PHYSICAL REVIEW A VOLUME 25, NUMBER 2 FEBRUARY 1982

Application of the adiabatic-nuclei approximation to energy-loss cross sections for collisions with molecules

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(Received March 23, 1981)

A general expression is derived for the energy-loss, or stopping, cross section for particles incident on linear or symmetric-top molecules, within the context of the adiabatic-nuclei approximation for vibration and rotation, or only rotation. The derivation is an alternative to that of Shimamura, and confirms his proof that the cross section is, when summed over all final rotor states, independent of the initial rotor state. It involves a sum rule for Clebsch-Gordan coefficients that, if not newly derived here, is certainly unfamiliar. The expression relating body-frame (fixed-nuclei) and laboratory-frame cross sections for linear and symmetric-top molecules is generalized to the asymmetric-top molecule, and it is shown that for this case the cross section for transitions between *any* rotational states can be written as a simple linear combination of the cross sections for the ground rotational state only in special circumstances. Application of Shimamura's theorem to this case leads to a general expression, applicable to all three classes of molecules, that is ideally suited to use with the results of standard fixed-nuclei scattering calculations. Applications near threshold and/or for polar molecules are discussed and illustrated for electron collisions with CO.

The energy-loss cross section for an inelastic collision is the product of the usual differential cross section and the energy lost (or gained) by the projectile. The stopping cross section is the energy-loss cross section integrated over all scattering angles. The energy loss per unit path length is this cross section multiplied by the number density of gas molecules, and the energy loss per unit time is this multiplied by the projectile velocity. For an ensemble of molecules the quantity of interest usually involves the average over the populations of molecular states in the gas, and some velocity distribution of the projectiles.[1] It has recently been shown[2] that the energy-loss and stopping (as well as the usual differential and integrated) cross sections for a given electronic state are, when summed over all final rotational states, independent of the initial rotational state of the molecule under conditions where rotational motion of the molecule is small or negligible during the collision process. The general proof applies to a broad range of molecules (linear, symmetric-top, asymmetric-top) and projectiles (charged and neutral structureless particles). Thus, when the slow-rotation assumption is deemed appropriate, the total differential and integrated cross sections and the energy loss per unit path length and time are independent of the rotational temperature of the gas—an extremely useful result. It not only simplifies interpretation of physical processes, but also the computation of the cross sections themselves.

Neglect of the rotational motion of the molecule during the collision amounts to treating the scattering event as for a molecule fixed in space (but perhaps vibrating) during the collision process, followed by an average over all orientations of the molecule relative to some coordinate system fixed in the laboratory. This is the usual adiabatic approximation,[3] which has been extensively applied[4] in electron-molecule collision theory and calculations. The purpose of the present note is to provide, for the two simplest molecular cases, a proof of the theorem stated above by a route alternative, but equivalent, to that of Shimamura, to consider its application to asymmetric-top molecules, and to present the resulting general expression for the energy-loss cross section in a form best suited to the exploitation of current computational techniques and available results. For symmetric-top and asymmetric-top molecules the discussion will be restricted to the case of a common initial and final electronic state, but this restriction will be relaxed for linear molecules. It will be assumed that the molecule is rigid with respect to rotational wave functions and energies, i.e., that vibrational and rotational motion are separable.

For linear[5] and symmetric-top molecules[6,7] the differential cross section in the slow-rotation (adiabatic-nuclei) approximation can be written

$$\frac{d\sigma_{avj,\alpha'v'j'}}{d\Omega}=\frac{k'}{k}\sum_{l_t}C(jl_tj';\Lambda\Lambda_t)^2\frac{d\sigma^{l_t,\Lambda_t}_{av,\alpha'v'}}{d\Omega}\ , \tag{1}$$

where $C(\cdots)$ is a Clebsch-Gordan coefficient, l_t is the angular momentum transferred during the collision[8] ($\vec{j}\,'=\vec{j}+\vec{l}_t,\Lambda'=\Lambda+\Lambda_t$), and k and k' are the initial and final relative momenta of the collision partners. These are related to the rotational (E_j) and vibronic (E_{av}) energies (in atomic units = 27.2 eV) of the molecule by

$$k'^2-k^2=2(E_{av}+E_j-E_{\alpha'v'}-E_{j'})\ . \tag{2}$$

The average over initial and sum over final degenerate magnetic sub-states has been taken in arriving at (1). For linear molecules Λ and Λ' specify the electronic angular momenta about the molecular symmetry axis, for symmetric-top (and spherical-top) molecules they specify the components of rotational angular momenta about this axis.

