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Resonant Scattering of Monochromatic Light in Gases*†

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The resonant scattering of monochromatic light in gases is analyzed. Explicit expressions for the differential cross section are obtained in the limits (Doppler width) ≫ (natural width) ≫ (collision width) and (collision width) ≫ (natural width) ≫ (Doppler width). In the former limit, the frequency distribution of scattered light is narrowed in the forward and backward directions, and has the full absorption width for right-angle scattering. In the collision-dominated limit, the cross section separates into a coherent and a fluorescent component. The motion of the atoms broadens the δ function distribution characterizing coherent scattering from a stationary target. The interference between light scattered by different atoms is assessed.

I. INTRODUCTION

In two recent papers[1,2] (hereafter referred to as I and II) the author developed a theory of the resonant scattering of light from perturbed atoms. The first of these papers dealt with the scattering from an atom which interacted with a crystal lattice. In II the theory was generalized to perturbations whose effect could be approximated by a randomly fluctuating term in the atomic level splitting. The approaches taken in both of these papers were especially suited to the description of scattering from paramagnetic ions imbedded in insulating crystals. In the present paper we will develop an analogous theory appropriate to the resonant scattering of light in gases.[3,4]

Light scattering in gases differs in two important ways from scattering in solids. First, the atoms of the gas are moving randomly with respect to source and detector. Second, the nature of the perturbations is qualitatively different. In a solid, typically, the atom is continually under the influence of the thermal vibrations of the lattice. In a gas, however, the atom undergoes random collisions with other atoms. These collisions are generally of brief duration and are widely separated in time. In the present paper we will develop a theory which incorporates these effects. Analytic expressions for the differential cross section will be obtained for several limiting cases. Interference effects between different scatterers will be assessed and there will be some discussion of the calculation of the fluorescence from nonresonant levels.

Before entering into the details of the analysis, we should like to make some brief comments about the spirit of our approach. Our main goal is to calculate the frequency dependence of the differential scattering cross section in the resonance region. We will show that the cross section can be characterized by the same parameters (shift, width, etc.) as characterize the absorption cross section. The parameters, themselves, we will not calculate. Applications of the theory to specific systems will be reported in subsequent publications.

II. THE UNPERTURBED STATIONARY ATOM

In this section we will consider the scattering from an unperturbed stationary atom. As shown in I, the differential cross section for a scattering process where the incoming photon has angular frequency ω_1, wave vector $\vec{k}_1$, and polarization $\vec{\epsilon}_1$ and the scattered one ω_2, $\vec{k}_2$, and $\vec{\epsilon}_2$ can be written as the Fourier transform of the induced dipole moment correlation function

$$d^2\sigma(\omega_1)/d\Omega_2 d\omega_2 = (\omega_1\omega_2^{\,3}/2\pi c^4)\int_{-\infty}^{\infty} dt\, e^{i(\omega_2-\omega_1)t}\langle P_{21}^{\,\dagger} P_{21}(t)\rangle , \tag{2.1}$$

where P_{21}, the induced dipole moment operator, is given by[5]

$$P_{21} = (i/\hbar)\int_{-\infty}^{0} [\vec{\epsilon}_2\cdot\vec{d}, e^{iH_0t'/\hbar}\vec{\epsilon}_1\cdot\vec{d}e^{-iH_0t'/\hbar}]e^{-i\omega_1t'}dt' , \tag{2.2}$$

and $P_{21}(t)$ is equal to $\exp[iH_0t/\hbar]P_{21}\exp[-iH_0t/\hbar]$. In Eq. (2.2) $\vec{d}$ denotes the dipole moment operator of the atom and H_0 is the atomic Hamiltonian. The brackets in (2.1) symbolize an ensemble average. In I and II allowance was made for situations where there might be an appreciable equilibrium population in the upper of the resonant levels. In this paper it will be assumed that the temperature of the gas is sufficiently low so that only the lower levels are populated.

In order to simplify the analysis, we will initially make the assumption that the upper and lower levels involved in the transition are themselves nondegenerate. This restriction will be removed in the more general treatment outlined in Sec. 5. Any degeneracy present can of course be removed by the application of an external magnetic field. The calculation of the differential cross section under these assumptions is relatively straightforward. Since a similar calculation is outlined in I and II, we present only the final results.

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1^4|\langle f|\vec{\epsilon}_2\cdot\vec{d}|i\rangle|^2|\langle f|\vec{\epsilon}_1\cdot d|i\rangle|^2}{\hbar^2c^4[(\omega_1-\omega_0)^2+\gamma_N^2]}\,\delta(\omega_1-\omega_2)\ . \tag{2.3}$$

Here $\langle f|\vec{\epsilon}_1\cdot\vec{d}|i\rangle$ and $\langle f|\vec{\epsilon}_2\cdot\vec{d}|i\rangle$ denote matrix elements of the dipole moment operator taken between the two resonant states which are separated in energy by $\hbar\omega_0$; γ_N denotes the natural linewidth. As noted in I, the light scattered from the unperturbed atom is unshifted in frequency, and its phase is coherent with respect to the phase of the incident light.

III. A GAS OF NONINTERACTING ATOMS

We wish to describe the scattering from atoms in an ideal classical gas. This calculation differs from the one in the preceding section in that the motion of the atoms is taken into account. It will become apparent that the translational motion gives rise to a shift and broadening of the frequency distribution of the scattered light. The results of our calculation will apply mainly to transitions whose breadth (in absorption) is determined by the Doppler width. We will first obtain an expression for the cross section for a single atom moving with velocity $\vec{v}$, and then average the resulting expression over the Maxwell-Boltzmann distribution. The end product of this averaging is an expression for the cross section which is appropriate to an ensemble of atoms as long as the effect of the interference between light scattered by different atoms may be neglected. Interference effects are discussed in Sec. 6.

