Theory of Low-Energy Electron Scattering by Polar Molecules

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The total diffusion cross section is calculated for low-energy impact of electrons upon polar molecules in an approximation which treats the molecules as fixed rotators. The amplitude is evaluated and the differential cross section corresponding to fixed orientation of the molecule is then averaged over the Maxwell distribution. It is shown how this simple approach follows from an adiabatic approximation to the excitation amplitudes. The results show excellent agreement with available data.

I. INTRODUCTION

IT is well known that the scattering problem for electron impact upon molecules, especially for low-energy electrons, is intractable since, in principle, the entire spectrum of the target molecule is involved in the calculation. But, in the case of molecules possessing a long-range interaction such as the dipole or quadrupole, analytical treatment becomes feasible because, after all, such moments are manifestations of the electronic configuration. Therefore, if most of the scattering should occur at long distances from the target, higher multipoles as well as exchange effects may become relatively unimportant. Such a point of view was first adopted[1] to calculate the rotational excitation efficiency for polar molecules in Born approximation, and more recently[2] considerable success using the same procedure was achieved in computing rotational excitation cross sections for molecules possessing quadrupole moments. However, in neither case was a total cross section attempted. In the case of polar molecules the excitation of rotational motion may be so efficient[1] that even for the very low-energy swarm experiments which measure the total diffusion cross section it cannot be supposed, as in the case of quadrupole molecules, that the elastic cross section approximates the total cross section. Consequently, the low-energy data which is available for H_2O and NH_3 has never been analyzed theoretically. It is the purpose of this paper to show how the diffusion cross section for polar molecules may be predicted quite simply if, as the starting point, an adiabatic approximation to the transition amplitudes, recently discussed by Chase,[3] is employed.

In Sec. II, the diffusion cross section is derived in the adiabatic approximation while application to polar molecules appears in Sec. III.

II. DERIVATION OF THE DIFFUSION CROSS SECTION

The scattering process which we consider treats the target molecule simply as a rotator which interacts with the incident electron by means of the potential $V(\mathbf{r},\tau)$. The spectrum of the rotator is defined by

$$H(\tau)\phi_n(\tau) = \epsilon_n\phi_n(\tau),$$

where the $\phi_n(\tau)$ shall be the well-known spherical harmonics for the rotational states. In the adiabatic approximation, the excitation amplitude for electron scattering from the target state i to n is given[3] by

$$f_{ni}(\theta,\phi) = \int d\tau \phi_n^*(\tau) f(\theta,\phi,\tau)\phi_i(\tau), \qquad (1)$$

where $f(\theta,\phi,\tau)$ is a τ-modulated adiabatic elastic scattering amplitude. That is, $f(\theta,\phi,\tau)$ represents the scatter of the electron with rotator coordinates held fixed. The validity criterion for this approximation is that the number of excited states of the target which contribute significantly to the total wave function is limited, and that the traversal time of the scattered particle through the interaction region is small compared with the period of the target motion excitable in the collision. The exact expression for the excitation amplitude is given by[4]

$$
\begin{aligned}
f_{ni} &= \frac{m}{2\pi\hbar^2}\int\int e^{-i\mathbf{k}_n\cdot\mathbf{R}}\phi_n^*(\tau)V(\mathbf{R},\tau)\Psi(\mathbf{R},\tau)d^3R\,d\tau \\
&= \frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{k}_n\cdot\mathbf{R}}\sum_\alpha F_\alpha(\mathbf{R})(n|V|\alpha),
\end{aligned}
\qquad (2)
$$

where $\Psi(\mathbf{R},\tau)$ is the total wave function for the process. It follows, for dipole interaction, that only those energy states immediately above and below those contained in $\Psi(\mathbf{R},\tau) = \sum F_\alpha(\mathbf{R})\phi_\alpha(\tau)$ can contribute to f_{ni}. That is, $n = \alpha \pm 1$ as a result of the well-known selection rule for the dipole matrix element $(n|V|\alpha)$. Consequently, if the α's involved in Ψ are limited, then so are the excitable states. Therefore, we may formally apply Eq. (1) to all n without violating the time of passage criterion. In fact, this criterion may be replaced by

$$\frac{\epsilon_{(n+1)}}{\hbar}\frac{R_0}{v}\ll 1, \qquad (3)$$

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[1] H. S. W. Massey, Proc. Cambridge Phil. Soc. **28**, 99 (1932).
[2] E. Gerjuoy and S. Stein, Phys. Rev. **97**, 1671 (1955).
[3] D. M. Chase, Phys. Rev. **104**, 838 (1956).