It will be seen that for asymmetric-top molecules (1) can be generalized to[9]

$$\frac{d\sigma_{avj,\alpha'v'j'}}{d\Omega}=\frac{k'}{k}\sum_{l_t}\sum_{\Lambda}\sum_{\Lambda''}\sum_{\Lambda'}\sum_{\Lambda'''}\Gamma^{j}_{\Lambda\tau}C(jl_tj';\Lambda\Lambda_t)\Gamma^{j'}_{\Lambda'\tau'}\Gamma^{j}_{\Lambda''\tau}C(jl_tj';\Lambda''\Lambda_t')\Gamma^{j'}_{\Lambda'''\tau'}\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{av,\alpha'v'}}{d\Omega}\ , \tag{3}$$

where $\Lambda'=\Lambda+\Lambda_t$ and $\Lambda'''=\Lambda''+\Lambda_t'$. The coefficients Γ are elements of the real, orthogonal transformation

$$\sum_{\Lambda'}H^j_{\Lambda\Lambda'}\Gamma^j_{\Lambda'\tau}=\Gamma^j_{\Lambda\tau}E_j\ , \tag{4}$$

where E_j are the rotational energies of the molecule (depending on both j and τ), and

$$H^j_{\Lambda\Lambda'}\equiv\langle j\Lambda m_j\,|\,H_{\text{rot}}\,|\,j\Lambda'm_j\rangle\ , \tag{5}$$

with H_{rot} the rotational Hamiltonian and $|j\Lambda m_j\rangle$ the rotational wave function for a *symmetric* top. Equation (1) is a special case ($H^j_{\Lambda\Lambda'}$ diagonal) of (3).

The precise definition of the dynamical partial cross sections $d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{av,\alpha'v'}/d\Omega$ in (3) is not of direct interest here, our only concern being that they exist and that the dependence on initial and final rotational states in (3) is confined solely to the kinematic ratio k'/k and the Clebsch-Gordan coefficients. This is the essential content of the adiabatic-nuclei approximation for rotation. There is no restriction on the degree of sophistication with which the dynamical cross sections are obtained. This is, of course, a subject of continued interest.[4]

It will be instructive, however, to pursue their definition a little further in order to fix ideas. Consistent with the adiabatic-nuclei approximation, they are most conveniently obtained from a scattering amplitude calculated in a coordinate frame fixed to the body of the molecule, assuming the molecule to be fixed in space, and then rotated geometrically to the laboratory-fixed coordinate frame. This amplitude is independent of rotational motion and can be written (for particular initial and final vibronic states av and $\alpha'v'$)

$$f_{av,\alpha'v'}(\hat{R})=\langle v\,|f_{\alpha,\alpha'}(\vec{R})\,|\,v'\rangle\ , \tag{6}$$

here $\vec{R}$ should be understood as shorthand for the collection of nuclear coordinates—only for a diatomic molecule is it a simple vector. Similarly $\hat{R}$ represents the simple polar angles (θ,ϕ) only for a linear molecule; it is, in general, the set of three Euler angles. The volume of angular space, V, for the linear molecule is 4π, but for the general case is $8\pi^2$. If the adiabatic approximation is made for rotation *only*, then the (6) is a formal representation of the scattering amplitude for a particular vibronic transition.[10] If the fixed-nuclei approximation is also made for vibration, then (6) involves a radial integral over vibrational wave functions of the scattering amplitude $f_{\alpha,\alpha'}(\vec{R})$ calculated for a range of internuclear separations.[11]

The scattering amplitude $f_{av,\alpha'v'}(\hat{R})$ is then multiplied by the product of initial and final rotational wave functions $R^j_{m_j\Lambda}(\hat{R})$ and $R^{j'}_{m_j'\Lambda'}(\hat{R})$ and integrated over all $\hat{R}$. If we take them to be normalized symmetric-top functions $D^j_{mm'}(\hat{R})$, as for linear and symmetric-top molecules, then their product can be written[12]

$$R^{j}_{m_j\Lambda}(\hat{R})R^{j'}_{m_{j'}\Lambda'}(\hat{R})^{*}=\frac{[(2j+1)(2j'+1)]^{1/2}}{V}(-1)^{m_{j'}-\Lambda'}\times\sum_{l_t}\sum_{M}\sum_{\Lambda_t}(2l_t+1)\begin{bmatrix} j & j' & l_t \\ m_j & -m_{j'} & \Lambda_t \end{bmatrix}\begin{bmatrix} j & j' & l_t \\ \Lambda & -\Lambda' & \Lambda_t \end{bmatrix}D^{l_t}_{M\Lambda_t}(\hat{R}) , \quad (7)$$

