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Semiclassical and Classical Spectrum in the Adiabatic Theory of Pressure Broadening

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The semiclassical spectrum, defined by use of WKB wave functions, and the classical expression of the spectrum are interpreted in terms of Feynman amplitudes. The radiative electronic transition may be considered to occur instantaneously, and the different times at which it can occur define different "paths" from initial to final state. During a collision of the radiating atom with a perturbing atom, the electronic transition occurs preferably when the relative distance between the two atoms is such that their relative velocity is conserved in the transition (Franck-Condon principle). In a given collision, there are several such preferred transition times which define as many preferred paths. Interference between these paths can result in interference patterns in the spectrum. In general, an interference structure, associated with the repulsive part of the interatomic potential difference, will appear in the violet wing of the spectral line. This forms a highly plausible explanation for the violet satellites observed in the spectrum of various gas mixtures. Not much regarding the shape of the interference structure can, in general, be deduced outside of numerical computations; nevertheless, the general dependence of the position of the violet satellites on parameters such as temperature, reduced mass, and size of the repulsive core of the potential difference can be inferred in a rough manner, and qualitative agreement with experiment be obtained.

I. INTRODUCTION

In recent years, much work has been done in formulating and interpreting the semiclassical theory of scattering phenomena,[1] which is derived from the quantum theory by use of the WKB approximation, or more generally via Feynman's formulation of quantum mechanics.[2] In this paper, we define and interpret the pressure-broadening analog of semiclassical scattering theory, and contrast it with the classical theory of pressure broadening. We restrict ourselves to the adiabatic theory of pressure effects.

The semiclassical spectrum shall be defined by the introduction of WKB wave functions in the quantum-mechanical expression of the spectrum. This approximation was made long ago by Jablonski[3]; however, his theory is generally referred to as a quantum-mechanical theory as opposed to classical path theories in which the translational motion of the atoms is treated classically.[4,5] But WKB wave functions imply classical trajectories, and Jablonski's theory is really a classical path theory. What distinguishes it, or equivalently the semiclassical theory, from the usual classical path theories is that in the latter, the influence of the electronic transition on the nuclear trajectories is neglected; the resulting spectrum is formally identical to that radiated by a classical charged oscillator of frequency and amplitude of oscillation modulated due to the influence of the perturbing atoms. This may therefore be termed the (fully) classical spectrum. The semiclassical spectrum is so called because, even though the trajectories are classical, the notion of an electronic transition, which is of purely quantum nature, is *explicitly* contained in its mathematical expression.

The semiclassical and classical expressions of the spectrum differ more by their external aspect, which allows one to be *interpreted* classically but not the other, than by their fundamental structure. In both cases, the spectrum is constructed in the manner familiar in Feynman's interpretation of quantum mechanics[2]: It is the absolute square of a sum of amplitudes (path integral), each associated with a possible manner (or path) for the system to pass from initial to final states; this is summed over final states and averaged over initial states. The semiclassical differential scattering cross section is constructed in the same way.[1] Moreover, the sum over amplitudes, or path integral, in the spectrum and that entering the scattering cross section are very similar in form; as a consequence, the special scattering effects which are directly related to the form of the path integral, namely, the rainbow and interference effects,[1] have analogs in the spectrum. The analog of the rainbow effect has been known for a long time: It is a statistical effect whereby an extremum (e.g., the minimum in a Lennard-Jones type of interaction) in the interatomic potential difference results in a sharp maximum in the spectrum.[6] This effect is responsible[7] for the red satellite observed in the spectrum of various gas mixtures,[4] in particular alkali–noble-gas mixtures.[8] The interference effect is less familiar in pressure-broadening theory; it will, in general, result in an interference structure in the violet wing of a pressure-broadened line, and it constitutes a highly plausible explanation for the violet satellites that appear in the spectrum of various gas mixtures.[4,8] It is the same interference effect which accounts for the oscillatory aspect of the spectrum when the initial potential has a deep attractive well above the repulsive part of the final potential curve, as discussed by Coolidge *et al.*[9] for bound-continuum emission and by Mies and Smith[10] for continuum-continuum emission. In this case, the spectrum somewhat "reflects" the nodal structure of the translational wave function above the well. For this reason, the interference pattern appeared to be a purely quantum-mechanical effect not to be expected in classical pressure-broadening theory. But the interference occurs equally well in the classical spectrum, and it is, in general, easier to discuss in that context.