[4] M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1953).

where n is the highest energy state contributing significantly to the total wave function. As a numerical example in the case of polar molecules, let R_0 be the classical distance of closest approach. Then

$$De/R_0^2 \simeq \tfrac{1}{2}mv^2,$$

or

$$\frac{R_0}{v} = \frac{1}{v^2}\left(\frac{2De}{m}\right)^{\frac{1}{2}}, \quad (4)$$

where D is the permanent dipole moment of the molecule. For a 0.15-ev electron, $v = 2.2 \times 10^7$ cm/sec, and in the case of H_2O where $D = 1.85 \times 10^{-18}$ (esu),

$$\frac{\epsilon_{(n+1)}}{\hbar}\frac{R_0}{v} \leq 5 \times 10^{-2}$$

for $n+1 \leq 10$. Thus, even for very slow electrons and strong dipole moments, the criterion (3) is well satisfied for as many as nine states present in the expansion for Ψ in (2).

As a result of these considerations, the total differential cross section may be written

$$\sigma_i(\theta,\phi) \equiv \sum_n |f_{ni}|^2 = \sum_n \int\int d\tau d\tau_0 \phi_n^*(\tau)\phi_n$$

$$\times (\tau_0)f(\theta,\phi,\tau)f^*(\theta,\phi,\tau_0)\phi_i^*(\tau_0)\phi_i(\tau), \quad (5)$$

and from the closure property $\sum_n \phi_n^*(\tau)\phi_n(\tau_0) = \delta(\tau-\tau_0)$, it follows that

$$\sigma_i(\theta,\phi) = \int d\tau |f(\theta,\phi,\tau)|^2 |\phi_i(\tau)|^2. \quad (6)$$

This is the expectation value for the differential cross section calculated with target coordinates held fixed. If the probability for finding targets in the ith state is denoted by p_i, then the total differential cross section for interception of the electron is given by

$$\sigma_t(\theta,\phi) = \sum_i p_i \sigma_i(\theta,\phi). \quad (7)$$

The quantity which is measured by the Townsend swarm method is the momentum transfer or diffusion cross section, defined by

$$Q = \int (1-\cos\theta)\sigma_t(\theta,\phi)d\Omega.$$

We note, furthermore, that it is this cross section which determines the collision frequency in electromagnetic conductivity theory for propagation in plasmas. In the next sect on we shall evaluate

$$Q = \int (1-\cos\theta)\sum_i p_i\sigma_i(\theta,\phi)d\Omega \quad (8)$$

for polar molecules.

III. APPLICATION TO POLAR MOLECULES

It is first necessary to evaluate the amplitude $f(\theta,\phi,\tau)$ for scattering in the field of a fixed dipole,

$$V(\mathbf{R},\tau) = -De\cos\omega/R^2. \quad (9)$$

That is, we seek a solution to the problem

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{R},\tau)\right)\psi(\mathbf{R}) = \psi(\mathbf{R}), \quad (10)$$

for fixed τ, subject to the outgoing boundary condition

$$\psi(\mathbf{R}) = e^{i\mathbf{k}_0\cdot\mathbf{R}} + f(\theta,\phi,\tau)e^{ik_0 R}/R. \quad (11)$$

The exact functional expression for $f(\theta,\phi,\tau)$ is given by the well-known expression[4]

$$f(\theta,\phi,\tau) = \frac{-m}{2\pi\hbar^2}\int d\mathbf{R}e^{-i\mathbf{k}\cdot\mathbf{R}}V(\mathbf{R},\tau)\psi(\mathbf{R}). \quad (12)$$

We shall evaluate f in Born approximation. Although justification for doing so is difficult, we shall first note in its defense that the energy dependence cannot change in any higher order approximation. For example, the second-order correction to the Born amplitude is given, apart from irrelevant constants, by

$$\int\int e^{-i\mathbf{k}\cdot\mathbf{R}}\frac{\cos\omega}{R^2}\frac{e^{ik_0|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\frac{\cos\omega'}{R'^2}e^{ik_0\cdot\mathbf{R}'}d\mathbf{R}d\mathbf{R}'$$

$$= \frac{1}{k_0}\int\int \exp(-i\mathbf{n}\cdot\boldsymbol{\varrho})\frac{\cos\omega}{\rho^2}\frac{\exp(i|\boldsymbol{\varrho}-\boldsymbol{\varrho}'|)}{|\boldsymbol{\varrho}-\boldsymbol{\varrho}'|}\frac{\cos\omega'}{\rho'^2}$$

$$\times \exp(i\mathbf{n}_0\cdot\boldsymbol{\varrho}')d\varrho d\varrho'. \quad (13)$$