where (· · ·) is a 3-*J* symbol. Combining this with (6), taking the mod-square, multiplying by k'/k, summing over $m_{j'}$ and averaging over m_j, and integrating over all $\hat{R}$ must yield (1). It follows that the partial cross section for angular momentum transfer in (1) can be written

$$\frac{d\sigma^{l_t,\Lambda_t}_{av,a'v'}}{d\Omega}=\sum_{M}|f^{l_t,\Lambda_t}_{av,a'v'}(M)|^{2} , \quad (8)$$

where

$$f^{l_t,\Lambda_t}_{av,a'v'}(M)\equiv\frac{(2l_t+1)^{1/2}}{V}\times\int f_{av,a'v'}(\hat{R})D^{l_t}_{M\Lambda_t}(\hat{R})d\hat{R} . \quad (9)$$

The integral (9) therefore effects the projection of a particular "harmonic" of $f_{av,a'v'}(\hat{R})$, and the partial cross sections are dependent on the projectile energy and initial and final vibronic (but not rotational) states.

Generalization to asymmetric-top molecules is straightforward if the wave function is taken[13] to be a linear combination of those for the symmetric top, i.e.,

$$R^{j}_{m_j\tau}(\hat{R})=\sum_{\Lambda}R^{j}_{m_j\Lambda}(\hat{R})\Gamma^{j}_{\Lambda\tau} . \quad (10)$$

Given the rotational Hamiltonian for the molecule in question, (10) results in the eigenvalue equation (4). Using (10) to generalize (7) yields (3), where now the dynamical cross section is

$$\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{av,a'v'}}{d\Omega}=\sum_{M}[f^{l_t,\Lambda_t}_{av,a'v'}(M)]^{*}f^{l_t,\Lambda_t'}_{av,a'v'}(M) , \quad (11)$$

still with the definition (9). These cross sections are, in general, complex quantities, but their imaginary parts make no contribution to (3), which must be purely real. The real part of (11) is clearly invariant under interchange of Λ_t and Λ_t'. If, in addition, the molecule has a plane of symmetry, then[9]

$$\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{av,a'v'}}{d\Omega}=(-1)^{\Lambda_t}\frac{d\sigma^{l_t,-\Lambda_t,\Lambda_t'}_{av,a'v'}}{d\Omega}=(-1)^{\Lambda_t'}\frac{d\sigma^{l_t,\Lambda_t,-\Lambda_t'}_{av,a'v'}}{d\Omega} . \quad (12)$$

The values of Λ_t and Λ_t' in (11) are also restricted by symmetry properties, e.g., the fact that Λ in (10) can take on only even, or only odd, values restricts $\Lambda_t-\Lambda_t'$ to even values or zero. These and other symmetry properties can be more easily exploited in actual computations by using, instead of (10), symmetry-adapted wave functions,[13] but this serves no purpose essential to our present concern. Equation (8) can now be considered a special case ($\Lambda_t=\Lambda_t'$) of (11).

For $j=\tau=0$, (3) reduces directly to

$$\frac{d\sigma_{av0,a'v'l_t}}{d\Omega}=\frac{k'}{k}\sum_{\Lambda_t}\sum_{\Lambda_t'}\Gamma^{l_t}_{\Lambda_t,\tau'}\Gamma^{l_t}_{\Lambda_t',\tau'}\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{av,a'v'}}{d\Omega} . \quad (13)$$

Unlike (1), (13) does not permit a unique identification of the dynamical cross section for arbitrary l_t,Λ_t,Λ_t' with a particular cross section for a transition out of the ground rotational state. If, however, the molecule has a plane of symmetry, the number of unique dynamical cross sections for $l_t\leq 4$ is sufficiently small that (13) is adequate for their determination if the cross sections for the ground state are known. It is also clear that for a molecule with a high degree of symmetry only the elements with $\Lambda_t=\Lambda_t'$ may contribute significantly in (13), in which case the simpler set of equations characteristic of the symmetric-top molecule may be an adequate approximation.