The motion of the center of mass of the atom is accounted for by multiplying the dipole moment components $\vec{\epsilon}_1\cdot\vec{d}$ and $\vec{\epsilon}_2\cdot\vec{d}$ by $\exp(i\vec{k}_1\cdot\vec{r})$ and $\exp(-i\vec{k}_2\cdot\vec{r})$, respectively. We will regard the position of the atom $\vec{r}$ as a classical variable determined by the classical equations of motion.[6] The frequency distribution of the cross section is then governed by the expression.

$$\int_{-\infty}^{\infty}e^{i(\omega_2-\omega_1)t}dt\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''e^{i(\omega_0-\omega_1)(t'-t'')}e^{-\gamma_N(|t'|+|t''|)}$$
$$\times\langle e^{-i\vec{k}_1\cdot\vec{r}(t'')}e^{i\vec{k}_2\cdot\vec{r}(0)}e^{-i\vec{k}_2\cdot\vec{r}(t)}e^{i\vec{k}_1\cdot\vec{r}(t+t')}\rangle\ . \tag{3.1}$$

As is appropriate for an ideal gas we will take $\vec{r}(t)$ to be equal to $\vec{v}t$, so that the origin of the coordinate system coincides with the position of the atom at $t=0$. The above expression then takes the form

$$\int_{-\infty}^{\infty}e^{i(\omega_2-\omega_1)t}dt\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''e^{i(\omega_0-\omega_1)(t'-t'')}e^{-\gamma_N(|t'|+|t''|)}$$
$$\times\langle\exp[i\vec{k}_1\cdot\vec{v}(t+t'-t'')-i\vec{k}_2\cdot\vec{v}t]\rangle\ , \tag{3.2}$$

where the average is now over a Maxwell-Boltzmann distribution in $\vec{v}$. After performing the average, the bracketed factor in (3.2) can be written

$$\exp\{-(k^2KT/2m)[t^2+(t+t'-t'')^2-2\cos\Theta\,(t^2+tt'-tt'')]\}\ , \tag{3.3}$$

where $k=|\vec{k}_1|\approx|\vec{k}_2|$, K is Boltzmann's constant, T is the temperature, and m is the mass of the atom. The symbol Θ denotes the scattering angle ($\Theta=0$ corresponds to forward scattering).

After inserting (3.3) into (3.2), the resulting multiple integral can be brought, without approximation, to the form

$$\frac{\sqrt{\pi}\,\gamma_N^{-1}\exp[-(\omega_2-\omega_1)^2/8a(1-\cos\Theta)]}{2[2a(1-\cos\Theta)]^{1/2}}\int_{-\infty}^{\infty}dy\,e^{-\gamma_N|y|}\exp[-\frac{i}{2}(2\omega_0-\omega_1-\omega_2)y-\frac{a}{2}(1+\cos\Theta)y^2]\ , \tag{3.4}$$

where $a=k^2KT/2m$. As long as $[a(1+\cos\Theta)]^{1/2}\gg\gamma_N$, we may neglect the factor $\exp(-\gamma_N|y|)$ in the integrand and thus obtain the expression

$$[\pi\gamma_N^{-1}/2a(1-\cos^2\Theta)^{1/2}]\exp[-(\omega_2-\omega_1)^2/8a(1-\cos\Theta)]\exp[-(2\omega_0-\omega_1-\omega_2)^2/8a(1+\cos\Theta)] \quad .$$

The differential cross section can be written

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2^3 A\gamma_N^{-1}}{4\hbar^2c^4a(1-\cos^2\Theta)^{1/2}}\exp\left(-\frac{(\omega_2-\omega_1)^2}{8a(1-\cos\Theta)}\right)\exp\left(-\frac{(2\omega_0-\omega_1-\omega_2)^2}{8a(1+\cos\Theta)}\right), \tag{3.6}$$

where A denotes the factor $|\langle f|\vec{\epsilon}_1\cdot\vec{\mathrm{d}}|i\rangle|^2\ |\langle f|\vec{\epsilon}_2\cdot\vec{\mathrm{d}}|i\rangle|^2$.

In the forward scattering limit, we obtain the expression

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2^3 A\gamma_N^{-1}}{4\hbar^2c^4a\Theta}\exp\left(-\frac{(\omega_2-\omega_1)^2}{4a\Theta^2}\right)\exp\left(-\frac{(\omega_1-\omega_0)^2}{4a}\right) \quad . \tag{3.7}$$

The frequency distribution of the light scattered in the forward direction is sharply peaked about the incident frequency. In the backward direction ($\Theta\approx\pi$) we have the result

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2^3 A\gamma_N^{-1}}{4\hbar^2c^4a(\pi-\Theta)}\exp\left(-\frac{(2\omega_0-\omega_1-\omega_2)^2}{4a(\pi-\Theta)^2}\right)\exp\left(-\frac{(\omega_1-\omega_0)^2}{4a}\right) \quad , \tag{3.8}$$

assuming $\sqrt{a}(\pi-\Theta)\gg\gamma_N$. The frequency distribution of the light scattered in the backward direction is peaked about the value $2\omega_0-\omega_1$. In other words, if the incident light has frequency $\omega_0-\Delta$, the distribution of the scattered light is centered about $\omega_0+\Delta$. At right angles ($\Theta=\pi/2$) the cross section becomes

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2^3 A\gamma_N^{-1}}{4\hbar^2c^4a}\exp\left(-\frac{(\omega_2-\omega_0)^2}{4a}\right)\exp\left(-\frac{(\omega_1-\omega_0)^2}{4a}\right) \quad , \tag{3.9}$$

with the result that the scattered light is peaked about ω_0 with the full Doppler width $\omega_1(KT/mc^2)^{1/2}$.

The frequency dependence displayed in Eqs. (3.7), (3.8), and (3.9) has a simple interpretation in terms of the scattering from an atom moving at constant velocity with respect to source and detector. If the frequency emitted by the source is $\omega_0-\Delta$, then the photons will be scattered most strongly if the atom has a velocity component $c\Delta/\omega_0$ in the direction of the source. As seen by the detector, the scattered radiation is radiation emitted with a frequency ω_0 which is Doppler shifted by an amount characteristic of the motion of the atom relative to the detector. If the detector is in the forward direction and the atom is receding, the frequency is shifted to $\omega_0-\Delta$, the source frequency. On the other hand, if the detector is in the backward direction and the atom is approaching, the shift is to $\omega_0+\Delta$. At right angles the effects of the motion of the atom with respect to detector and source are independent of one another as is apparent from the cross section which becomes the product of two probability distributions, one for the incoming and one for the outgoing photon.

