Semiclassical Treatment of Strong Collisions in Pressure Broadening*

T. A. Dillon, E. W. Smith, and J. Cooper
National Bureau of Standards, Boulder, Colorado 80302

and

M. Mizushima
Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80302

(Received 28 January 1970)

The classical-path approximation reduces the problem of pressure broadening of spectral lines to the evaluation of matrix elements of the scattering operator. If the intermolecular potential is long range and the interaction volume is large, the broadening is caused by distant or weak collisions. In this case, the scattering operator can be approximated by a second-order expansion, and the perturber trajectories can be taken to be straight paths. For neutral atoms or molecules, the intermolecular potential is short range and broadening arises from close or "strong" collisions. In this paper it is shown how classical trajectories, determined by a "scalar interaction" (i.e., one that does not depend upon the state of the radiator), can be used to expand the scattering operator in the sum of operators characteristic of the radiator's internal states.

I. INTRODUCTION

The classical-path impact theory of pressure broadening was developed by Anderson[1] for the case of well-resolved lines. This theory was extended by Baranger[2] to include the case of overlapping lines as well as formulation of a quantum-mechanical impact theory.[3] A similar theory was developed simultaneously by Kolb and Griem,[4] who applied the theory to a calculation of the Stark broadening of plasma lines. However, the most general formulation of pressure broadening is the relaxation theory of Fano.[5] Most pressure-broadening calculations are performed using a classical-path impact theory where the quantities of interest are matrix elements of the scattering operator. A great many line-shape calculations use a second-order expansion of the S matrix to describe those collisions whose impact parameter is greater than some critical value ρ_0 (i.e., weak collisions). The S matrix is assumed to be effectively zero for collisions whose impact parameter is less than ρ_0 (i.e., strong collisions). This approximation is useful in treating the Stark broadening of spectral lines emitted from plasmas because the Coulomb forces are long range, and the broadening is dominated by many distant or weak collisions.

Since the forces between neutral atoms and molecules are short range, the pressure broadening of molecular lines is dominated by a few strong collisions. Nonetheless, most calculations of molecular lines follow Anderson's approach,[6] using straight paths for the perturber trajectories and treating the S matrix by the second-order expansion approximation. This procedure is difficult to justify for the cases where strong collisions make an important contribution, and calculations following this prescription have had only moderate success. In this paper an alternative treatment of the scattering operator is proposed which retains a full exponential form for the scattering operator and employs classical trajectories for the perturbing molecules. In this procedure, the scattering operator is calculated for all values of the impact parameter. The classical-path impact theory with general classical trajectories for perturbers is derived and compared with Fano's expression for the line shape. The results are equivalent to retaining first-order terms in the density expansion of the relaxation operator. Justification is presented for using an un-time-ordered exponential for the scattering operator. Finally, some practical methods for evaluating S matrix elements are discussed.

A. Line Shape

The fraction of molecules in a gas actually radiating (emitting or absorbing) is assumed to be so small that a bath of perturber particles can be associated with each radiator. The gas is regarded as a number of statistically independent cells,[7] each consisting of a single radiator and a bath of perturbing particles which do not interact with the radiation. The Hamiltonian H for a given cell is a sum of of an unperturbed radiator Hamiltonian H_0^a, an unperturbed Hamiltonian for the bath of perturbers H_0^p, and an interaction V between the radiator and perturbers. The scalar part of the interaction V_0 (that part which does not operate on radiator states) is added to H_0^p to form a "thermal-bath" Hamiltonian H_0^b. If the motion of the radiator is ignored (i.e., Doppler broadening), the remaining part of the interaction $V_1 = V - V_0$ gives the total Hamiltonian as a

sum of two independent unperturbed terms and a coupling perturbation V_1:

$$H = H_0^a + H_0^b + V_1 \quad . \tag{1.1}$$

The spectral distribution of power radiated is usually written in the form

$$P(\omega) = (4\omega^4/3c^3)NF(\omega) \quad , \tag{1.2}$$

where N is the number of radiators and $F(\omega)$ is called the spectrum or line shape. The spectrum[2] is given as the Fourier transform of a dipole autocorrelation function $\Phi(s)$:

$$F(\omega) = \pi^{-1}\,\mathrm{Re}\int_0^\infty e^{i\omega s}\Phi(s)\,ds \quad . \tag{1.3}$$

Since the interaction of perturbers with the radiation is ignored, $\Phi(s)$ can be expressed in terms of the radiator dipole moment $\vec{d}$ and the density operator for the cell ρ[5]:

$$\Phi(s) = \mathrm{Tr}\{\vec{d}\cdot\vec{D}(s)\} \quad , \tag{1.4}$$

$$\vec{D}(s) = e^{-iHs}(\rho\vec{d})e^{iHs} \quad . \tag{1.5}$$

The trace is taken over states of the cell (radiator and perturber states), and the operator $\vec{D}(s)$ will satisfy an Heisenberg equation of motion. The equation for $\vec{D}(s)$ can be formally simplified by introducing an Hermitian Liouville operator defined by its operation on an arbitrary operator A:

$$LA = [H, A] \quad . \tag{1.6}$$

It is easy to verify that

$$\vec{D}(s) = e^{-iLs}(\rho\vec{d}) \tag{1.7}$$

by differentiating (1.5) and using (1.6). The Fourier transform (1.3) can be performed:

$$F(\omega) = \pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}\{\vec{d}(\omega - L)^{-1}\rho\vec{d}\} \quad , \tag{1.8}$$

giving a formal solution for the line shape.