It will be helpful to have the definition

$$\frac{d\sigma_{av,a'v'}}{d\Omega}\equiv\sum_{l_t}\sum_{\Lambda_t}\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t}_{av,a'v'}}{d\Omega}=\frac{1}{V}\int|f_{av,a'v'}(\hat{R})|^{2}d\hat{R} . \quad (14)$$

This simple reduction follows from the completeness of the *D* matrices over the space $V=\int d\hat{R}$

(for linear molecules the sum over Λ_t is constrained to only one value, but since $\hat{R}$ is two-dimensional the D matrices still comprise a complete set). Thus (14) is simply a cross section for a vibronic transition in a fixed molecule, averaged over all orientations of the molecule. If electronic and vibrational motion are uncoupled, we can also sum (14) over v' to define

$$\frac{d\sigma_{\alpha v,\alpha'}}{d\Omega} \equiv \sum_{l_t} \sum_{\Lambda_t} \frac{d\sigma_{\alpha v,\alpha'}^{l_t,\Lambda_t,\Lambda_t}}{d\Omega}$$

$$= \frac{1}{V} \int \langle v \| f_{\alpha,\alpha'}(\hat{R}) |^2 | v \rangle d\hat{R} \ , \qquad (15)$$

which follows from the completeness of the vibrational wave functions. It will be noted that (14) is simply the trace of the matrix of partial cross section defined by (11). Thus if only a *total* cross section is desired, necessary computational effort is greatly reduced for an asymmetric-top molecule.

Now let us assume that the projectile kinetic energy is sufficiently high that k'/k can be taken as constant with respect to *rotational* contributions. Then (3) can be summed over all final rotational states, neglecting contributions from the kinematic factor. This will be indicated by the single summand $J'(=j', j'\Lambda'$ or $j'\tau'$ for the three types of molecules). For linear molecules we simply use the sum rule for Clebsch-Gordan coefficients to obtain immediately

$$\sum_{J'} \frac{d\sigma_{\alpha vj,\alpha' v' j'}}{d\Omega} = \frac{k'}{k} \frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega} \ . \qquad (16)$$

Thus the total cross section is independent of j, a well known result.[4] For symmetric-top molecules the sum over j' also effects the elimination of the Clebsch-Gordan coefficients, and the sum over Λ' for fixed Λ amounts to summing over all possible Λ_t. Thus the result is also (16). For asymmetric-top molecules, summing (3) over τ' and using the orthogonality of the transformation (10) introduces $\delta_{\Lambda'''}^{\Lambda'}$. The sum over j' reduces to $\delta_{\Lambda''}^{\Lambda}\delta_{\Lambda_t'}^{\Lambda_t}$, and that over Λ of the remaining product $(\Gamma_{\Lambda\tau}^{j})^2$ is unity. The result is again (16). Thus the total cross sections for symmetric-top and asymmetric-top molecules are also independent of the initial rotational states, as previously shown.[2]

It has also been shown[14] that this fact combined with the factorization (1) can be exploited to analyze rotationally unresolved energy-loss spectra for electron collisions with linear and symmetric-top molecules in order to extract *absolute* rotational cross sections. The key to this technique is the fact that only a few quantities, the cross sections defined by (8), depend on the collision dynamics. It follows from (3), and the J independence of the total cross section for asymmetric-top molecules, that this approach may prove useful for this case as well, where now the unknowns to be determined by the analysis are the cross sections defined by (11). Even if individual rotational cross sections are not of direct interest, the technique can have great value in providing the factorization of a total cross section into contributions for particular transfer of angular momentum, as in (14).

Now we can consider the rotational energy-loss cross section, which for a particular transition $\alpha vj \rightarrow \alpha' v'$ is given by

$$\frac{dS_{\alpha vj,\alpha' v'}}{d\Omega} \equiv \sum_{J'} \tfrac{1}{2}(k^2 - k'^2) \frac{d\sigma_{\alpha vj,\alpha' v' j'}}{d\Omega} \ . \qquad (17)$$

Separating (17) into rotational and vibronic components, the latter reduce immediately using (16). The rotational energy differences for linear and symmetric-top molecules can be written (ignoring dependence of A_α and B_α on v)

$$E_{j'} - E_j = B_{\alpha'} j'(j'+1) + (A_{\alpha'} - B_{\alpha'})\Lambda'^2$$

$$- B_\alpha j(j+1) - (A_\alpha - B_\alpha)\Lambda^2 \ . \qquad (18)$$

For symmetric-top molecules A_α corresponds to the second principal moment of inertia of the nuclei and is generally comparable to B_α (if smaller than B_α it is often called C_α, if equal to B_α we have the case of the spherical top). For linear molecules A_α corresponds to the moment of inertia of the electrons about the internuclear axis, and is generally much larger than B_α and strongly dependent on α. Consistent with the assumption of only two degrees of freedom for the linear molecule, the terms in A_α and $A_{\alpha'}$ in (18) will henceforth be neglected for this case (more properly, subsumed in the vibronic energies). To evaluate the sum over J' of the first term in (18) we use the sum rule (A5) derived in the Appendix. The result, for linear molecules, is