The term on the right follows immediately upon making the simple transformation $k_0\mathbf{R} = \boldsymbol{\varrho}$, $k_0\mathbf{R}' = \boldsymbol{\varrho}'$. The vectors $\mathbf{n}$ and $\mathbf{n}_0$ are unit vectors in the direction of scattering and incidence respectively. The same k_0^{-1} dependence arises in the same way for all terms of the perturbation expansion. Encouraged to the extent that the correct energy dependence follows in Born approximation, we may obtain further justification[5] if

$$|\Phi(\mathbf{R})| \ll |e^{i\mathbf{k}_0\cdot\mathbf{R}}| = 1 \quad (14)$$

for all $\mathbf{R}$, where

$$\Phi(\mathbf{R}) = \frac{m}{2\pi\hbar^2}De\int d^3\mathbf{R}'\frac{e^{ik_0|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\frac{\cos\omega'}{R'^2}e^{ik_0\cdot\mathbf{R}'},$$

which is the full scattered wave in Born approximation. But

$$|\Phi(\mathbf{R})| \lesssim \frac{mDe}{2\pi\hbar^2}\int \frac{d\mathbf{R}'\cos\omega'}{|\mathbf{R}-\mathbf{R}'|R'^2}$$

$$= \frac{mDe}{2\pi\hbar^2}\cos\alpha\int\frac{d\mathbf{R}'}{R'^2}\sum_{l=0}^{\infty}\frac{1}{r}\left(\frac{r_<}{r_>}\right)^l P_l(\cos\theta')\cos\theta',$$

[5] D. Bohm, Quantum Theory (Prentice-Hall, Inc., New York, 1951), p. 551.

where α is the angle between the direction of the dipole moment and $\mathbf{R}$; $r_>$, $r_<$ mean, respectively, the larger and smaller of R and R', and the polar axis lies along the direction of $\mathbf{R}$. Thus, it follows by the remaining elementary integration that

$$|\Phi(\mathbf{R})| \leq (mDe/\hbar^2) \cos\alpha \tag{15}$$

for all k_0 and R. For H_2O, $D = 1.85 \times 10^{-18}$ (esu), and

$$|\Phi(\mathbf{R})| \leq 0.72 \cos\alpha. \tag{16}$$

This result shows that the largest value of $|\Phi(\mathbf{R})|$ is comparable with unity but that a large range of dipole orientations, α, exists for which the magnitude of the scattered wave is everywhere much less than unity. Although this does not in fact guarantee the validity of the Born approximation, it affords some indication of its validity especially when it is realized that the criterion (14) is often too stringent a condition.[6,7] One further observation which encourages the employment of Born approximation is that terms of order D^3 in $|f(\theta,\phi,\tau)|^2$ vanish identically in the averaging indicated in (7). That is, if f could be calculated to second order in D, the cross term in $|f|^2$ makes no contribution to the final answer. This result is expected from the parity of the dipole and can be demonstrated, but the detailed proof will be omitted.

Accordingly, let us proceed with the evaluation of the amplitude in (12) based upon the replacement of $\psi(\mathbf{R})$ by $\exp(i\mathbf{k}_0\cdot\mathbf{R})$. The integration is elementary and leads to

$$f(\mathbf{k},\mathbf{k}_0) = \frac{2iDem \cos\gamma}{\hbar^2} \int_0^\infty j_1(qR)dR = \frac{2iDem}{\hbar^2} \frac{\cos\gamma}{q}, \tag{17}$$

where γ is the angle between the fixed direction of the dipole moment and the direction of momentum change,
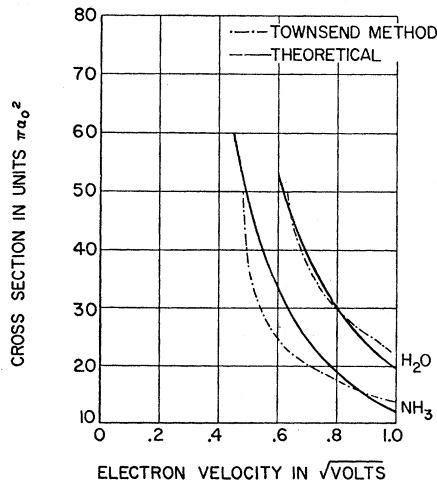

FIG. 1. Diffusion cross section for slow electrons.

[6] Reference 5, p. 553.
[7] P. M. Morse, Revs. Modern Phys. 4, 591 (1932).