There are two additional features of the analysis which also merit comment. First, if the natural width is much greater than the Doppler width, i.e., $\gamma_N\gg\sqrt{a}$, the differential cross section can be written

$$\begin{aligned}\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}&=\frac{\omega_1\omega_2^3 A\exp[-(\omega_2-\omega_1)^2/8a(1-\cos\Theta)]}{\sqrt{\pi}\hbar^2c^4[8a(1-\cos\Theta)]^{1/2}[\frac{1}{4}(2\omega_0-\omega_1-\omega_2)^2+\gamma_N^2]}\\&\approx\frac{\omega_1\omega_2^3 A\exp[-(\omega_2-\omega_1)^2/8a(1-\cos\Theta)]}{\sqrt{\pi}\hbar^2c^4[8a(1-\cos\Theta)]^{1/2}[(\omega_0-\omega_1)^2+\gamma_N^2]} \quad .\end{aligned} \tag{3.10}$$

Equation (3.10) is to be compared with (2.3). It is seen that even if lifetime broadening is the dominant linewidth mechanism, the motion of the atoms still influences the scattering cross section to the extent of broadening the δ function into a Gaussian.

The second comment pertains to the integrated intensity. If we approximate the multiplicative factor $\omega_1\omega_2^3$ in (3.6) by ω_1^4, we may integrate the resulting expression over ω_2 to obtain the equation

$$\frac{d\sigma(\omega_1)}{d\Omega_2}=\int_{-\infty}^{\infty}d\omega_2\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1^4 A\gamma_N^{-1}\pi^{1/2}}{2\hbar^2c^4a^{1/2}}\exp\left(-\frac{(\omega_0-\omega_1)^2}{4a}\right) \quad . \tag{3.11}$$

Apart from the matrix elements, the integrated cross section is independent of scattering angle. This result is not surprising, since if we integrate again over $d\Omega_2$ we obtain a total scattering cross section which in the absence of nonradiative decay processes (e.g., inelastic collisions) is equal to the absorption cross section. The latter, in the Doppler limit, has the familiar exponential form displayed in Eq. (3.11).

IV. COLLISION BROADENING

In this section we will examine the effects of collisions on the differential cross section. Our first calculation will be appropriate to a stationary target. We will then incorporate the motion of the scatterers. We utilize a very simple model for the collisions. We assume elastic collisions with the atoms of a buffer gas and neglect inelastic effects entirely. We will also neglect collisions between resonant atoms where the nonradiative transfer of excitation may be important. The collisions themselves we will treat in an impact approximation similar to that introduced by Anderson.[7] It is beyond the scope of this paper to discuss in detail the situations where the model is appropriate. Typically it has the same range of validity as the corresponding model for the absorption cross section, i.e., fast collisions and frequencies near ω_0.

Our analysis of the problem parallels the formulation of the impact model which was outlined by Kubo.[8] We assume that the effects of the collisions can be represented by a fluctuating term in the level splitting $\delta\omega_0(t)$. A formal expression for the cross section in the presence of a time-dependent splitting was obtained in II. In the notation of this paper it is written

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2{}^3A}{2\pi c^4\hbar^2}\int_{-\infty}^{\infty}dt\,e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\exp[i(\omega_0-\omega_1)(t'-t'')-\gamma_N(|t'|+|t''|)]$$
$$\times\langle\exp[-i\int_0^{t''}\delta\omega_0(\bar{t})+i\int_t^{t'+t}\delta\omega_0(\bar{t})d\bar{t}]\rangle, \tag{4.1}$$

where the brackets now refer to an average over the fluctuations in $\delta\omega_0$.

In II it was assumed that the frequency fluctuations had a Gaussian spectrum in which case $\langle\exp[\cdots]\rangle$ was replaced by $\exp\langle\frac{1}{2}[\cdots]^2\rangle$. The Gaussian model, while useful in many solid-state problems, is unsatisfactory for the characterization of atomic collisions. As emphasized in Ref. 8, it is the Poisson rather than the Gaussian distribution which is appropriate for collision broadening. In averaging over a Poisson distribution,

$$\langle\exp[-i\int_0^{t''}\delta\omega_0(\bar{t})d\bar{t}+i\int_t^{t+t'}\delta\omega_0(\bar{t})d\bar{t}]\rangle$$

is replaced by the expression

$$\exp\{N\langle\exp[-i\int_0^{t''}\delta\omega_{01}(\bar{t})d\bar{t}+i\int_t^{t'+t}\delta\omega_{01}(\bar{t})d\bar{t}]-1\rangle\}, \tag{4.2}$$

where N is the number of perturbing atoms and $\delta\omega_{01}$ is the frequency fluctuation associated with a single perturber.

The calculation of the average in (4.2) parallels the calculation of the corresponding average in the absorption analysis. In the latter problem the expression analogous to (4.2) is

$$\exp\{N\langle\exp[i\int_0^{t}\delta\omega_{01}(\bar{t})d\bar{t}]-1\rangle\}, \tag{4.3}$$

which after averaging has the form

$$\exp(i\Delta_c t-\gamma_c|t|), \tag{4.4}$$

where Δ_c is the shift in frequency coming from the collisions, and γ_c is the collision width. As shown in Ref. 8, these parameters can be expressed as integrals over the collision cross section.[9] To perform the average in (4.2), it is convenient to separate the calculation into several parts which are determined by the relative magnitudes of t, t', and t''. A straightforward application of the analysis outlined in Ref. 8 leads to the result

$$\exp\{N\langle\exp[-i\int_0^{t''}\delta\omega_{01}(\bar{t})d\bar{t}+i\int_t^{t'+t}\delta\omega_{01}(\bar{t})d\bar{t}]-1\rangle\}$$
$$=\exp[i\Delta_c(t'-t'')-\gamma_c(|t'|+|t''|)-\gamma_c(|t+t'-t''|+|t|-|t'+t|-|t''-t|)]. \tag{4.5}$$

We may verify the correctness of (4.5) for $t=0$. The left-hand side has the value

$$\exp\{N\langle\exp[i\int_{t''}^{t'}\delta\omega_{01}(\bar{t})d\bar{t}]-1\rangle\}, \tag{4.6}$$

while the right-hand side can be written

$$\exp[i\Delta_c(t'-t'')-\gamma_c|t'-t''|], \tag{4.7}$$

in agreement with what would be predicted from (4.3) and (4.4).