$$\frac{dS_{\alpha vj,\alpha' v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t} B_{\alpha'} l_t(l_t+1)\frac{d\sigma_{\alpha v,\alpha' v'}^{l_t,\Lambda_t}}{d\Omega}\right.$$
$$\left.+[(B_{\alpha'}-B_\alpha)j(j+1)-B_{\alpha'}\Lambda'^2+B_\alpha\Lambda^2+2B_{\alpha'}\Lambda\Lambda_t+E_{\alpha' v'}-E_{\alpha v}]\frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega}\right] . \tag{19}$$

Now supposing that $B_{\alpha'}=B_\alpha=B$, (19) reduces to

$$\frac{dS_{\alpha vj,\alpha' v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t} Bl_t(l_t+1)\frac{d\sigma_{\alpha v,\alpha' v'}^{l_t,\Lambda_t}}{d\Omega}+(E_{\alpha' v'}-E_{\alpha v}-B\Lambda_t^2)\frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega}\right] . \tag{20}$$

For symmetric-top molecules, with the restriction to the case $\alpha=\alpha'$, we use the identity

$$2B\Lambda(\Lambda'-\Lambda)+(A-B)(\Lambda'^2-\Lambda^2)\equiv 2A\Lambda\Lambda_t+(A-B)\Lambda_t^2 ,$$

and note that the first of these terms vanishes when averaged (the energy E_j being independent of the sign of Λ) over $\pm\Lambda$ for fixed Λ_t. The result is

$$\frac{dS_{\alpha vj,\alpha' v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t}\sum_{\Lambda_t}[Bl_t(l_t+1)+(A-B)\Lambda_t^2]\frac{d\sigma_{\alpha v,\alpha' v'}^{l_t,\Lambda_t}}{d\Omega}+(E_{\alpha' v'}-E_{\alpha v})\frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega}\right] . \tag{21}$$

Equations (20) and (21) are, as (16), independent of J. Thus we have, for linear and symmetric-top molecules, an alternative proof of Shimamura's theorem,[2] here slightly generalized to include electronic transitions for linear molecules. This generalization required the use of symmetric-top functions rather than spherical harmonics to represent the rotational wave functions, without which the term in Λ_t^2 in (20) would not have been correctly obtained. Generalization to electronic transitions in nonlinear molecules will necessarily require the use of more sophisticated representations of the rotational wave function, but this will not be pursued further here.

A similar reduction of the energy-loss cross section for asymmetric-top molecules has not been attempted [further generalization of the sum rule (A5) would be required], but this is no doubt possible. We will rather *apply* Shimamura's theorem, and seek the result analogous to (20) and (21). If the rotational contribution is independent of J it must equal the value for $J=0$. Thus using (12)

$$\frac{dS_{\alpha v0,\alpha' v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t}\sum_{\tau'}\sum_{\Lambda_t}\sum_{\Lambda_t'}\Gamma_{\Lambda_t\tau'}^{l_t}\Gamma_{\Lambda_t'\tau'}^{l_t}E_{l_t}\frac{d\sigma_{\alpha v,\alpha' v'}^{l_t,\Lambda_t,\Lambda_t'}}{d\Omega}+(E_{\alpha' v'}-E_{\alpha v})\frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega}\right] . \tag{22}$$

Using (4), the sum over τ' can be carried out to yield

$$\frac{dS_{\alpha v0,\alpha' v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t}\sum_{\Lambda_t}\sum_{\Lambda_t'}H_{\Lambda_t,\Lambda_t'}^{l_t}\frac{d\sigma_{\alpha v,\alpha' v'}^{l_t,\Lambda_t,\Lambda_t'}}{d\Omega}+(E_{\alpha' v'}-E_{\alpha v})\frac{d\sigma_{\alpha v,\alpha' v'}}{d\Omega}\right] . \tag{23}$$

The elements of $H^{l_t}_{\Lambda_t,\Lambda_t'}$ are simply expressed[13] in terms of l_t,Λ_t,Λ_t' and the three principal moments of inertia of the molecule. It is noteworthy that only elements with $|\Lambda_t'-\Lambda_t|=0$ and 2 are nonzero. Equation (23) is the general expression sought. It reduces to (21) if $H^{l_t}_{\Lambda_t,\Lambda_t'}$ is diagonal, and to (20) if, in addition, the sum over Λ_t is restricted to a single term and the restriction $\alpha=\alpha'$ is relaxed.