Recently, Takeo[11] has made a numerical calculation of the classical spectrum with a Lennard-Jones interaction; in his results there appear one red satellite and two violet satellites, in qualitative agreement with many experimental observations.[4,8] Though it is extremely satisfying to know that the theory does yield such features, it is useful to have a simple understanding of why they are obtained and what are the basic mechanisms responsible for them. Margenau's statistical approximation[12,13] together with its "rainbow effect" provides such an understanding as far as the red satellite is concerned.[7] Our discussion of the interference effect allows us to understand the formation of violet satellites in the classical spectrum and also to infer the general dependence of their position on parameters such as temperature, reduced mass, and size of the repulsive core of the interatomic potential difference, in qualitative agreement with experiment.

In Sec. II, the basic quantities are defined and the quantum-mechanical expression for the spectrum is written down. In Sec. III, the semiclassical spectrum is defined and interpreted in terms of Feynman amplitudes; the classical spectrum is derived and interpreted in Sec. IV. Finally, in Sec. V, the rainbow and interference effects are discussed, and the latter is used to understand qualitatively some general properties of violet satellites.

II. BASIC EXPRESSIONS: QUANTUM-MECHANICAL SPECTRUM

Let us consider an optically active atom, the radiator, immersed in a gas of other atoms, the perturbers. Let $U_e(r)$ be the interatomic potential, calculated via the Born-Oppenheimer approximation, acting between the radiator and a perturber when the former is in the electronic state e; r is the distance separating the two atoms (spherical symmetry is assumed). We shall denote by $(4\omega^4/3c^3)\,I(\omega)$ (c is the velocity of light) the power radiated at the frequency ω as a result of radiative transitions from initial electronic state i to final state f, to which correspond the respective potentials $U_i(r)$ and $U_f(r)$. The transition energy depends on the translational states of the atoms before and after the transition, which results in a spreading of the radiated frequencies.

At perturber densities sufficiently low that (almost) only binary collisions occur, the wings of the spectrum $I(\omega)$ are described by the intensity distribution $J(\omega)$ radiated if only one perturber is present[3]; more generally, the full spectrum $I(\omega)$ is usually expressed[4,5,14] (following a set of simplifying assumptions) as the Nth convolution power of $J(\omega)$, where N is the total number of perturbers. For our purposes, it is therefore sufficient to consider only the one-perturber distribution $J(\omega)$; this is[3] (units are chosen such that $\hbar = 1$, and constant factors are neglected)

$$J(\omega) = \int_0^\infty dk_i\,\rho(\epsilon_i) \sum\nolimits_l (2l+1) \int_0^\infty dk_f \left| \langle \psi^l_{k_f} | D | \psi^l_{k_i} \rangle \right|^2 \times \delta(\pm\omega - \epsilon_f + \epsilon_i) \,. \quad (2.1)$$

Here ω is the frequency measured relative to the unperturbed line, that is, relative to the energy separating the electronic states i and f of the isolated radiator; the plus and minus signs correspond to absorption and emission, respectively; $D(r)$ is the matrix element of the dipole moment operator between initial and final electronic states when the perturber is (fixed) at a distance r from the radiator; $\psi^l_{k_e}$ $(e = i, f)$ are radial wave functions of the radiator-perturber couple, corresponding to electronic state e, and for angular momentum l and translational energy $\epsilon_e = k_e^2/2m$, m being the reduced mass; thus, the ψ's are solutions of the Schrödinger equation

$$\left(\frac{d^2}{dr^2} + k_e^2(r;\epsilon_e, l) \right) \psi^l_{k_e}(r) = 0 \,,$$

where the wave number

$$k_e(r;\epsilon_e, l) \equiv (2m)^{1/2} [\epsilon_e - U_e(r) - l(l+1)/2mr^2]^{1/2} \,, \quad (2.2)$$

and $\rho(\epsilon_i)$ are the statistical weights for the initial translational states $\psi^l_{k_i}$.