B. Fano's Relaxation Theory

The Liouville operator is an example of a tetradic operator which is discussed in some detail in the Appendix. Because of the linear property of commutators, L can be written as a sum analogous to the Hamiltonian:

$$LA = [H_0^a, A] + [H_0^b, A] + [V_1, A]$$

$$= (L_0^{(a)} + L_0^{(b)} + L_1)A = (L_0 + L_1)A \quad . \tag{1.9}$$

Fano's method assumes that the density operator can be written in a product form

$$\rho \sim \exp(-\hbar H/kT)$$

$$\approx \exp(-\hbar H_0^a/kT)\,\exp(-\hbar H_0^b/kT) \sim \rho^a\rho^b \quad . \tag{1.10}$$

This is called "neglect of back reaction in the density matrix" since the effect of V_1 on the statistics is ignored. The trace can be factored into traces over radiator and bath states. Introducing the operator $M(\omega)$ by

$$(\omega - L)^{-1} = (\omega - L_0)^{-1}[1 + M(\omega)(\omega - L_0)^{-1}] \tag{1.11}$$

simplifies the line-shape expression

$$F(\omega) = \pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}_a\{\vec{d}(\omega - L_0^{(a)})^{-1}$$

$$\times [1 + \langle M(\omega)\rangle(\omega - L_0^{(a)})^{-1}]\rho^{(a)}\vec{d}\} \quad . \tag{1.12}$$

The angular brackets denote the thermal-bath average

$$\langle M(\omega)\rangle = \mathrm{Tr}_b\{M(\omega)\rho^{(b)}\} \quad . \tag{1.13}$$

The line shape is written in terms of a relaxation operator $\langle M_c(\omega)\rangle$ obtained by "reentangling" $\langle M(\omega)\rangle$ and $L_0^{(a)}$,[5]

$$(\omega - L_0^{(a)})^{-1}[1 + \langle M(\omega)\rangle(\omega - L_0^{(a)})^{-1}]$$

$$= [\omega - L_0^{(a)} - \langle M_c(\omega)\rangle]^{-1} \quad . \tag{1.14}$$

This gives an equation for $\langle M_c(\omega)\rangle$

$$\langle M_c(\omega)\rangle = [1 + \langle M(\omega)\rangle(\omega - L_0^{(a)})^{-1}]^{-1}\langle M(\omega)\rangle \quad , \tag{1.15}$$

which Fano uses to obtain a solution by performing an expansion of $\langle M(\omega)\rangle$ in powers of gas density.

The interaction term V_1 is given as the sum of interactions V_1^i between the ith perturber and the radiator, and so L_1 is given as a sum of L_1^i. Retaining only terms first order in gas density n gives the relaxation operator as $n\{m(\omega)\}_{\mathrm{av}}$ where the av denotes a one-body thermal average and $m(\omega)$ is given as the solution of a Lippmann-Schwinger equation,

$$m(\omega) = L_1^i(\omega - L_0^i - L_1^i)^{-1}(\omega - L_0^i)$$

$$= (\omega - L_0^i)(\omega - L_0^i - L_1^i)^{-1}(\omega - L_0^i) - (\omega - L_0^i) \quad , \tag{1.16}$$

$$F(\omega) = \pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}_a\{\vec{d}[\omega - L_0^a - n\{m(\omega)\}_{\mathrm{av}}]^{-1}\rho^a\vec{d}\} \quad . \tag{1.17}$$

Fano obtains a solution of these equations in a time-independent formalism. In Sec. II the relaxation operator is obtained from a more familiar time-dependent formulation.

II. TIME-DEPENDENT FORMULATION

The line shape is given (1.8) by the thermal-bath average of $(\omega - L)^{-1}$, which can be written as the Fourier transform of the tetradic time-evolution operator, e^{-iLt}. Since the average $\langle(L_0^b)^n A\rangle$ vanishes for arbitrary operators A, it is possible to transform e^{-iLt} to the interaction picture, $e^{-iL_0t}\mathfrak{U}(t;0)$:

$$[\omega - L_0^a - \langle M_c(\omega)\rangle]^{-1} \equiv \langle(\omega - L)^{-1}\rangle$$

$$= -i\int_0^\infty \exp[i(\omega - L_0^a)t]\langle\mathfrak{U}(t;0)\rangle\,dt \quad . \tag{2.1}$$

The tetradic $\mathfrak{U}(t;0)$ satisfies the familiar differential

equation

$$i\frac{\partial \mathfrak{U}}{\partial t}(t;0)=e^{iL_0t}L_1e^{-iL_0t}\mathfrak{U}(t;0)\equiv\tilde{L}(t)\mathfrak{U}(t;0)\ , \quad (2.2)$$

which can be written as an integral equation

$$\mathfrak{U}(t;0)=1-i\int_0^t\tilde{L}(s)\mathfrak{U}(s,0)\,ds\ . \quad (2.3)$$

Since L_1 is given as a sum of N_p single-particle L^i's, the operator $\mathfrak{U}(t;0)$ is given as a time-ordered product of single perturber $\mathfrak{U}^i(t;0)$,

$$\mathfrak{U}(t;0)=\mathcal{O}\prod_{i=1}^{N_p}\mathfrak{U}^i(t;0)\ . \quad (2.4)$$