An expression for the cross section is obtained by combining (4.1) and (4.5). The triple integral can be evaluated with the help of Eq. (A3) with $\alpha=\omega_2-\omega_1$, $\beta=\omega_0+\Delta_c-\omega_1$, $A=\gamma_c$, $B=\gamma_c$, $C=\gamma_N+\gamma_c$, and $D=-\gamma_c$. The result takes the form

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2{}^3A}{\hbar^2c^4[(\omega_1-\omega_0-\Delta_c)^2+(\gamma_c+\gamma_N)^2]}\left(\delta(\omega_1-\omega_2)+\frac{\gamma_c}{\gamma_N}\frac{(\gamma_c+\gamma_N)/\pi}{(\omega_2-\omega_0-\Delta_c)^2+(\gamma_c+\gamma_N)^2}\right). \tag{4.8}$$

Equation (4.8) is to be compared with Eq. (2.11) of II ($\hbar\omega_0/KT\gg 1$). It is evident that the impact model yields the same result as the Gaussian model when the latter is evaluated in the motional narrowing limit. This is not surprising since both models give a lorentzian shape for the absorption cross section. As noted in II, the two terms in the bracketed factor on the right-hand side of (4.8) characterize the coherent scattering and the resonance fluorescence.

Equation (4.8) was obtained for a stationary target. As a first step in amalgamating the effects of the target motion with the effects of collisions, we may combine the collision broadening with the Doppler analysis of the preceding section. The resulting cross section takes the form

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2{}^3A}{2\pi\hbar^2c^4}\int_{-\infty}^{\infty}dt\,e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\exp\{-(k^2KT/2m)[t^2+(t+t'-t'')^2-2\cos\Theta(t^2+tt'-tt'')]\}$$
$$\times\exp[i(\omega_0+\Delta_c-\omega_1)(t'-t'')-(\gamma_N+\gamma_c)(|t'|+|t''|)]\exp[-\gamma_c(|t+t'-t''|+|t|-|t'+t|-|t''-t|)]. \tag{4.9}$$

There is an important assumption which is implicit in this equation. In obtaining the kinematical factor

$$\exp\{-(k^2KT/2m)[t^2+(t+t'-t'')^2-2\cos\Theta(t^2+tt'-tt'')]\},$$

we have assumed that the atom is moving with uniform velocity. The resulting cross section is then averaged over a Maxwell-Boltzmann distribution. In reality the same collisions which perturb the electronic transitions will also influence the motion of the atoms. However if the resonant atoms are much more massive than the perturbing atoms, the influence of the collisions on the motion of the former is slight. In such a situation (4.9) becomes a reasonable approximation.

In the limit as Δ_c and γ_c approach zero, (4.9) reduces to (3.6). In the opposite limit, where the collision width is much greater than the Doppler width, the motion of the atoms has little effect on the resonance fluorescence, but it does broaden the δ-function in the coherent cross section. The magnitude of this effect can be ascertained by replacing the kinematical factor in (4.9) by its limiting form for $t\gg t'$, t'', an approximation which is appropriate whenever $\gamma_c+\gamma_N\gg\omega_1(KT/mc^2)^{1/2}$. Then we have

$$\delta(\omega_1-\omega_2)\to(2\pi)^{-1}\int_{-\infty}^{\infty}e^{i(\omega_2-\omega_1)t}\exp[-(k^2KT/m)(1-\cos\Theta)t^2]\,dt$$
$$=\frac{1}{2\pi^{1/2}}\frac{\exp[-(\omega_2-\omega_1)^2/(4k^2KT/m)(1-\cos\Theta)]}{[(k^2KT/m)(1-\cos\Theta)]^{1/2}}. \tag{4.10}$$

It is evident that the amount of broadening depends not only on the average speed but also on the scattering angle with the δ function being recovered in the forward scattering limit.

The equations derived in this section were obtained under the assumption that the perturbing collisions were elastic. If inelastic collisions are present as well, they influence the cross section in two ways. First, in (4.8)–(4.10) the natural linewidth γ_N is replaced by $\gamma_N+\gamma_{ci}$, where γ_{ci} is the inelastic collision width. Second, in addition to the resonance fluorescence centered about ω_0, there will also be fluorescence at frequencies ω_a, ω_b, etc., where the levels a, b, ... are the terminating states for inelastic transitions from the resonant level.

The cross sections for the fluorescent transitions are readily derived by means of the following argument. Since the fluorescence is an incoherent process, the cross section for emission from level a is the product of four factors: (1) a factor associated with the probability of absorbing a photon while making a transition to the upper resonant level, (2) a branching ratio which is equal to the fraction of transitions depopulating the resonant level which terminate at level a, (3) a factor proportional to the fraction of transitions from the level a which involve radiative emission terminating at the ground level, and (4) a lorentzian factor characterizing the frequency distribution of the emitted photon. That is, we have

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_a\propto\frac{|\langle 0|\vec{\epsilon}_1\cdot\vec{d}\,|g\rangle|^2(\gamma_N{}^0+\gamma_{ci}{}^0+\gamma_c{}^0)R_{0\to a}}{[(\omega_1-\omega_0-\Delta_c{}^0)^2+(\gamma_N{}^0+\gamma_{ci}{}^0+\gamma_c{}^0)^2](\gamma_{ci}{}^0+\gamma_N{}^0)}$$

$$\times \frac{|\langle g|\vec{\epsilon}_2\cdot\vec{d}\,|a\rangle|^2(\gamma_N{}^a+\gamma_{ci}{}^a+\gamma_c{}^a)}{(\gamma_N{}^a+\gamma_{ci}{}^a)[(\omega_2-\omega_a-\Delta_c{}^a)^2+(\gamma_N{}^a+\gamma_{ci}{}^a+\gamma_c{}^a)^2]} , \tag{4.11}$$

where $R_{0\to a}$ is the transition rate from the resonant level to level a, $\gamma_N{}^a$, $\gamma_{ci}{}^a$, $\gamma_c{}^a$, and $\Delta_c{}^a$ are the natural width, the inelastic width and the elastic width, and shift of a; $\gamma_N{}^0$, $\gamma_{ci}{}^0$, $\gamma_c{}^0$, and $\Delta_c{}^0$ are the corresponding parameters for the resonant level, and g denotes the ground state.