Equation (2.1) is analogous to the spectrum radiated by a diatomic molecule, with the difference that in the latter continuum-continuum transitions are excluded; for simplicity, we consider only continuum-continuum transitions, but the inclusion of bound states is straightforward and our discussion of the semiclassical spectrum covers that case also, provided obvious modifications are made. For definiteness, only absorption shall be considered.

III. SEMICLASSICAL SPECTRUM

The semiclassical spectrum is obtained by substituting in the quantum-mechanical spectrum (2.1) WKB wave functions of which only the parts covering classically accessible regions are retained, namely,

$$\psi^{l}_{k_e\,\mathrm{WKB}}(r) = [k_e/k_e(r;\epsilon_e,l)]^{1/2} \times\cos\Big[\int_{b_e(\epsilon_e,l)}^{r} dr'\,k_e(r';\epsilon_e,l)+\tfrac{1}{4}\pi\Big]; \tag{3.1}$$

$k_e(r;\epsilon_e,l)$, defined in Eq. (2.2), is the radial component of the classical momentum at r, and $b_e(\epsilon_e,l)$ is the classical turning point defined by

$$k_e(b_e;\epsilon_e,l)=0\ . \tag{3.2}$$

In Feynman's interpretation of quantum mechanics,[2] a probability amplitude is associated with each possible manner, or path, for a system to pass from a given initial state to a given final state. The total transition amplitude is the sum of the amplitudes corresponding to all possible paths connecting the initial and final states; the transition probability is equal to the absolute square of that sum. By stationary phase integration, the sum over all paths is reduced to the sum over only the *classical* paths connecting the two states; this is usually equivalent to the use of WKB wave functions and defines the semiclassical approximation in general.[2]

For instance, in potential scattering, the initial and final states for constructing the differential cross section are, respectively, defined by the incident and outgoing velocities (i.e., energy and direction) of the beam particle; the classical trajectories, for a given incident velocity, are uniquely determined by the angular momentum, or equivalently by the impact parameter. The semiclassical amplitude for scattering in a given angle is, therefore, expressed as the sum over impact parameters of the amplitudes associated with classical trajectories having the same deflection angle.[1]

In our case we have an analogous situation, with the main difference that during a collision of the perturber with the radiator, the latter may suffer a radiative electronic transition, which changes the interatomic potential; also, the initial and final states are not specified in the same manner as in potential scattering. The initial and final states, for constructing the intensity radiated at the frequency ω, are specified by (i) the electronic states of the radiator; (ii) the initial and final states of the radiation field which differ by a photon of frequency ω; (iii) the angular momentum of the perturber, which is conserved throughout (the radiator is assumed fixed in space to simplify the discussion); and (iv) the initial translational energy ϵ_i of the perturber, the final energy ϵ_f being determined by energy conservation: $\epsilon_f=\epsilon_i+\omega$.

A typical path connecting the states (i,ϵ_i,l) and (f,ϵ_f,l) is as follows: The perturber travels from infinity up to a distance r from the radiator, following a classical trajectory determined by ϵ_i, l, and the potential $U_i(r)$; when the perturber is at r, the electronic transition $i\to f$ occurs (instantaneously), and the perturber then follows a trajectory determined by ϵ_f, l, and the potential $U_f(r)$, and returns to infinity. The amplitude associated with such a path is equal to the product of three amplitudes: the amplitude for coming from infinity to r, the amplitude $T_{i\to f}(r)$ for the electronic transition to occur at r, and the amplitude for returning from r to infinity.