If the collisions are statistically independent, there is nothing to distinguish between perturbers when an average over-all possible perturber motion is performed. Using $\mathfrak{U}^i=1+\varphi^i$, we obtain

$$\begin{aligned}\langle\mathfrak{U}^i(t;0)\rangle&=\mathcal{O}\prod_{j=1}^{N_p}\langle 1+\varphi^i(t;0)\rangle\\&=\mathcal{O}\left[1+n\{\varphi^i(t;0)\}_{\rm av}/N_p\right]^{N_p}\\&\xrightarrow[\lim N_p\to\infty]{}\mathcal{O}\exp[n\{\mathfrak{U}^i(t;0)-1\}_{\rm av}]\ ,\end{aligned} \quad (2.5)$$

where the one-body spatial distribution[8] n/N_p was factored out of the one-body average to give the one-body thermal average $\{\cdots\}_{\rm av}$. The integral relation (2.3) and the identity[9] $\mathfrak{U}(t;0)=e^{iL_0t}\mathfrak{U}(0,-t)e^{-iL_0t}$ give

$$\langle\mathfrak{U}(t;0)\rangle=\mathcal{O}\exp[-in\int_0^t\exp(iL_0^as)\times\{\tilde{L}_1^i(0)\mathfrak{U}^i(0,-s)\}_{\rm av}\exp(-iL_0^as)\,ds]\ , \quad (2.6)$$

which is equivalent to Fano's result (1.16). The impact approximation assumes that the quantity $\{L_1^i\mathfrak{U}^i(0;-s)\}_{\rm av}$ increases to a constant value $\{L_1^iU^i(0;-\infty)\}_{\rm av}$ in a time τ such that

$$\{L_1^i\mathfrak{U}^i(0;-\infty)\}_{\rm av}\tau\ll 1\ . \quad (2.7)$$

Assuming that $t\gg\tau$, we replace $\{L_1^i\mathfrak{U}^i(0,-s)\}_{\rm av}$ by the constant $\{L_1^i\mathfrak{U}^i(0,-\infty)\}_{\rm av}$. Equation (2.6) thus becomes

$$\langle\mathfrak{U}(t;0)\rangle=\exp(iL_0^at)\exp(-i[L_0^a+n\{L_1^i\mathfrak{U}^i(0;\infty)\}]_{\rm av}t)\ . \quad (2.8)$$

If this result is substituted into (2.1) and compared with Fano's result it can be seen that m is simply $L_1^i\mathfrak{U}^i(0,-\infty)$. The same result is obtained by Fourier transforming (1.16), using the interaction picture and noting that $\langle\tilde{L}_1^i(t)\mathfrak{U}^i(t;0)\tilde{L}_1^i(0)\rangle_1$ is an autocorrelation function with a correlation time τ on the same order as the correlation time for $\langle\tilde{L}_1^i(t)\tilde{L}_1^i(0)\rangle_1$.

The one-body thermal average can be expressed as integrals over the classical variables $\vec{x}$ and $\vec{v}$ which denote the position and velocity of the perturber at the time $t=0$.[7] The position $r(t)$ of the perturber at time t is a uniquely determined function of $\vec{x}$, $\vec{v}$, and t. For distant (weak) collisions the perturber trajectory is taken to be a straight line $\vec{r}(t)=\vec{x}+\vec{v}t$; however, for close (strong) collisions the perturber trajectory is determined by the scalar part of the interaction V_0. The instantaneous radial velocity $\dot{r}$ for a particle moving under the influence of a central potential is[10]

$$\dot{r}=\frac{dr}{dt}=\left[\frac{2}{\mu}\left(E-V_0-\frac{l^2}{2\mu r^2}\right)\right]^{1/2}\ , \quad (2.9)$$

where μ is the reduced mass, l is the angular momentum, and E is the total energy. The position of a particle is determined by two integral equations

$$t-t_c=\int_{r_0}^{r(t)}dr/\dot{r}\ , \quad (2.10)$$

$$\theta(t)-\theta_c=\int_{r_0}^{r(t)}(l/\mu r^2\dot{r})\,dr\ , \quad (2.11)$$

and the azimuthal angle is a constant φ_c, since scattering occurs in a plane. The point of closest approach r_0 is a root of the equation $\dot{r}=0$. It is convenient to write $\vec{x}$ in cylindrical coordinates where $d^3\vec{x}$ is given as $-v\rho\,d\rho\,dt_0\,d\alpha$; the velocity is written in spherical coordinates so that $d^3\vec{v}$ becomes $v^2\sin\beta\,dv\,d\beta\,d\gamma$.[11] These are the familiar collision variables, where ρ is the impact parameter for the collision (provided the perturber is outside the range $r_{\max}$ of V_0 at time $t=0$). If the perturber trajectory was a straight line, $\vec{r}(t)=\vec{\rho}+\vec{v}(t-t_0)$, the "time of closest approach" would be t_0. The difference between the actual "time of closest approach" t_c and t_0 is simply the constant K,

$$K=t_c-t_0=(r_{\max}^2-\rho^2)^{1/2}/v-\int_{r_0}^{r_{\max}}dr/\dot{r}\ . \quad (2.12)$$

It can be seen from (2.10) that r and therefore θ, $V_1(r)$, and $L_1^i(r)$ depend upon time only in the combination $(t-t_c)$ making it easy to show that

$$\{\tilde{L}_1^i(0)\mathfrak{U}^i(0;-\infty)\}_{\rm av}=\{L_1^i(t_c)\mathfrak{U}^i(t_c;-\infty)\}_{\rm av}\ .$$

The integration over t_0 can be performed explicitly using the change of variable $t_c=K+t_0$:

$$\begin{aligned}\int_{-\infty}^{\infty}\tilde{L}_1^i(t_c)\mathfrak{U}^i(t_c,-\infty)\,dt_c&=i\int_{-\infty}^{\infty}\frac{d\mathfrak{U}^i(t_c,-\infty)}{dt_c}\,dt_c\\&=i[\mathfrak{U}^i(\infty;-\infty)-1]\equiv\bar{m}(\alpha,\beta,\gamma,\rho,v)\ .\end{aligned} \quad (2.13)$$

The average over angles (α,β,γ) is equivalent to averaging over values of the magnetic quantum numbers of the radiator states[12] so that the thermal average is given by integrals over ρ and v. It is shown in the Appendix that $\mathfrak{U}(\infty;-\infty)$ is given simply as a direct product of scattering operators, S_iS_r. If it is assumed that the scattering matrices will be averaged over magnetic quantum numbers, we have

$$n\{m\}_{\rm av}=\int_0^\infty dv\,v^2f(v)nv2\pi\int_0^\infty\rho\,d\rho[S_iS_r-1]\ , \quad (2.14)$$

where the one-body velocity distribution $f(v)$ is a Maxwellian,

$$f(v) = (\mu/2\pi kT)^{3/2} e^{-\mu v^2/2kT} \quad . \tag{2.15}$$

The resulting line shape (1.17) is equivalent to the result of Baranger and reduces the problem of line shape to calculating matrix elements of the scattering operator.