V. GENERALIZATION

The results presented in the preceding sections were obtained from a rather simple model in which we assumed nondegenerate initial and final states and rectilinear motion of the atom as a whole. We wish to generalize our findings to more realistic situations where there are overlapping lines and where there may be changes in velocity resulting from collisions with the perturbers.

Our approach to the more general problem is founded on the assumptions that first, we can represent the effects of the collisions on the transition by a time-development operator having matrix elements between the electronic states of the atom and second, that we can separate the average over the motion of the atoms from the average over the time-development operator. The significance and appropriateness of the first assumption has been discussed by Baranger in connection with the calculation of the absorption lineshape.[10] The second assumption is somewhat more severe, since as noted, collisions which affect the motion generally affect the electronic transitions as well. In way of justification we may say that not infrequently there are situations where over a given time interval only a small fraction of the collisions which perturb the transition also significantly influence the motion. In this limit we may neglect the contribution of the velocity changing collisions to the time-development operator. The velocity changing collisions appear only in the kinematic factor which may then be averaged separately.

We summarize the discussion of the preceding paragraph by presenting the expression for the differential cross section which is obtained when we apply the two approximations to the Kramers-Heisenberg formula

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2{}^3}{2\pi c^4\hbar^2}\int_{-\infty}^{\infty}dt\,e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\langle e^{-i\vec{k}_1\cdot\vec{r}(t'')}e^{i\vec{k}_2\cdot\vec{r}(0)}e^{-i\vec{k}_2\cdot\vec{r}(t)}e^{i\vec{k}_1\cdot\vec{r}(t+t')}\rangle$$

$$\times\frac{1}{N_g}\sum_{\substack{\alpha\beta\\ \gamma\delta\mu}}\sum_{ABCD}e^{-i\omega_1(t'-t'')}\langle\alpha|T(t'')|\mu\rangle\langle\mu|\vec{\epsilon}_1\cdot\vec{d}\,|D\rangle\langle D|T^\dagger(t'')|C\rangle\langle C|\vec{\epsilon}_2\cdot\vec{d}\,|\delta\rangle$$

$$\times\Big\langle\langle\delta|T(t)|\gamma\rangle\langle\gamma|\vec{\epsilon}_2\cdot\vec{d}\,|B\rangle\langle B|T(t')|A\rangle\langle A|\vec{\epsilon}_1\cdot\vec{d}\,|\beta\rangle\langle\beta|T^\dagger(t+t')|\alpha\rangle\Big\rangle_{\text{ave}} . \tag{5.1}$$

Here α, β, ... denote states of the ground manifold, which are assumed to be equally populated with a weighting factor $N_g{}^{-1}$, and A, B, ... denote states of the resonant excited manifold. The symbol $T(t)$ denotes the time development operator for the atom which reduces to $\exp(-iH_0t)$ in the absence of perturbations (H_0 is the electronic part of the free atom Hamiltonian). It is assumed to have no matrix elements between the ground and excited manifold. The subscript ave denotes an average over collisions which perturb the electronic transition.

The calculation of the full cross section even with the approximations embodied in (5.1) appears to be prohibitively complex, apart from the special cases considered previously. A partial solution to the problem is possible however. If we omit the kinematical factor for the moment, we may separate the cross section into its coherent and incoherent parts, a procedure which was discussed in detail in I. The coherent cross section takes the form

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{coh}}=\frac{\omega_1\omega_2{}^3}{2\pi c^4\hbar^2}\int_{-\infty}^{\infty}e^{i(\omega_2-\omega_1)t}dt\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\,e^{-i\omega_1(t'-t'')}$$

$$\times N_g{}^{-1}\Big\langle\sum_{\alpha,\beta}\sum_{A,B}\langle\alpha|\vec{\epsilon}_2\cdot\vec{d}\,|B\rangle\langle B|T(t')|A\rangle\langle A|\vec{\epsilon}_1\cdot\vec{d}\,|\beta\rangle\langle\beta|T^\dagger(t')|\alpha\rangle\Big\rangle_{\text{ave}}$$

$$\times N_g{}^{-1}\Big\langle\sum_{\alpha,\beta}\sum_{A,B}\langle\alpha|\vec{\epsilon}_2\cdot\vec{d}\,|B\rangle\langle B|T(t'')|A\rangle\langle A|\vec{\epsilon}_1\cdot\vec{d}\,|\beta\rangle\langle\beta|T^\dagger(t'')|\alpha\rangle\Big\rangle^*_{\text{ave}} . \tag{5.2}$$

Equation (5.2) can also be written

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{coh}} = (\omega_1/c)^4 |\vec{\epsilon}_2 \cdot \overleftrightarrow{\chi}^{TD}(\omega_1) \cdot \vec{\epsilon}_1|^2 \delta(\omega_1 - \omega_2) , \tag{5.3}$$

where $\overleftrightarrow{\chi}^{TD}(\omega_1)$ is the electric susceptibility of the atom calculated in the time-development approximation

$$\overleftrightarrow{\chi}^{TD}(\omega_1) = \frac{i}{\hbar}\int_{-\infty}^{0} dt' e^{-i\omega_1 t'} N_g^{-1} \left\langle \sum_{\alpha,\beta} \sum_{A,B} \langle\alpha|\vec{d}|B\rangle\langle B|T(t')|A\rangle\langle A|\vec{d}|\beta\rangle\langle\beta|T^\dagger(t')|\alpha\rangle \right\rangle_{\text{ave}} . \tag{5.4}$$

Equation (5.3) is the generalization of the delta function term in (4.8). As shown by (4.10), the motion of the atom has the effect of broadening the delta function. To see how this comes about in the general case, we evaluate the average over the velocities in (5.1) using a Gaussian approximation similar to that employed in calculating neutron scattering cross sections.[11] Thus we write

$$\langle e^{-i\vec{k}_1\cdot\vec{r}(t'')} e^{i\vec{k}_2\cdot\vec{r}(0)} e^{-i\vec{k}_2\cdot\vec{r}(t)} e^{i\vec{k}_1\cdot\vec{r}(t+t')}\rangle = \exp\left[-\frac{1}{2}\left\langle\left(\vec{k}_1\cdot\int_{t''}^{t'+t}\vec{v}(\bar{t})d\bar{t} - \vec{k}_2\cdot\int_0^t \vec{v}(\bar{t})d\bar{t}\right)^2\right\rangle\right]. \tag{5.5}$$