We shall denote by $\langle r_1\to r_2\rangle_e$ the amplitude associated with the motion of the perturber from r_1 to r_2 along the classical trajectory determined by $U_e(r)$, ϵ_e, and l, provided r_1 and r_2 are on the same side of the turning point b_e; if not, that is, if the perturber passes through b_e in going from r_1 to r_2, then we write the amplitude as $\langle r_1\to b_e\to r_2\rangle_e$. The amplitude $\langle r_1\to r_2\rangle_e$ has a phase[2] equal to the classical action from r_1 to r_2:

$$\langle r_1\to r_2\rangle_e \sim \exp\Big[i\,\Big|\int_{r_1}^{r_2} dr\,k_e(r)\Big|\Big] \tag{3.3}$$

(the dependences on ϵ_e and l shall no longer be written explicitly when obvious). If r_3 lies between r_1 and r_2, we have the relation

$$\langle r_1\to r_2\rangle = \langle r_1\to r_3\rangle\langle r_3\to r_2\rangle\ . \tag{3.4}$$

However, if the perturber passes through the turning point b in going from r_1 to r_2, an extra phase factor $e^{i\pi/2}$ is picked up, that is, $e^{i\pi/2}$ is the amplitude associated with passing through a turning point[15]; thus we have

$$\begin{aligned}\langle r_1\to b\to r_2\rangle &= \langle r_1\to b\rangle\, e^{i\pi/2}\langle b\to r_2\rangle\\ &= \exp\Big[i\int_b^{r_1} k(r)\,dr+\tfrac{1}{2}i\pi+i\int_b^{r_2} k(r)\,dr\Big].\end{aligned} \tag{3.5}$$

The phase factor $e^{i\pi/2}$ is a direct consequence of the fact that quantum mechanically there is some barrier penetration at the turning point.

Let us write for instance the amplitude for the perturber to be at r; this is

$$A(r) = (\langle\infty\to r\rangle + \langle\infty\to b\to r\rangle)\,[k/k(r)]^{1/2}, \tag{3.6}$$

that is, the total amplitude for coming from infinity to r, both directly and after being reflected at the turning point, multiplied by the factor $[k/k(r)]^{1/2}$ which, when squared, measures the relative time spent at r [$k(r)/m$ is the velocity at r] and might be called the amplitude for staying at r. Now we can write, according to (3.4),

$$\langle\infty\to r\rangle=\langle\infty\to b\rangle\langle r\to b\rangle^{-1}\ ;$$

Eq. (3.6) then becomes

$$A(r)=\langle\infty\to b\rangle(\langle r\to b\rangle^{-1}+e^{i\pi/2}\langle b\to r\rangle)[k/k(r)]^{1/2}$$
$$=\langle\infty\to b\rangle 2e^{i\pi/4}\psi_{\text{WKB}}(r)\ .$$

Thus the semiclassical amplitude to be at r is equal (up to a constant factor) to the WKB wave function, and the nodal structure of $|\psi(r)|^2$, which results from the interference between incident and reflected waves, may also be interpreted as the result of interference between amplitudes associated with the two classical paths available to the perturber for reaching r.

Let us now construct the amplitudes associated with different paths connecting the initial state (i, ϵ_i, l) and the final state (f, ϵ_f, l). Different paths are distinguished by the value of r at which the electronic transition occurs and also by the *signs* of the radial velocity immediately before and after the transition. We distinguish four cases: In the first two, the electronic transition occurs before the perturber has reached the turning point b_i, so that the radial velocity immediately before the transition is $\dot{r}=-k_i(r)/m$ (a dot over a quantity shall always indicate differentiation with respect to time); immediately after the transition, the perturber is still at r, but its radial velocity has been changed to either (a) $\dot{r}=-k_f(r)/m$, in which case the perturber will pass through the turning point b_f before heading to infinity, or (b) $\dot{r}=+k_f(r)/m$; that is, the sign of the radial velocity has been reversed, and the perturber heads directly to infinity.

