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COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in The Physical Review or Physical Review Letters; (2) addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.

Generalization of Resonant Scattering Calculations

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Previous calculations of the differential cross section for the resonant scattering of monochromatic light in gases are generalized. The connection between the integrated and coherent cross sections and the absorption line shape is displayed.

In a recent paper,[1] we have outlined a calculation of the differential cross section characterizing the resonant scattering of light by the atoms in a gas. In Ref. 1, the collisions of the scattering atom with its perturbers were treated in the impact approximation. The purpose of this paper is to generalize the theory to make it applicable to a broader spectrum of experimental configurations. We do this by rewriting the cross section in such a way as to specifically display its dependence on the potential characterizing the interaction between the scattering atom and its perturbers. In addition, we derive expressions for the integrated and coherent cross sections which may be useful in making comparisons between experiment and theory.[2]

The starting point is Eq. (4.1) of Ref. 1, as modified by Eq. (4.2) of the same paper.

$$\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2} = \frac{\omega_1\omega_2{}^3 A}{2\pi\hbar^2 c^4}\int_{-\infty}^{\infty} dt\, e^{i(\omega_2-\omega_1)t}\int_{-\infty}^{0} dt'\int_{-\infty}^{0} dt''\exp[i(\omega_0-\omega_1)(t'-t'')+\gamma(t'+t'')]$$
$$\times \exp\{N\langle \exp[-i\int_0^{t''}\delta\omega_{01}(\bar{t})d\bar{t}+i\int_t^{t+t'}\delta\omega_{01}(\bar{t})d\bar{t}]-1\rangle\}\,. \quad (1)$$

Here, A denotes a product of the squares of the matrix elements of the dipole moment operator, ω_0 is the resonant frequency, ω_1 and ω_2 are the frequencies of the incoming and outgoing photons, γ is the lifetime in the upper state as determined by both radiative and nonradiative processes, $\delta\omega_{01}(t)$ is the frequency fluctuation associated with a single perturber, and N is the number of perturbers. If the potential energy associated with the interaction between the perturber and the resonant scatterer is written $v(r_{12})$ then the average appearing in (1), when written explicitly, takes the form[3]

$$\langle \exp[-i\int_0^t \delta\omega_{01}(\bar{t})d\bar{t} + i\int_t^{t+t'} \delta\omega_{01}(\bar{t})d\bar{t}] - 1\rangle = \frac{2\pi}{V}\int_0^\infty \rho\, d\rho \int_{-\infty}^{\infty} dx_0$$
$$\times\left[\exp\left(-i\int_0^{t''} \frac{v}{\hbar}\{[\rho^2+(x_0+\langle s\rangle\bar{t})^2]^{1/2}\}d\bar{t} + i\int_t^{t+t'} \frac{v}{\hbar}\{[\rho^2+(x_0+\langle s\rangle\bar{t})^2]^{1/2}\}d\bar{t}\right) - 1\right], \tag{2}$$

where $\langle s\rangle$ is the average speed of the perturbers relative to the scattering atoms, and V is the volume of the system.

Since the frequency of the scattered photon, ω_2, is close to ω_1, we can obtain an expression for the frequency-integrated intensity by replacing $\omega_1\omega_2^3$ by ω_1^4 in Eq. (1) and then integrating over ω_2 from minus infinity to plus infinity. We obtain the result

$$\frac{d\sigma(\omega_1)}{d\Omega_2} = \frac{\omega_1^4 A}{\hbar^2 c^4}\int_{-\infty}^0 dt' \int_{-\infty}^0 dt'' \exp[i(\omega_0-\omega_1)(t'-t'')+\gamma(t'+t'')]\exp\{N\langle \exp[i\int_{t''}^{t'} \delta\omega_{01}(\bar{t})d\bar{t}] - 1\rangle\}. \tag{3}$$

After averaging, the bracketed factor in (3) is a function only of the difference $(t'-t'')$. Because of this we introduce the variables $x=-(t'+t'')$ and $y=(t'-t'')$, and rewrite the double integral in (3)

$$\tfrac{1}{2}\int_0^\infty e^{-\gamma x}dx\int_{-x}^{x} dy\, e^{i(\omega_0-\omega_1)y}\exp\{N\langle\exp[i\int_0^y \delta\omega_{01}(\bar{t})d\bar{t}] - 1\rangle\}.$$

Integrating this expression by parts leads to the result

$$\frac{d\sigma(\omega_1)}{d\Omega_2} = \frac{\omega_1^4\pi|\langle i|\vec{\epsilon}_1\cdot\vec{d}|f\rangle|^2 f(\omega_1)|\langle i|\vec{\epsilon}_2\cdot\vec{d}|f\rangle|^2}{\hbar^2 c^4\gamma}, \tag{4}$$

where we have written A explicitly as a product of matrix elements.[4] Here $f(\omega_1)$ is the normalized lineshape function

$$f(\omega_1) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx\, e^{i(\omega_0-\omega_1)x-\gamma|x|}\exp\{N\langle\exp[i\int_0^x \delta\omega_{01}(\bar{t})d\bar{t}] - 1\rangle\}, \tag{5}$$

with $\int_{-\infty}^{\infty} du\, f(u) = 1.$ (6)