We may combine the results of (5.2) and (5.5) to obtain an expression for what we choose to call the quasi-coherent cross section.[12]

$$\begin{aligned}\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{qua-coh}} &= \frac{\omega_1\omega_2^3}{2\pi c^4}\int_{-\infty}^{\infty} dt\, e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0} dt' \int_{-\infty}^{0} dt'' e^{-i\omega_1(t'-t'')} \\ &\times \exp\left[-\frac{1}{2}\left\langle\left(\vec{k}_1\cdot\int_{t''}^{t'+t}\vec{v}(\bar{t})d\bar{t} - \vec{k}_2\cdot\int_0^t\vec{v}(\bar{t})d\bar{t}\right)^2\right\rangle\right] \\ &\times N_g^{-1}\left\langle\sum_{\alpha,\beta}\sum_{A,B}\langle\alpha|\vec{\epsilon}_2\cdot\vec{d}|B\rangle\langle B|T(t')|A\rangle\langle A|\vec{\epsilon}_1\cdot\vec{d}|\beta\rangle\langle\beta|T^\dagger(t')|\alpha\rangle\right\rangle_{\text{ave}} \\ &\times N_g^{-1}\left\langle\sum_{\alpha,\beta}\sum_{A,B}\langle\alpha|\vec{\epsilon}_2\cdot\vec{d}|B\rangle\langle B|T(t'')|A\rangle\langle A|\vec{\epsilon}_1\cdot\vec{d}|\beta\rangle\langle\beta|T^\dagger(t'')|\alpha\rangle\right\rangle^*_{\text{ave}} .\end{aligned} \tag{5.6}$$

The integrals over t' and t'' in (5.6) have their major contribution from the intervals $-\gamma_c^{-1} \lesssim t', \ t'' \leq 0$, where γ_c is a measure of the collision width. On the other hand, the integral over t has its major contribution from the interval $-\lambda^{-1} \lesssim t \lesssim \lambda^{-1}$, where λ is a measure of the width of the quasi-coherent distribution (λ is on the order of $\omega_1(KT/mc^2)^{1/2}$ for rectilinear motion). If $\gamma_c \gg \lambda$, as in the case when collision broadening is dominant, we may set t' and t'' equal to zero in the kinematical factor in (5.6). As a result we obtain the cross section

$$\begin{aligned}\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{qua-coh}} &= \frac{\omega_1\omega_2^3}{2\pi c^4}|\vec{\epsilon}_2\cdot\overleftrightarrow{\chi}^{TD}(\omega_1)\cdot\vec{\epsilon}_1|^2 \\ &\times \int_{-\infty}^{\infty} dt\, e^{i(\omega_2-\omega_1)t}\exp[-k^2(1-\cos\Theta)\int_0^t\int_0^t \langle V_\parallel(t_1)V_\parallel(t_2)\rangle\, dt_1 dt_2] ,\end{aligned} \tag{5.7}$$

where $V_\parallel$ is the component of velocity along the direction $\vec{k}_1 - \vec{k}_2$.

Equation (5.6) indicates how the motion of the resonant atom broadens the coherent cross section. The width of the distribution is seen to depend on the velocity autocorrelation function $\langle V_\parallel(t_1)V_\parallel(t_2)\rangle$. If $(\omega_2 - \omega_1)^{-1}$ is much less than the mean time between kinetic collisions, we may approximate $\langle V_\parallel(t_1)V_\parallel(t_2)\rangle$ by $\langle V_\parallel^2\rangle$ ($=KT/m$) and thus obtain the Gaussian shape of (4.10). On the other hand, if $(\omega_2 - \omega_1)^{-1}$ is much greater than the mean time between collisions, the diffusion approximation is valid and we may set $\langle V_\parallel(t_1)V_\parallel(t_2)\rangle$ equal to $2\mathfrak{D}\delta(t_1 - t_2)$, where $\mathfrak{D}$ is the diffusion constant. We then have

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{qua-coh}} = \frac{2\omega_1\omega_2^3|\vec{\epsilon}_2\cdot\overleftrightarrow{\chi}^{TD}(\omega_1)\cdot\vec{\epsilon}_1|^2\mathfrak{D}k^2(1-\cos\Theta)}{\pi c^4\{(\omega_2-\omega_1)^2 + [2\mathfrak{D}k^2(1-\cos\Theta]^2\}} , \tag{5.8}$$

in agreement with the quasi-coherent component in (A7).

Two final comments are appropriate here. First, the quasi-coherent cross section characterizes only part of the distribution of scattered radiation. As noted in I the remainder is associated with the fluctuations of the induced dipole moment about its average value. Second, we emphasize that Eq. (5.7) was derived under the assumption that collision broadening is the dominant linewidth mechanism. A model calculation where this assumption is not made is outlined in Appendix A.

VI. INTERFERENCE

In an actual experiment light is scattered from a large number of atoms. If the wavelength of the light is comparable with the inter-atom spacing, the interference between the light scattered by different atoms must be taken into account. In this section we will indicate how the interference affects the intensity of scattered light.

We begin by discussing interference in the collision-dominated limit analyzed in Sec. 5. As noted there and discussed in greater detail in I and II, the single atom cross section can be separated into a coherent and an incoherent component. The coherent component is associated with the ensemble (= time) average of the induced dipole moment, while the incoherent component arises from fluctuations in the induced moment. Such a separation is also possible in the many-atom cross section. If the fluctuations in the induced dipole moments of the different atoms are independent of one another, a reasonable assumption for gases, the incoherent cross section for the ensemble will be the sum of the incoherent cross sections for the various atoms.