The associated amplitudes are

$$\text{(a)}\ \langle\infty\to r\rangle_i\, T_{i\to f}(r)\,\langle r\to b_f\to\infty\rangle_f\ ,$$

$$\text{(b)}\ \langle\infty\to r\rangle_i\, T_{i\to f}(r)\,\langle r\to\infty\rangle_f\ ,$$

where $T_{i\to f}(r)$ is the amplitude for undergoing the electronic transition at r. In the third and fourth cases, the electronic transition occurs after the perturber has gone through b_i, that is, when it is on its way back to infinity and its radial velocity is $+k_i(r)/m$; again, the radial velocity immediately after the transition can be either (c) outgoing, $\dot{r}=+k_f(r)/m$, or (d) incoming and equal to $-k_f(r)/m$. The corresponding amplitudes are

$$\text{(c)}\ \langle\infty\to b_i\to r\rangle_i\, T_{i\to f}(r)\,\langle r\to\infty\rangle_f\ ,$$

$$\text{(d)}\ \langle\infty\to b_i\to r\rangle_i\, T_{i\to f}(r)\,\langle r\to b_f\to\infty\rangle_f .$$

We make use of the relations

$$\langle\infty\to r\rangle_i=\langle\infty\to b_i\rangle_i\langle r\to b_i\rangle_i^{-1}\ ,$$

$$\langle\infty\to b_i\to r\rangle_i=\langle\infty\to b_i\rangle_i e^{i\pi/2}\langle b_i\to r\rangle_i\ ,$$

$$\langle r\to b_f\to\infty\rangle_f=\langle r\to b_f\rangle_f e^{i\pi/2}\langle b_f\to\infty\rangle_f\ ,$$

$$\langle r\to\infty\rangle_f=\langle b_f\to r\rangle_f^{-1}\langle b_f\to\infty\rangle_f\ ,$$

and drop the constant phase factor $\langle\infty\to b_i\rangle_i\langle b_f\to\infty\rangle_f$ common to all amplitudes. We further express the amplitudes $\langle b_e\to r\rangle_e$ by means of (3.3) and the amplitudes (a)–(d) take the form

$$T_{i\to f}(r)\exp\Big[i\int_{b_i}^{r}(\pm)k_i(r')\,dr'-i\int_{b_f}^{r}(\pm)k_f(r')\,dr'+\tfrac{1}{2}in\pi\Big],$$

where n is the number of times the perturber passes through a turning point; the signs preceding $k_i(r)$ and $k_f(r)$ are the respective signs of the radial velocity immediately before and after the transition; the signs and the values of n are (–, –, 1), (–, +, 0), (+, +, 1), and (+, –, 2) for the respective cases (a)–(d).

In order to construct the sum over paths, we integrate the amplitudes (a)–(d) over r from b^* to ∞ where b^* is the maximum of b_i and b_f, and sum. The integral is from b^* rather than from b_i to ∞, for if r is smaller than $b_f(\epsilon_f, l)$, the final state (f, ϵ_f, l) is not accessible, that is $T_{i\to f}(r;\epsilon_i,\epsilon_f,l)=0$. There results exactly the overlap integral $\langle\psi^l_{k_f\text{WKB}}|D|\psi^l_{k_i\,\text{WKB}}\rangle$, provided $T_{i\to f}(r)$ is identified with $D(r)[k_ik_f/k_i(r)k_f(r)]^{1/2}$. This identification agrees with one's intuitive feeling for the probability for the transition to occur at r is then $|D(r)|^2k_ik_f/k_i(r)k_f(r)$: $|D(r)|^2$ represents a transition probability per unit time, so that it must be multiplied by the relative time spent at r, namely, $k_i/k_i(r)$. $k_f/k_f(r)$ plays the role of a density of final states: Among all the final states (f, ϵ_f, l) available, those for which the perturber stays longer at r are chosen preferably. In particular if the state (ϵ_f, l) is such that $b_f>r$, the perturber spends no time at r in that state and $T_{i\to f}(r)=0$.