III. S MATRIX

The scattering operator is represented by a time-ordering exponential denoted by

$$S = \mathcal{O} \exp[-i \int_{-\infty}^{\infty} \tilde{V}_1(t)\, dt] \quad , \tag{3.1}$$

where

$$\tilde{V}_1(t) = \exp(iH_0^a t) V_1 \exp(-iH_0^a t) \quad . \tag{3.2}$$

For weak collisions the average interaction strength $\overline{V}$ is much less than the inverse of the collision duration time τ_c^{-1}, and the scattering operator can be approximated by the first few terms in its series expansion. This approximation sacrifices the unitarity of the scattering operator and necessitates lower-limit cutoffs on the impact parameter. This approach is useful for Stark broadening, a process dominated by weak collisions, but it provides a poor approximation for strong collision processes. Gases of neutral particles interact via short-range forces, and the pressure broadening is dominated by strong collisions. In this case it is desirable to guarantee unitarity of the scattering operator and avoid cutoffs on the impact parameter. To develop such an alternative approximation, consider the following identity for S-matrix elements:

$$\langle a|S|b\rangle = \langle a|b\rangle - i\sum_c \int_{-\infty}^{\infty} e^{i\omega_{ac}t} \times \langle a|V_1|c\rangle\langle c|U(t;-\infty)|b\rangle\, dt \quad . \tag{3.3}$$

The contribution to the S matrix from the intermediate states $|c\rangle$ for which $\omega_{ac}\tau \gg 1$ can be neglected because of the rapid oscillation of the exponential in the integral. For intermediate states such that $\omega_{ac}\tau \sim 1$, assume that the interaction is weak (i.e. $\langle a|V_1|c\rangle\tau \ll 1$), so they can also be ignored. This assumption is not generally valid but is useful for a great many cases of interest. Intermediate states for which $\omega_{ac}\tau \ll 1$ are the only ones that contribute to (3.3), hence the exponential can be replaced by unity. These conditions can be stated formally by defining a projection operator[13] which selects only those intermediate states which will contribute:

$$\begin{aligned} &\langle a|\mathcal{P}V|c\rangle = \langle a|V_1|c\rangle \quad \text{for} \quad \omega_{ac}\tau_c \ll 1 \ , \\ &\langle a|\mathcal{P}V_1|c\rangle = 0 \qquad\quad \text{for} \quad \omega_{ac}\tau_c \gtrsim 1 \ . \end{aligned} \tag{3.4}$$

The scattering operator can now be written in the form

$$S = \mathcal{O} \exp(-i \int_{-\infty}^{\infty} \mathcal{P}V_1\, dt) \quad , \tag{3.5}$$

where time ordering is retained since in general $\mathcal{P}V_1$ does not commute with itself at all times

A review article by Buckingham[14] gives intermolecular potentials for many common cases in terms of molecular moments and the variables $r(t)$ and $\chi(t)$ shown in Fig. 1. The situations are such that one angle-dependent term dominates the intermolecular potential which is given by a first- or second-order Legendre polynomial (a caret is used to denote an operator on radiator states):

$$V = \eta_0 V_0(r) + V_1(r)\eta_n \hat{P}_n(\cos\chi(t)) \quad . \tag{3.6}$$

The factors $V_0(r)$ and $V_1(r)$ are scalar quantities on the rotational and vibrational states of the atom. The terms η_0 and η_n contain time-independent molecular moments which are scalar quantities on rotational states but in general are operators on vibrational states. The moments can be expressed as sums of a scalar part η' and an operator part $\hat{\eta}$,[15]

$$\eta_0 = \eta_0' + \sum \left(\frac{\partial \eta_0}{\partial Q_k}\right)_{eq} \hat{Q}_k = \eta_0' + \hat{\eta}_0 \quad , \tag{3.7}$$

where $\hat{Q}_k$ is the kth normal coordinate. The operator $\mathcal{P}V_1(r)$ is

$$\mathcal{P}V_1(r) = V_0(r)\mathcal{P}\hat{\eta}_0 + V_1(r)\mathcal{P}(\eta_n' + \hat{\eta}_n)\hat{P}_n(\cos\chi(t)) \quad , \tag{3.8}$$

and the scalar part V_0 is given as $V_0(r)\eta_0'$.

