattices. The triple-dipole term is found to be quite small, of the order of 2% of the ground-state energy of liquid He^4.

I. INTRODUCTION

The magnitude of the contribution of three-body interactions to the ground-state energy of helium has become a more important question because the two-body potential is being determined more accurately[1,2] and because recent ground-state energy calculations[3] have been accurate enough to distinguish between various proposed forms of the two-body potential. In this paper, we will present detailed calculations of the contribution of the triple-dipole dispersion term to the ground-state energy of liquid He^4 and solid He.

The Hamiltonian H for a set of N helium atoms of mass m in a volume V is

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + U \quad , \qquad (1)$$