Shimamura's result can be expressed

$$\frac{dS_{\alpha vj,\alpha'v'}}{d\Omega}=\frac{k'}{k}\left[\frac{1}{V}\int [f_{\alpha v,\alpha v'}(\hat{R})]^* H_{\text{rot}} f_{\alpha v,\alpha v'}(\hat{R})d\hat{R}+(E_{\alpha'v'}-E_{\alpha v})\frac{d\sigma_{\alpha v,\alpha v'}}{d\Omega}\right], \tag{24}$$

where the scattering amplitude in (24) is that defined by (6). In deriving (24) it was assumed that both initial and final states are eigenfunctions of the same H_{rot}, equivalent to our assumption that

$$(A_{\alpha v},B_{\alpha v})=(A_{\alpha'v'},B_{\alpha'v'}) .$$

Shimamura also noted that the first term in (24) may be small "if the amplitude $f_{\alpha'v',\alpha v}(\hat{R})$ depends weakly on the molecular orientation." In (23) this corresponds to only the harmonics with $l_t \gtrsim 0$ being significant.

The major advantage of (23) is that the partial cross sections defined by (11) are usually, or can easily be made, a direct by-product of fixed-nuclei calculations. Their value is already apparent from (1) and (3). This becomes even more useful if vibration as well as rotation is treated with, or can be assumed to satisfy, the adiabatic approximation. Since the sum over v' of the energy-loss cross section may be of interest, we can take

$$E_{\alpha'v'}-E_{\alpha v}\simeq E_{\alpha'}+E_{v'}-E_{\alpha}-E_{v}$$

and use (15) for the electronic terms. It is also easily shown, given the completeness of the vibrational wave functions, that

$$\sum_{v'}(E_{v'}-E_{v})\frac{d\sigma_{\alpha v,\alpha'v'}}{d\Omega}=\frac{k'}{k}\frac{1}{V}\int \langle v[f_{\alpha,\alpha'}(\vec{\mathrm{R}})]^*[H_{\text{vib}},f_{\alpha,\alpha'}(\vec{\mathrm{R}})]\,|\,v\rangle d\hat{R} , \tag{25}$$

where the scattering amplitude in (25) is that in the right-hand side of (6), and H_{vib} is the vibrational Hamiltonian. Calculations in the body frame are required over a range of values of $\vec{\mathrm{R}}$ in order to evaluate the integrals in (6) and (15), but it may well be both easier and more accurate to evaluate the right-hand side of (25) than the left-hand side. In this case, we can represent the sum over v' of (23) by

$$\frac{dS_{\alpha v,\alpha'}}{d\Omega}\equiv\sum_{v'}\frac{dS_{\alpha vo,\alpha'v'}}{d\Omega}=\frac{k'}{k}\left[\sum_{l_t}\sum_{\Lambda_t}\sum_{\Lambda_t'}H^{l_t}_{\Lambda_t,\Lambda_t'}\frac{d\sigma^{l_t,\Lambda_t,\Lambda_t'}_{\alpha v,\alpha'}}{d\Omega}+(E_{\alpha'}-E_{\alpha})\frac{d\sigma_{\alpha v,\alpha'}}{d\Omega}\right.$$
$$\left.+\frac{1}{V}\int \langle v[f_{\alpha,\alpha'}(\vec{\mathrm{R}})]^*[H_{\text{vib}},f_{\alpha,\alpha'}(\vec{\mathrm{R}})]\,|\,v\rangle d\vec{\mathrm{R}}\right] . \tag{26}$$

If the vibrational wave function is well-localized about the internuclear separation R_α (as for the ground state), then (15) may be adequately approximated by the results of calculations at R_α only, and it may also be adequate to approximate H_{vib} in (26) by the harmonic oscillator Hamiltonian.