The classical expression for $\dot{r}$, (2.9), can be used to change the variable of integration in (3.7) from t to r:

$$\int_{-\infty}^{\infty} \mathcal{P}V(r)\, dt = 2\int_{r_0}^{\infty} \frac{V_0(r)\, dr}{\dot{r}}\, \mathcal{P}\hat{\eta}_0 + \mathcal{P}\int_{r_0}^{\infty} \frac{V_1(r)[\hat{P}_n(\cos\chi(t)) + \hat{P}_n(\cos\chi(-t))]\, dr}{\dot{r}} (\eta_n' + \hat{\eta}_n) \quad . \tag{3.9}$$

The geometry of Fig. 2 and the addition theorem[16] for spherical harmonics give

$$\hat{P}_n(\cos\chi(t)) = \frac{4\pi}{2n+1} \sum_{m=-n}^{n} Y_{nm}^*(\theta(t), \varphi_c)\hat{Y}_{nm}(\theta_N, \varphi_N) \quad , \tag{3.10a}$$

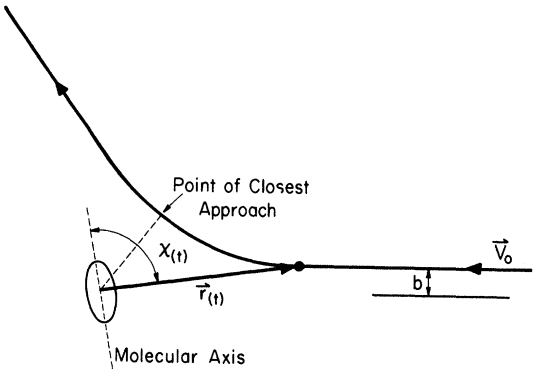

FIG. 1. Geometry of a collision.

$$\hat{P}_n(\cos\chi(-t)) = \frac{4\pi}{2n+1}\sum_{m=-n}^{n} Y^*_{nm}(2\theta_c - \theta(t), \varphi_c) \times \hat{Y}_{nm}(\theta_N, \varphi_N) \ , \qquad (3.10b)$$

where θ_N and φ_N are angles of molecular orientation.

However, for small n, $\hat{P}_n(\cos\chi(\pm t))$ varies slowly compared to the factor $V_1(r)\dot{r}^{-1}$, which is sharply peaked at r_0 where $\dot{r}$ vanishes. The main contribution to the integral (3.9) occurs when $\theta(t)=\theta_c$. Since the Z axis in Fig. 2 was chosen parallel to the impact axis $\theta(\infty)=0$, the orbit equation (2.11) can be used to evaluate θ_c and the variable χ^0,

$$\hat{P}_n(\cos\chi^0) = [4\pi/(2n+1)]\textstyle\sum_m Y^*_{nm}(\theta_c, \varphi_c)\hat{Y}_{nm}(\theta_N, \varphi_N) , \qquad (3.11)$$

which is independent of time. The scattering operator is now given by an un-time-ordered exponential

$$S = \exp[-iK_0\mathcal{P}\hat{\eta}_0 - iK_1\mathcal{P}(\eta_n' + \hat{\eta}_n)P_n(\cos\chi^0)] , \qquad (3.12)$$

since there are no time-dependent operators. The integrals K_i are simply

$$K_i = 2\int_{r_0}^{\infty} dr V_i(r)/\dot{r} \ . \qquad (3.13)$$

This approximation works best for close or strong collisions where $\theta(t)$ varies slowly compared with $V_1(r)\dot{r}^{-1}$. Even for the worst case of distant or weak collisions, comparison with the straight-path approximation shows the discrepancy to be less than 25%. Since the contribution of weak collisions is small (for neutral particles), this error is unimportant.

If $V_0(r)$ is a polynomial in $1/r$ (i.e., Lennard-Jones), the K_i are hyperelliptic integrals and the quadratures are straightforward (the root r_0 can be factored out of the denominator and removed by a change of the integration variable).

For rotational lines, both $\hat{\eta}_0$ and $\hat{\eta}_n$ vanish and the scattering operator can be expanded as a sum of Legendre polynomials:

$$S = \exp[-iK_1\eta_n'\mathcal{P}P_n(\cos\chi^0)] = \textstyle\sum_j \tau_j^{(n)}\mathcal{P}P_j(\cos\chi^0) \ . \qquad (3.14)$$

This relation gives a differential equation for S in terms of the variable $x=\cos\chi^0$:

$$\frac{dS}{dx} = -iK_1\eta_n'\mathcal{P}\frac{dP_n(x)}{dx}S \qquad (3.15)$$

or

$$\sum_j \tau_j^{(n)}\mathcal{P}\frac{dP_j(x)}{dx} = -iK_1\eta_n'\mathcal{P}\frac{dP_n(x)}{dx}\left(\sum_j \tau_j^{(n)}\mathcal{P}P_j(x)\right) \ . \qquad (3.16)$$

Multiplying by $P_l(x)(x^2-1)$ and integrating over x from -1 to 1, we obtain a recursion relation for the τ's:

$$\tau_{l-1}^{(n)}\left(\frac{(l-1)l}{(2l-1)}\right) - \tau_{l+1}^{(n)}\left(\frac{(l+1)(l+2)}{(2l+3)}\right) = -iK_1\eta_n'\left(\frac{n(n+1)(2l+1)}{(2n+1)}\right) \times \sum_j \tau_j^{(n)}\left[\begin{pmatrix} n+1 & l & j \\ 0 & 0 & 0\end{pmatrix}^2 + \begin{pmatrix} n-1 & l & j \\ 0 & 0 & 0\end{pmatrix}^2\right] \ . \qquad (3.17)$$

In practice we are concerned with first- and second-order Legendre polynomials in the exponential. In these cases it is easier to obtain a recursion relation by direct application of the orthogonality relation

$$\tau_j^{(n)} = \tfrac{1}{2}(2j+1)\int_{-1}^{1} P_j(x)\exp[-iK_1\eta_n'P_n(x)]dx \ . \qquad (3.18)$$

A recursion relation can be obtained from integration by parts. For a first-order polynomial the scattering operator is

$$S = \exp\{-iK_1\eta_1'\mathcal{P}P_1(x)\} = \sum_{j=0}^{\infty}\tau_j^{(1)}\mathcal{P}P_j(x) \ , \qquad (3.19)$$