The scattering associated with the average of the induced moments will display the effects of interference. In order to assess their importance, it is convenient to examine the integrated (over ω_2) intensity of the coherent scattering. This is easily obtained from Eq. (5.7) if we first, set $\omega_2=\omega_1$ in the factor $\omega_1\omega_2^3$ and second, integrate over ω_2 from minus to plus infinity. The cross section that results can be written

$$\left.\frac{d\sigma(\omega_1)}{d\Omega_2}\right|_{\text{qua-coh}} = \frac{\omega_1}{c^4} N \left|\vec{\epsilon}_2\cdot\overleftrightarrow{\chi}^{TD}(\omega_1)\cdot\vec{\epsilon}_1\right|^2 \left\langle \sum_{j=1}^{N} e^{i(\vec{k}_1-\vec{k}_2)\cdot(\vec{r}_i-\vec{r}_j)}\right\rangle . \tag{6.1}$$

where $\overleftrightarrow{\chi}^{TD}(\omega_1)$ is the susceptibility of a single atom in the time-development approximation. The sum is over the N resonant atoms (nonresonant scattering is neglected). The factor in brackets in (6.1) is the atomic interference function for the resonant component of the gas.[13] Away from the forward direction, this function has a value close to unity. Interference effects are negligible, and the total cross section is the sum of the coherent cross sections for the N resonant atoms.[13] In the forward scattering limit, $\vec{k}_1=\vec{k}_2$, the interference function has the value N and the cross section is factor of N greater than in the absence of interference.

The effect of interference on the ideal gas cross section can be determined in much the same way. Separating the cross section into its coherent and incoherent parts leads to the result

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2} = \frac{AN\omega_1\omega_2^3}{2\pi\hbar^2c^4}\int_{-\infty}^{\infty}dt\, e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\, e^{i(\omega_0-\omega_1)(t'-t'')-\gamma_N(|t'|+|t''|)}$$
$$\times\Big(\langle\exp[-i\vec{k}_1\cdot\vec{v}t''-i\vec{k}_2\cdot\vec{v}t+i\vec{k}_1\cdot\vec{v}(t+t')]\rangle$$
$$+\Big\langle\sum_{j=1}^{N} e^{i(\vec{k}_1-\vec{k}_2)\cdot(\vec{r}_i-\vec{r}_j)}-1\Big\rangle\langle e^{-i\vec{k}_1\cdot\vec{v}t''}\rangle\langle e^{i\vec{k}_2\cdot\vec{v}(t+t')}\rangle\Big). \tag{6.2}$$

With the assumption of complete disorder, as is appropriate for a spatially homogeneous ideal gas, the factor $\langle\sum_{j=1}^{N}\exp[i(\vec{k}_1-\vec{k}_2)\cdot(\vec{r}_i-\vec{r}_j)]-1\rangle$ is zero for $\vec{k}_1$ different from $\vec{k}_2$.[13] Thus we have

$$d^2\sigma(\omega_1)/d\Omega_2 d\omega_2 = N d^2\sigma(\omega_1)/d\Omega_2 d\omega_2\big|_{\text{atom}}, \quad (\vec{k}_1\neq\vec{k}_2), \tag{6.3}$$

where the single-atom cross section is given by (3.6). Thus in a spatially homogeneous ideal gas interference effects vanish except in the forward direction.

VII. CONCLUSION

In the preceding sections we have outlined calculations of the differential cross section characterizing the resonant scattering of light in gases. It is to be noted that the scattering cross section contains much more information about the target than is to be found in the absorption cross section. This is evident, for example, in Eq. (4.8). Were one to integrate the differential cross section over ω_2 and the solid angle, one would obtain an absorption cross section proportional to $[(\omega_1 - \omega_0 - \Delta_C)^2 + (\gamma_C + \gamma_N)^2]^{-1}$. In the absorption cross section it is the sum of the natural width and the collision width which enters, whereas in the scattering cross section both the sum and the ratio of the widths appear. Thus measurements of the scattering cross section permit one to determine, in principle, distinct values for the two widths.

In measurements of the cross section it is important that the incident light be very close to monochromatic. As pointed out in I, if there is a distribution in the frequency of the incident light, the time average of the scattering rate is proportional to the average of the cross section over the distribution. If the distribution is broad, considerable information will be lost in the averaging process. For this reason lasers are especially promising as sources.

It should also be mentioned that the theory applies with minor modifications to the resonant scattering of gamma rays by nuclei. Here the effects of collisions on the transition are negligible, and the cross section is determined primarily by the intrinsic lifetime and the kinematics. The modifications that are necessary come about because of the recoil of the atom. The effect of the recoil on the ideal-gas cross section is discussed in Appendix B.

APPENDIX A. INTEGRAL EVALUATION AND MODEL CALCULATION

Here we outline the evaluation of a triple integral which arises in the calculation of the differential cross section. The integral I is written

$$I = \int_{-\infty}^{\infty} dt\, e^{i\alpha t} \int_{-\infty}^{0} dt' \int_{-\infty}^{0} dt''\, e^{i\beta(t'-t'')} \exp[-A|t| - B|t+t'-t''| - C(|t'| + |t''|) - D(|t+t'| + |t''-t|)], \tag{A1}$$

where α, β, A, B, C, and D are real. As a first step we rewrite I in the form

$$I = 2\,\mathrm{Re}\left(\int_0^{\infty} e^{i\alpha t} \int_{-\infty}^{0} dt' \int_{-\infty}^{0} dt''\, e^{i\beta(t'-t'')} \exp[\cdots] \right), \tag{A2}$$

where Re means the real part of the expression in parentheses. The integration in (A2) is most conveniently performed by first integrating over t' and t'' and finally over t. As a result we obtain the expression

$$\begin{aligned} I = 2\,\mathrm{Re}\{&\tfrac{1}{2}(C+D)^{-1}(A+C+D-i\alpha+i\beta)^{-1}[(B+C+D+i\beta)^{-1} + (B-C-D-i\beta)^{-1}] \\ &+ (B+C+D-i\beta)^{-1}(A+C+D-i\alpha+i\beta)^{-1}[(B-C+D-i\beta)^{-1} - (B-C-D-i\beta)^{-1}] \\ &- (B+C+D-i\beta)^{-1}(B-C+D-i\beta)^{-1}(A+B+2D-i\alpha)^{-1}\}. \end{aligned} \tag{A3}$$