Concerning the validity of the adiabatic approximation itself, it is generally expected to break down: (i) near threshold, (ii) near a resonance, and (iii) for polar molecules. In all cases this is because the interaction time is not, in a classical sense, short compared to the molecular rotational or vibrational periods. Problems (i) and (ii) may be somewhat mitigated by use of the energy-modified adiabatic approximation.[15] Problem (iii) is particularly acute, as (11) diverges for forward scattering and the angular integration of (11) is infinite, for $l_t=1$. This problem, as well as (i), may be partially solved by use of the multipole-extracted adiabatic-nuclei approximation.[16] In this approach the dominant long-range interactions are treated with full account of the rovibrational dynamics, but in some simple approximation such as the first Born approximation. Then all of the above discussion can be applied to the *corrections* to these approximate cross sections, these corrections still being obtained with the adiabatic approximation but with the dominant long-range interactions extracted in a self-consistent manner. The dependence of the energy-loss or stopping cross section on initial rotational state would then be, in this example, that associated with the first Born approximation. This could be useful information, even if the absolute magnitude of the cross section is unknown. Following Shimamura,[2] we note finally that the above discussion is not limited to electrons as projectiles. They could be positrons or heavy structureless particles as well. The range of validity over which the adiabatic approximation is valid may, of course, be different.

To illustrate, we consider electron collisions with CO. Cross sections for transitions involving the lowest few rotational states of the ground vibrational state are available[17] from quite sophisticated calculations *not* involving the adiabatic approximation. Stopping cross sections S_j computed for initial states $j=0$ and $j=1$ from these results are compared as a test of the theorem in Table I. The dipole-extracted stopping cross sections (S_j less the first Born approximation FBA) are defined by

$$\Delta S_j \equiv S_j - 2B[(j+1)\sigma^{\mathrm{FBA}}_{j,j+1} - j\sigma^{\mathrm{FBA}}_{j,j-1}] \; , \tag{27}$$

where

$$\sigma^{\mathrm{FBA}}_{j,j'} = \frac{8\pi}{3}\frac{D^2}{k^2}\frac{j_>}{2j+1}\ln\frac{k+k'}{|k-k'|} \tag{28}$$

is the first Born approximation for the cross section[4] in units of $a_0^2(=0.2800\times10^{-20}\ \mathrm{m}^2)$, $D(=0.044$ a.u.) is the dipole moment of CO used in the original calculations, and $j_>$ is the larger of j and j'. The cross sections S_0 and S_1 are seen to be in reasonable agreement only at the highest energies tabulated, but the cross sections ΔS_0 and ΔS_1 are in excellent agreement at all energies. The first Born approximation appears to be adequate for energies less than 0.005 eV. Thus we conclude that the stopping cross section for the energy range $2B$ to 0.6 eV can be obtained to good accuracy (assuming the original results to be correct) from the expression

$$S_j(E) = \Delta S_0(E) + 2B[(j+1)\sigma^{\mathrm{FBA}}_{j,j+1}(E) - j\sigma^{\mathrm{FBA}}_{j,j-1}(E)] \; , \tag{29}$$

and the values of ΔS_0 in Table I. For higher energies the agreement of S_1 and S_0 is excellent, but the original results do not extend to high enough rotational levels that the results for S_j could be considered well converged. The moral here for future calculations is that it may take more values of l_t to converge (23) than, for example, (1), (3), or (14). Likewise, if fixed-nuclei calculations are being made for vibration, the little additional effort required to evaluate the right-hand side of (25) may be quite valuable.

This work was supported by the U.S. Department of Energy (Office of Basic Energy Sciences).

TABLE I. The stopping cross section (meV Å^2) for electrons scattered by CO. The incident electron energy is E for initial state $j=0$ and $E-2B$, for $B=0.238$ meV, for $j=1$. S_j is the stopping cross section, and ΔS_j is the stopping cross section less the contribution from the first Born approximation for the dipole ($\Delta j=\pm1$) transition.

E (eV)	S_0	ΔS_0	S_1	ΔS_1
0.005	22.1	0.4	16.7	0.4
0.010	13.5	0.5	10.9	0.6
0.030	6.05	0.64	5.16	0.64
0.050	4.26	0.71	3.72	0.71
0.100	2.83	0.85	2.56	0.85
0.600	2.34	1.92	2.30	1.93

APPENDIX

In a footnote, Shimamura[6] attributed to Takayanagi the observation that the sum

$$\sum_{j'} C(jl_tj';\Lambda\Lambda'-\Lambda)C(jl_tj';\Lambda''\Lambda'-\Lambda'')[j'(j'+1)-j(j+1)]$$

is independent of j for $l_t=1,2$ and 3 for the case $\Lambda'=\Lambda=\Lambda''=0$, and stated that it is possible to extend the result for $l_t\geq 4$. In this appendix some of the standard formulas of Racah algebra are used to prove the j independence of this sum for any l_t for the case $\Lambda=\Lambda''\neq 0$ and $\Lambda'\neq 0$, and to provide a simple expression for its value in the general case. The resulting expression is a simple generalization of that provided for the case $\Lambda'=0$ by Choi *et al.*[18]