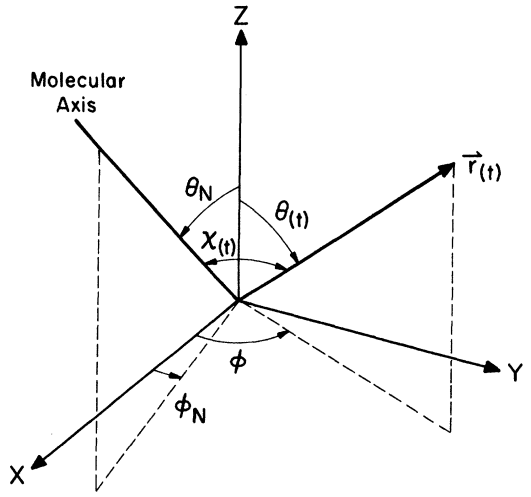

FIG. 2. Geometry for the addition theorem.

$$\tau_j^{(1)} = \tau_{j-2}^{(1)}(2j+1)/(2j-3) - i\tau_{j-1}^{(1)}(2j+1)/K_1\eta_1' \quad , \quad (3.20)$$

where $\tau_0^{(1)}$ and $\tau_1^{(1)}$, needed to generate the recursion relation, are obtained by direction integration:

$$\tau_0^{(1)} = \frac{\sin(K_1\eta_1')}{K_1\eta_1'} ,$$

$$\tau_1^{(1)} = \frac{3i}{K_1\eta_1'}\left(\cos(K_1\eta_1') - \frac{\sin(K_1\eta_1')}{K_1\eta_1'}\right) . \quad (3.21)$$

A second-order polynomial can be expanded in terms of even-ordered polynomials only,

$$S = \exp[-iK_1\eta_2'\mathcal{P}P_2(x)] = \textstyle\sum_j \tau_{2j}^{(2)}\mathcal{P}P_{2j}(x) \quad , \quad (3.22)$$

$$\tau_{2j}^{(2)} = \frac{(4j+1)(4j-1)}{4j}\left(\frac{(2j-3)}{(4j-5)(4j-7)}\tau_{2j-4}^{(2)} + \frac{1}{(4j-5)(4j-1)}\tau_{2j-2}^{(2)} - \frac{i}{2K_1\eta_2'}\tau_{2j-2}^{(2)}\right) , \quad (3.23)$$

where $\tau_0^{(2)}$ and $\tau_2^{(2)}$ are again obtained by direct integration:

$$\tau_0^{(2)} = \tfrac{1}{2}\int_{-1}^{1} \exp[-i\tfrac{1}{2}K_1\eta_2'(3x^2-1)]\,dx$$

$$= \exp(i\tfrac{1}{2}K_1\eta_2')(\pi/3K_1\eta_2')^{1/2}F(\tfrac{3}{2}K_1\eta_2') . \quad (3.24)$$

The Fresnel integral defined by

$$F(x) = \int_0^x dt\, e^{-it}/(2\pi t)^{1/2} \quad (3.25)$$

is given by a polynomial approximation[17] with an accuracy of better than 10^{-9}, and $\tau_2^{(2)}$ is obtained by integration by parts:

$$\tau_2^{(2)} = \tfrac{5}{2}[(i/K\eta_2')\exp(-iK_1\eta_2') - (i/K_1\eta_2')\tau_0 - \tau_0] . \quad (3.26)$$

All of these recursion relations are unstable for small values of $|K_1\eta_n'|$, but in that region a power-series expansion of S will converge rapidly since $|P_n(x)| \leq 1$. The case for a second-order Legendre polynomial is treated explicitly:

$$\exp(-iK_1\eta_2'\mathcal{P}P_2(x)) = \sum_{n=0}^{N}(-iK_1\eta_2)^n\frac{\mathcal{P}[P_2(x)]^n}{n!} + R_N , \quad (3.27)$$

where

$$|R_N| < \exp(|K_1\eta_2|)|K_1\eta_2|^{N+1}/(N+1)! \quad (3.28)$$

and for $|3K_1\eta_2'| \leq 1$ and $N = 10$ the error $|R_N|$ is less than 10^{-13}. Since any power of $P_2(x)$ can be expanded as a sum of even-ordered Legendre polynomials[18]:

$$[P_2(x)]^n = \sum_{j=0}^{n} C_{2j}^n P_{2j}(x) \quad , \quad (3.29)$$

the sum in (3.27) can be rearranged to give

$$\exp[-iK_1\eta_2'\mathcal{P}P_2(x)] = \sum_{j=0}^{N}\left(\sum_{n=j}^{N}(-iK_1\eta_2')^n\frac{C_{2j}^n}{n!}\right)\mathcal{P}P_{2j}(x) \quad (3.30)$$

or the following expressions for the τ's:

$$\tau_{2j}^{(2)} = \sum_{n=j}^{N}(-iK_1\eta_2')^n C_{2j}^n/n! , \quad 0 \leq j \leq N$$
$$\tau_{2j}^{(2)} = 0, \quad j > N . \quad (3.31)$$

The coefficients $(C_{2j}^n/n!)$ are given in Table I. A prescription has been given for expanding the scattering operator as a sum of Legendre polynomials and has reduced the problem of calculating S-matrix elements to the calculation of matrix elements of spherical harmonics.[19] For finite rotational quantum numbers, the triangle condition will truncate the apparent infinite series (3.14). The case of vibrational lines can be handled in a fashion completely

TABLE I. Table of $C_{2j}^n/n!$.