As an application of (A3) we evaluate the differential cross section of an atom which is perturbed by collisions in the manner outlined in Sec. 4, and whose velocity autocorrelation function has the form

$$\langle V_i(t_1) V_j(t_2) \rangle = 2\mathfrak{D}\delta_{ij}\delta(t_1 - t_2), \quad (i, j = x, y, z), \tag{A4}$$

where $\mathfrak{D}$ is a diffusion constant. The cross section that results can be written[14]

$$\begin{aligned} \frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2} = \frac{\omega_1 \omega_2^3 A}{2\pi\hbar^2 c^4} &\int_{-\infty}^{\infty} e^{i(\omega_2-\omega_1)t} dt \int_{-\infty}^{0} dt' \int_{-\infty}^{0} dt''\, e^{i(\omega_0+\Delta_c-\omega_1)(t'-t'')} \\ &\times \exp\{-\mathfrak{D}k^2[|t+t'-t''| + |t| - \cos\Theta(|t-t''| + |t'+t| - |t'| - |t''|)]\} \\ &\times \exp[-(\gamma_N+\gamma_c)(|t'| + |t''|) - \gamma_c(|t+t'-t''|) + |t| - |t'+t| - |t''-t|)] \,. \end{aligned} \tag{A5}$$

The integral in (A5) is easily evaluated with the help of (A3). Since the resulting expression is rather cumbersome, we consider only the limiting cases $\mathfrak{D}k^2 \gg \gamma_N \gg \gamma_C$ and $\gamma_C \gg \mathfrak{D}k^2$, γ_N. In the limit $\mathfrak{D}k^2 \gg \gamma_N \gg \gamma_C$ we have

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2} = \frac{\omega_1 \omega_2^3 A \gamma_N^{-1}}{2\pi\hbar^2 c^4}\,\mathrm{Re}\left(\frac{1}{Dk^2 - i(\omega_2-\omega_0)}\right)\left(\frac{1}{Dk^2 + i(\omega_0-\omega_1)} + \frac{1}{Dk^2 - i(\omega_0-\omega_1)}\right)$$

$$=\frac{\omega_1\omega_2{}^3A\gamma_N{}^{-1}}{\pi\hbar^2c^4}\left(\frac{\mathfrak{D}k^2}{(\mathfrak{D}k^2)^2+(\omega_2-\omega_0)^2}\right)\left(\frac{\mathfrak{D}k^2}{(\mathfrak{D}k^2)^2+(\omega_1-\omega_0)^2}\right). \tag{A6}$$

It is apparent that the diffusive motion of the atom has destroyed the coherence between the incident and scattered wave so that the cross section becomes the product of two lorentzians, one characterizing absorption and the other emission.

In the limit $\gamma_c \gg \mathfrak{D}k^2$, γ_N we obtain the result

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}=\frac{\omega_1\omega_2{}^3}{\pi\hbar^2c^4[(\omega_1-\omega_0-\Delta_c)^2+\gamma_c{}^2]}\left(\frac{2\mathfrak{D}k^2(1-\cos\Theta)}{(\omega_2-\omega_1)^2+[2\mathfrak{D}k^2(1-\cos\Theta)]^2}+\frac{\gamma_c}{\gamma_N}\frac{\gamma_c}{(\omega_0+\Delta_c-\omega_2)^2+\gamma_c{}^2}\right). \tag{A7}$$

In this limit the only effect the motion has on the cross section is to broaden the delta function into a Lorentzian, in agreement with the results of Sec. 5.

APPENDIX B. THE EFFECT OF RECOIL ON THE IDEAL-GAS CROSS SECTION

In order to incorporate the effects of target recoil on the cross section for scattering from an ideal gas, it is necessary to treat the vector $\vec{r}(t)$ appearing in (3.1) as a quantum-mechanical operator whose evolution is determined by the Hamiltonian $p^2/2m$. We then have

$$\exp[-i\vec{k}_1\cdot\vec{r}(t'')]\exp[i\vec{k}_2\cdot\vec{r}(0)]\exp[-i\vec{k}_2\cdot\vec{r}(t)]\exp[i\vec{k}_1\cdot\vec{r}(t+t')]$$

$$=\exp(ip^2t''/2m\hbar)\exp(-i\vec{k}_1\cdot\vec{r})\exp(-ip^2t''/2m\hbar)\exp(i\vec{k}_2\cdot\vec{r})\exp(ip^2t/2m\hbar)\exp(-i\vec{k}_2\cdot\vec{r})$$

$$\times\exp(-ip^2t/2m\hbar)\exp[ip^2(t+t')/2m\hbar]\exp(i\vec{k}_1\cdot\vec{r})\exp[-ip^2(t+t')/2m\hbar]\;. \tag{B1}$$

If we make use of the operator identity

$$\exp(-i\vec{k}\cdot\vec{r})f(\vec{p}\,\vec{r}),\;\exp(i\vec{k}\cdot\vec{r})=f(\vec{p}+\hbar\vec{k},\vec{r})\;, \tag{B2}$$

with $f(\vec{p},\vec{r})$ being a function of momentum and position operators, we find that (B1) can be written

$$\exp[-i\vec{k}_1\cdot\vec{r}(t'')]\exp[i\vec{k}_2\cdot\vec{r}(0)]\exp[-i\vec{k}_2\cdot\vec{r}(t)]\exp[i\vec{k}_1\cdot\vec{r}(t+t')]$$

$$=\exp[i\vec{p}\cdot\vec{k}_1(t+t'-t'')/m-i\vec{p}\cdot\vec{k}_2t/m]\exp[i\hbar(\vec{k}_1-\vec{k}_2)^2t/2m+i\hbar k_1{}^2(t'-t'')/2m]. \tag{B3}$$

The first factor in (B3) is the result obtained when recoil effects are neglected. The second factor gives rise to the frequency shifts associated with the recoil. These are negligible for electronic transitions, but may be important in γ-ray scattering. If we replace the momentum operators by the classical variables and subsequently average over a Maxwell-Boltzmann distribution, we obtain an equation similar to (3.6) but with ω_2 replaced by $\omega_2+\hbar(\vec{k}_1-\vec{k}_2)^2/2m$ and ω_0 by $\omega_0+\hbar k_1{}^2/2m$.

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$$\int_a^b\int_c^d dx_1dx_2\delta(x_1-x_2)$$
$$=\tfrac{1}{2}[|d-a|+|c-b|-|d-b|-|c-a|].$$