The reduced matrix element of $\vec{\mathrm{j}}\cdot\vec{\mathrm{l}}_t$ can be written[12]

$$\langle jl_tj'||\vec{\mathrm{j}}\cdot\vec{\mathrm{l}}_t||jl_tj'\rangle=\tfrac{1}{2}[j'(j'+1)-j(j+1)-l_t(l_t+1)]\ , \tag{A1}$$

and also written

$$\langle jl_tj'||\vec{\mathrm{j}}\cdot\vec{\mathrm{l}}_t||jl_tj'\rangle=(-1)^{j+l_t+j'}W(jjl_tl_t;lj')(2j+1)^{1/2}\langle j||\vec{\mathrm{j}}||j\rangle(2l_t+1)^{1/2}\langle l_t||\vec{\mathrm{l}}_t||l_t\rangle\ , \tag{A2}$$

where $W(\cdots)$ is a Racah coefficient. Using the relation $\langle L||\vec{\mathrm{L}}||L\rangle=[L(L+1)]^{1/2}$ for the reduced matrix elements in (A2), and equating (A1) and (A2), yields

$$j'(j'+1)=j(j+1)+l_t(l_t+1)\ +2(-1)^{j+l_t+j'}W(jjl_tl_t;lj')[(2j+1)(j+1)j(2l_t+1)(l_t+1)l_t]^{1/2}\ . \tag{A3}$$

Now consider $j'(j'+1)$ multiplied by

$$C(jl_tj';\Lambda\Lambda'-\Lambda)C(jl_tj';\Lambda''\Lambda'-\Lambda'')$$

and summed over all j'. The first two terms in (A3) reduce immediately. The third reduces, using a standard contraction formula[12] for the sum of the product of two Clebsch-Gordan coefficients and a Racah coefficient, to

$$-2[(2j+1)(j+1)j(2l_t+1)(l_t+1)l_t]^{1/2}(-1)^{\Lambda'+j+l_t+\Lambda+\Lambda''}\begin{bmatrix} j & j & 1\\ \Lambda & -\Lambda'' & \epsilon\end{bmatrix}\begin{bmatrix} l_t & l_t & 1\\ \Lambda-\Lambda' & \Lambda'-\Lambda'' & \epsilon\end{bmatrix}, \tag{A4}$$

and evaluating the Clebsch-Gordan coefficients in (A4) yields the final result for the sum rule[19]

$$\begin{aligned}\sum_{j'} C(jl_tj';\Lambda\Lambda'-\Lambda)C(jl_tj';\Lambda''\Lambda'-\Lambda'')j'(j'+1)&=[j(j+1)+l_t(l_t+1)+2\Lambda(\Lambda'-\Lambda)]\delta_{\Lambda\Lambda''}\\ &\quad-\{[j(j+1)-\Lambda\Lambda''][l_t(l_t+1)-(\Lambda-\Lambda')(\Lambda''-\Lambda')]\}^{1/2}\delta_{\Lambda\Lambda''\pm 1}\ .\end{aligned} \tag{A5}$$

In addition to the use to which (A5) is put in this paper, it will find application in the l_z-conserving modification of fixed-nuclei calculations.[20] Here the relevant sum can be expressed, using (A5) as

$$\sum_j \left[\frac{2j+1}{2J+1}\right]C(jlJ;\Lambda m)^2Bj(j+1)=B[l(l+1)+J(J+1)-2m(\Lambda+m)]\ . \tag{A6}$$

Thus for the *diagonal* (in J,m and Λ) elements of the fixed-nuclei channel energies, we have simply $k_{l'}^2-k_l^2=B[l(l+1)-l'(l'+1)]$.

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[6] I. Shimamura, *Symposium on Electron-Molecule Collisions,* edited by I. Shimamura and M. Matsuzawa (University of Tokyo, Tokyo, 1979), p. 13.

[7] This can also be inferred from the work of Y. Itikawa [J. Phys. Soc. Jpn. 30, 835 (1971)], who considered the problem of electron collisions with symmetric-top molecules in the first Born approximation.

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[19] The right-hand side of Eq. (A5) was also obtained (again for the case $\Lambda'=0$) by J. M. Launay [J. Phys. B 9, 1823 (1976)], but not identified as a simple sum rule.

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