$\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$; and, since $|\mathbf{k}_0| = |\mathbf{k}|$, $q = k_0[2(1-\cos\theta)]^{\frac{1}{2}}$. If the coordinates of the target are measured relative to the fixed direction of $\mathbf{q}$, then the total differential cross section, Eq. (7), may be expressed as

$$\sigma_T = 4\left(\frac{Dem}{\hbar^2}\right)^2 \frac{1}{q^2} \sum_{l=0}^\infty \sum_{m=-l}^l p_{lm} \int |\Theta(lm)|^2 \cos^2\gamma \, d\Omega, \tag{18}$$

where $\Theta(lm)$ is the rotator eigenfunction. The integral is easily evaluated by means of the identity[8]

$$\cos\gamma\,\Theta(lm) = \Theta(l+1\;m)\left[\frac{(l+1-m)(l+1+m)}{(2l+1)(2l+3)}\right]^{\frac{1}{2}}$$
$$+\Theta(l-1\;m)\left[\frac{(l-m)(l+m)}{(2l-1)(2l+1)}\right]^{\frac{1}{2}}.$$

The result is

$$\int |\Theta(lm)|^2 \cos^2\gamma \, d\Omega$$
$$= \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} + \frac{l^2 - m^2}{(2l-1)(2l+1)}. \tag{19}$$

Now, the probability distribution for nondegenerate energy states of the rotators under equilibrium conditions is independent of m. Therefore,

$$p_{lm} \equiv p_l = \exp\left(\frac{-E_l}{kT}\right) \Big/ \sum_{l,m} \exp\left(\frac{-E_l}{kT}\right)$$
$$= \exp\left(\frac{-E_l}{kT}\right) \Big/ \sum_{l=0}^\infty (2l+1) \exp\left(\frac{-E_l}{kT}\right). \tag{20}$$

From this expression for p_{lm} together with (19), it follows in a straightforward manner that

$$\sum_{l=0}^\infty \sum_{m=-l}^l p_l \int |\Theta(lm)|^2 \cos^2\gamma \, d\Omega = \tfrac{1}{3}, \tag{21}$$

independent of T. This is precisely the same as the classical space average of $\cos^2\gamma$. Therefore (18) reduces to

$$\sigma_T = \frac{4}{3}\left(\frac{Dem}{\hbar^2}\right)^2 \times \frac{1}{2k_0^2(1-\cos\theta)}, \tag{22}$$

and, finally, the diffusion cross section, Eq. (8), becomes

$$Q = \frac{8\pi}{3}\left(\frac{Dem}{\hbar^2 k_0}\right)^2 = \frac{8\pi}{3}\left(\frac{De}{hv}\right)^2 \text{ (cgs);} \tag{23}$$

or, in units of πa_0^2 ($a_0 = $ Bohr radius),

$$Q = 5.60(D^2/E). \tag{24}$$

[8] E. U. Condon and G. H. Shortley, Theory of Atomic Spectra (Cambridge University Press, New York, 1953), p. 53.

Here, D is in units of 10^{-18} (esu) and E is the electron energy in ev.

The measured dipole moments[9] in esu units are $D(H_2O) = 1.85 \times 10^{-18}$ and $D(NH_3) = 1.47 \times 10^{-18}$. Upon using these values, the theoretical curves based upon Eq. (24) together with the available experimental[10] cross sections are portrayed in Fig. 1. The agreement between theory and experiment is remarkably good.

IV. CONCLUSION

A possible source of error apart from the use of the Born approximation is the extrapolation of pure dipole interaction all the way to the origin. An order-of-magnitude estimate of this error has been carried out by choosing a cut-off point at a distance equal to $2a_0$. The method was similar to that employed by Gerjuoy and Stein[2] where the potential in the near-region is represented by an expansion in spherical harmonics. It was found that all higher order harmonics become negligible compared with the contribution to the amplitude from the spherically symmetric part of the potential as the incident energy diminishes toward zero. In fact, the main correction to the diffusion cross section is energy-independent and is given by

$$\Delta Q \equiv 4\pi \left(\frac{16}{3} \frac{m}{\hbar^2} a_0^3 V_0 \right)^2, \qquad (25)$$

[9] U. S. Department of Commerce, National Bureau of Standards, Circular No. 537 (1953).

[10] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 208.

where V_0 is an assumed constant potential for the spherically symmetric part of the potential. The details for the derivation of (25) are omitted since it merely amounts to retracing the steps for the deduction of (23) after introducing the cutoff. Even for V_0 as high as 5 ev, the correction in (25) amounts to $4\pi a_0^2$ which is small compared with the cross sections given by (24) especially for the lower incident energies. Conversely, we may infer that in the case of very weak dipole moments the near-field corrections can diminish the accuracy of the present theory.

Finally, this simplified model of the electron-molecule collision process cannot be regarded as confirmed, not only because the quoted experimental data are meager and unconfirmed, but the analysis of the raw data in swarm experiments is complicated and involves assumptions about the velocity distribution function of the electrons which in turn depends upon the differential cross section for the scattering. However, for the purpose of further experiment, it is well to emphasize that the electron energies should not greatly exceed vibrational thresholds but be sufficiently large in order that the criterion (3) be fulfilled. Consequently, the majority of the targets should be in energy states well below that of the primary electron. Furthermore, in order to avoid the inaccuracies relative to the near-field correction, future experiments should involve molecules with large dipole moments.