Equation (4) has a simple physical interpretation. The factor $|\langle i|\vec{\epsilon}_1\cdot\vec{d}|f\rangle|^2 f(\omega_1)$ is a measure of the probability that a photon is absorbed, while $|\langle i|\vec{\epsilon}_2\cdot\vec{d}|f\rangle|^2/\gamma$ is a measure of the probability that the atom in the upper state returns to the ground state by emitting a photon.[5]

As noted previously,[6] the cross section for phase coherent scattering is obtained from the ensemble average of the induced dipole moment operator. In the present analysis it takes the form

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{coh}} = \frac{\delta(\omega_1-\omega_2)\omega_1^4 A}{\hbar^2 c^4}\left|\int_{-\infty}^0 dt'\, e^{i(\omega_0-\omega_1)t'+\gamma t'}\exp\{N\langle\exp[i\int_0^{t'} \delta\omega_{01}(\bar{t})d\bar{t}] - 1\rangle\}\right|^2. \tag{7}$$

By first introducing the unit step function and then writing $\theta(x)$ as an integral, i.e.,

$\theta(x) = 1, \quad x>0; \quad \theta(x)=0, \quad x<0,$

$$\theta(x) = (1/2\pi i)\int_{-\infty}^{\infty} du\, e^{iux}/(u-i\epsilon), \tag{8}$$

where the limit $\epsilon\to 0+$ is understood, we can rewrite (7) as follows:

$$\left.\frac{d^2\sigma(\omega_1)}{d\Omega_2 d\omega_2}\right|_{\text{coh}} = \frac{\delta(\omega_1-\omega_2)\omega_1^4 A\pi^2}{\hbar^2 c^4}\left[f(\omega_1)^2 + \left(\frac{P}{\pi}\int_{-\infty}^{\infty}\frac{du\, f(u)}{u-\omega_1}\right)^2\right]. \tag{9}$$

In obtaining (9), we have made use of the symbolic identity

$$\lim_{\epsilon \to 0} 1/(\omega - i\epsilon) = P/\omega + i\pi\delta(\omega), \tag{10}$$

where P denotes the principal value. The results displayed in Eqs. (4) and (9) are the appropriate generalizations of the findings reported in Sec. 4 of Ref. 1. Moreover, the functional dependence of the coherent cross section on $f(\omega_1)$ is indicative of the fact that the real and imaginary parts of the electric susceptibility are connected by Kramers-Kronig relations.[7]

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[4]The notation for the matrix elements is the same as in Ref. 1.

[5]A result similar to Eq. (4) is obtained if the target atoms are in motion provided $f(\omega_1)$ is interpreted as a line-shape function which folds in both Doppler and collision broadening.

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[7]The relationship between the coherent cross section and the electric susceptibility tensor is discussed in Ref. 6.

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Some Remarks on Projection Operators and Theories of Dissociative Attachment*

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A difficulty recently pointed out in O'Malley's theory for dissociative attachment can be removed by employing the truncated diagonalization method.

I. INTRODUCTION

The theory of dissociative attachment presented by O'Malley[1] seems particularly convenient for many applications. Recently, Chen and Mittleman[2] pointed out a difficulty which occurs in this theory and proposed an alternate procedure. It is the purpose of this paper, first, to remove the difficulty in O'Malley's theory, and then, to make an observation about Chen and Mittleman's procedure.

The reaction considered is

$$AB + e \to A + B^-.$$

The process is envisioned as the approach of an electron to a stable diatomic molecule with the formation of an unstable AB^- ion. The AB^- ion can then either eject an electron and the system returns to reactants, or the AB^- can dissociate to an A atom and a B^- ion. (Only reactions are considered in which B^- is stable with respect to ejecting an electron.) If this mechanism is valid and if only one negative-ion electronic state is involved, a curve crossing – between the neutral and ionic potential curves – must occur in some sense. This follows, since at the initial internuclear separation when AB^- is formed, this ion is unstable with respect to AB, and at the final internuclear separation the system is stable.

By considering the AB^- curve as representing the eigenenergy, not of the full electronic Hamiltonian but as an eigenenergy of a projected electronic Hamiltonian, O'Malley arrives at an ionic curve which can freely cross the $AB + e$ curve.[1,3]

It is important to note that from this point of view, the AB^- curve only partially characterizes the resonance. The wave function which belongs with this curve is one of possibly many zero-order solutions of the electronic wave equation which form an expansion basis for the final solution. By means of such a basis of electronic wave functions parametrically depending on nuclear coordinates, a coupled set of partial dif-