n j	0	1	2	3	4	5
0	1.000 000 +0					
1	0.000 000 +0	1.000 000 +0				
2	1.000 000 −1	1.428 571 −1	2.571 428 −1			
3	9.523 803 −3	7.142 857 −2	4.675 323 −2	3.896 103 −2		
4	3.571 428 −3	1.082 251 −2	1.528 471 −2	7.792 204 −3	4.195 804 −3	
5	4.329 004 −4	2.206 127 −3	2.397 602 −3	2.062 642 −3	8.833 267 −4	3.507 328 −4
6	7.325 979 −5	2.913 753 −4	4.010 694 −4	3.176 389 −4	2.050 581 −4	7.624 626 −5
7	8.325 008 −6	2.876 841 −5	5.056 861 −5	4.724 377 −5	3.063 298 −5	1.616 421 −5
8	9.692 103 −7	4.231 233 −6	5.992 458 −6	5.637 785 −6	4.194 888 −6	2.338 219 −6
9	1.076 900 −7	4.701 370 −7	6.658 286 −7	6.264 206 −7	4.660 987 −7	3.006 030 −7
10	8.645 034 −9	3.923 429 −8	5.749 567 −8	5.914 575 −8	4.870 324 −8	3.253 965 −8

nj	6	7	8	9	10
6	2.396 311−5				
7	5.325 135−6	1.384 535−6			
8	1.055 846−6	3.125 369−7	6.930 377−8		
9	1.480 850−7	5.887 321−8	1.584 086−8	3.060 166−9	
10	1.809 554−8	8.023 768−9	2.863 128−9	7.061 921−10	1.208 798−10

analogous to the rotational case. In this case a normal-mode displacement coordinate appears in the exponential. This is a first-order Hermite polynomial, and a recursion relation can be derived for the expansion coefficients of S as a sum of Hermite polynomials. Again for finite vibrational quantum numbers, the apparent infinite series will truncate. A final remark is in order here since in general there will be a term in the potential characteristic of the perturber orientation. If this term is a separate additive term, it can be neglected since in that case S will factor into the product of an S operator which depends on the radiative states $S^{(a)}$ and an S operator which depends on the perturber states $S^{(b)}$:

$$S = S^{(a)} S^{(b)} \quad . \tag{3.32}$$

However, since only matrix elements of the product $SS^{\dagger}$ need to be computed, the contribution will be a factor

$$\sum_{\alpha\beta} \langle \alpha | S^{(b)} | \beta \rangle \langle \beta | S^{(b)\dagger} | \alpha \rangle \langle \alpha | \rho_{\rm int}^{(b)} | \alpha \rangle = \sum_{\alpha} \langle \alpha | S^{(b)} S^{(b)\dagger} | \alpha \rangle \langle \alpha | \rho_{\rm int} | \alpha \rangle = 1 \ , \tag{3.33}$$

which is trivial.

APPENDIX

Comparison of matrix elements of (1.6) and interpretation of L as a tetratic or four-index operator on a vector space of two-index matrices gives

$$[LA]_{mn} = \sum_{m'n'} L_{mn;m'n'} A_{m'n'} \ , \tag{A1}$$

where

$$L_{mn;m'n'} = H_{mm'} \delta_{nn'} - \delta_{mm'} H^{*}_{nn'} \quad . \tag{A2}$$

Each of the terms in (A2) has the form of a direct product of a matrix H with a unity matrix I. A doubled or "dual" space is defined as a product space

$$|mn\rangle\rangle = |m\rangle |n\rangle \ , \tag{A3a}$$

and "left" and "right" operators are defined as direct products of operators with the unit operator

$$\mathcal{O}_l = \mathcal{O} \otimes I \ , \tag{A3b}$$

$$\mathcal{O}_r = I \otimes \mathcal{O}^{*} \ . \tag{A3c}$$

The usual rules for forming matrix elements in a direct product space give

$$\langle\langle mn | \mathcal{O}_l | m'n' \rangle\rangle = \langle m | \mathcal{O} | m' \rangle \langle n | n' \rangle \ , \tag{A4a}$$

$$\langle\langle mn | \mathcal{O}_r | m'n' \rangle\rangle = \langle m | m' \rangle \langle n | \mathcal{O} | n' \rangle^{*} \ , \tag{A4b}$$

from which it is clear that

$$L = H_l - H_r \ . \tag{A5}$$

If the dual space is formed from eigenvectors of the Hamiltonian, L will be diagonal with eigenvalues corresponding to transition frequencies ω_{mn}. Since the Hamiltonian is given as a sum, the Liouville operator is also a sum,

$$L = L_0^{(a)} + L_0^{(b)} + L_I = L_0 + L_I \ . \tag{A6}$$

In practice matrix elements are evaluated in the dual space formed from eigenvectors of the unperturbed Hamiltonian H_0. In this case L_0 is diagonal with eigenvalues corresponding to observed transition frequencies, and this dual space is frequently referred to as "line space". We shall recall some basic properties of direct products,[20] and use them to prove some useful relationships for tetradic operators:

$$(A \otimes 1)(1 \otimes B) = (1 \otimes B)(A \otimes 1) = A \otimes B \ , \tag{A7}$$

$$(A \otimes 1)^n = A^n \otimes 1 \ , \tag{A8}$$

$$e^{A \otimes 1} = e^{A} \otimes 1 \ , \tag{A9}$$

$$\frac{d(A \otimes 1)}{dx} = \frac{dA}{dx} \otimes 1 \ . \tag{A10}$$

The relation (A7) says that all left operators commute with all right operators which gives an expression of $\tilde{L}_1(t)$

$$\begin{aligned} \tilde{L}_1(t) &= \exp\{i[H_{0l} - H_{0r}]t\}(V_{1l} - V_{1r}) \exp\{-i[H_{0l} - H_{0r}]t\} \\ &= \exp(iH_0 t)_l \exp(iH_0 t)_r (V_{1l} - V_{1r}) \\ &\quad \times \exp(-iH_0 t)_r \exp(-iH_0 t)_l \\ &= \tilde{V}_1(t)_l - \tilde{V}_1(t)_r \ . \end{aligned} \tag{A11}$$

This relationship allows us to show that $\mathfrak{U}(t;t')$ obeys the same equation as $U(t;t')_l U(t;t')_r$:

$$i \frac{\partial}{\partial t} \mathfrak{U}(t;t') = \tilde{L}_1(t) \mathfrak{U}(t;t') \ , \tag{A12a}$$

$$i \frac{\partial}{\partial t} U(t;t') = \tilde{V}_1(t) U(t;t') \ . \tag{A12b}$$

Application of (A10) gives

$$\begin{aligned} & i \frac{\partial}{\partial t} [U(t;t')_l U(t;t')_r] \\ &= \left[i \frac{\partial}{\partial t} U(t;t')_l \right] U(t;t')_r + U(t;t')_l \left[i \frac{\partial}{\partial t} U(t;t')_r \right] \\ &= [\tilde{V}_1(t) U(t;t')]_l U(t;t')_r - U(t;t')_l [\tilde{V}_1(t) U(t;t')]_r \\ &= [\tilde{V}_1(t)_l - \tilde{V}_1(t)_r] U(t;t')_l U(t;t')_r \\ &= \tilde{L}_1(t) U(t;t')_l U(t;t')_r \ , \end{aligned} \tag{A13}$$

$$\mathfrak{U}(t;t') = U(t;t')_l U(t;t')_r \ , \tag{A14}$$

which has the special case

$$\mathfrak{U}(\infty;-\infty) = S_l S_r \ . \tag{A15}$$

*Work partially supported by N. I. H. Grant No. GM 11123.

[1]P. W. Anderson, Phys. Rev. 76, 647 (1949).
[2]M. Baranger, Phys. Rev. 111, 494 (1958).
[3]M. Baranger, Phys. Rev. 112, 855 (1958); 111, 481 (1958).
[4]A. C. Kolb and H. Griem, Phys. Rev. 111, 514 (1958).
[5]U. Fano, Phys. Rev. 131, 259 (1963).
[6]C. J. Tsao and B. Curnutte, J. Quant. Spectry. Radiative Transfer 2, 41 (1962).
[7]E. W. Smith, C. R. Vidal, and J. Cooper, J. Res. Natl. Bur. Std. (U. S.) 73A, 389 (1969).
[8]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 183.
[9]P. Roman, *Advanced Quantum Theory* (Addison-Weslsy, Reading, Mass., 1965), p. 310.
[10]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1950), p. 62.
[11]See page 419 of Ref. 7.
[12]J. Cooper, Rev. Mod. Phys. 39, 167 (1967).
[13]M. Mizushima, Progr. Theoret. Phys. (Kyoto) Suppl. 40, 207 (1967).
[14]A. D. Buckingham, in *Advances in Chemical Physics XII*, edited by J. O. Hirschfelder (Interscience, New York, 1967), p. 107.
[15]G. Herzberg, *Molecular Spectra and Molecular Structure II Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, N. J., 1945), p. 244.
[16]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 67.
[17]J. Boersma, Math. Computation 14, 380 (1960).
[18]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Dept. of Commerce, Natl. Bur. Std., Washington, D. C., 1964), p. 798.
[19]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957), p. 111.
[20]P. R. Halmos, *Finite Dimensional Vector Spaces* (Van Nostrand, New York, 1958), p. 95.

PHYSICAL REVIEW A VOLUME 2, NUMBER 5 NOVEMBER 1970

Intermediate-Energy Electron-Atom Scattering. I

Marvin H. Mittleman
The City College of the City University of New York, New York, New York 10031
(Received 13 May 1970)

The problem of electron-atom scattering in the energy range where both high- and low-energy methods are unreliable is considered. A previously proposed equation is made tractable by a separable approximation on the electron-electron correlation function. This results in a pair of coupled equations in which all inelastic channels are lumped into one effective one. The equations are then reduced to a tractable form by some drastic approximations and solved by an eikonal approximation. The results are good in a restricted angular range, and the restrictions are shown to be due to the "drastic approximations" and the eikonal approximation, neither of which is really necessary.

When a particle is scattered by a target with internal degrees of freedom, the energy scale can be set in terms of an average excitation energy of the medium. When the incident energy is smaller than, or of the order of, this excitation energy, so that only a few channels are open, then there are reliable calculational methods for obtaining scattering amplitudes. For example, for the problem of electron-atom scattering the close coupling method[1] or its modifications[2] gives good results with a reasonable expenditure of computing effort when only a few channels are open. As the energy goes up and the number of open channels increases, the amount of computing time necessary for any given accuracy of the results becomes prohibitively large.

At high energies the Born approximation or its modifications[3] give good results, but as the energy is lowered approaching, say, ten times the scale energy, these methods also become less reliable. There is then a large energy region where there is a need for more reliable methods.

Chase[4] seems to have been the first to have suggested an approximation in which the target particles are frozen in a given configuration, and then the amplitude for scattering from this configuration is calculated. If we denote this amplitude for scattering from P_i to P_f by $f(P_f, P_i; X)$, where X represents the (fixed) coordinates of the target particles, then the theory gives a result for the inelastic (or elastic) scattering amplitude:

$$f_{n',n}(P_f, P_i) = \int (dX)\varphi_{n'}^*(X) f(P_f, P_i; X)\varphi_n(X), \quad (1)$$

where the $\varphi_s(X)$ are the target wave functions. The method has been generalized,[5] so that not all the target degrees of freedom have to be treated by this approximation. This is particularly useful in electron-molecule scattering where rotational and electronic degrees of freedom have widely different time scales (or energy scales).

This is a high- or intermediate-energy method,