Thus the four terms in the overlap integral $\langle\psi^l_{k_f\,\text{WKB}}|D|\psi^l_{k_i\,\text{WKB}}\rangle$, obtained by writing the cosines in the wave functions as the sum of two exponentials, have been interpreted as corresponding to the possible signs of the radial velocities immediately before and after the electronic transition, and the integration variable r as the position of the perturber when the transition takes place. A similar analysis would apply if either the initial or final, or both, states are bound.

We note that in the four integrals

$$\int_{b^*}^{\infty}dr\exp\left(i\int_{b_i}^{r}(\pm)k_i(r')\,dr'-i\int_{b_f}^{r}(\pm)k_f(r')\,dr'+\tfrac{1}{2}in\pi\right)$$
$$\times\ D(r)\left(\frac{k_ik_f}{k_i(r)k_f(r)}\right)^{1/2}\qquad(3.7)$$

the integrands are oscillating functions of r, of varying frequency equal to $(\pm)k_i(r)-(\pm)k_f(r)$, that is, to the difference of the radial momenta immediately before and after the electronic transition. The main contribution to the integrals comes from the regions where the phase of the integrand is stationary, that is, where $(\pm)k_i(r)-(\pm)k_f(r)\approx 0$, or, in other words, the dominant transitions are those which conserve the instantaneous velocity (Franck-Condon principle). The terms corresponding to a reversal of the sign of the radial velocity [cases (b) and (d)] are accordingly small; they contribute the integral

$$\int_{b^*}^{\infty} dr \cos\left(\int_{b_i}^{r} k_i(r')\,dr' + \int_{b_f}^{r} k_f(r')\,dr' + \tfrac{1}{2}\pi\right) \times D(r)\left(\frac{k_i k_f}{k_i(r)k_f(r)}\right)^{1/2} ,$$

which is usually neglected.[3] The two other terms contribute

$$\int_{b^*}^{\infty} dr \cos\left(\int_{b_i}^{r} k_i(r')\,dr' - \int_{b_f}^{r} k_f(r')\,dr'\right) \times D(r)\left(\frac{k_i k_f}{k_i(r)k_f(r)}\right)^{1/2} , \qquad (3.8)$$

an expression familiar from Jablonski's theory.[3]

IV. CLASSICAL SPECTRUM

The semiclassical spectrum may be simplified by assuming the kinetic-energy difference

$$[k_f^2(r)-k_i^2(r)]/2m=\epsilon_f-\epsilon_i-U(r)\ , \quad U\equiv U_f-U_i$$

small compared to $k_i^2(r)/2m$, and treating it as a perturbation[16]. One then sets

$$k_f(r\,;\,\epsilon_f,\,l)=\{k_i^2(r\,;\,\epsilon_i,\,l)+2m[\epsilon_f-\epsilon_i-U(r)]\}^{1/2}$$

$$\simeq k_i(r\,;\,\epsilon_i\,,\,l)+[\epsilon_f-\epsilon_i-U(r)]m/k_i(r)\ ,$$

$$b_f(\epsilon_f\,,\,l)\simeq b_i(\epsilon_i\,,\,l)$$

in the phase of $\psi^{l}_{k_f\,\mathrm{WKB}}(r)$, and $k_f(r)\simeq k_i(r)$ in its amplitude; this is essentially the Born approximation[17] to the WKB wave function for a perturbation $\epsilon_f-\epsilon_i-U$. One also neglects the terms for which the sign of the radial velocity is reversed by the electronic transition. The overlap integral is thus given by (3.8) modified by the above approximations, that is

$$(k_i k_f)^{1/2}\int_{b_i}^{\infty} D(r)\frac{dr}{k_i(r)} \times \cos\left(\int_{b_i}^{r}\frac{m\,dr'}{k_i(r')}\,[\epsilon_f-\epsilon_i-U(r')]\right).$$

Introducing the time t defined by $dr/dt=k_i(r)/m$ and the condition that $t=0$ when the perturber passes through the turning point b_i, we obtain

$$m^{-1}(k_i k_f)^{1/2}\int_0^{\infty} dt\, D(r(t))\cos\left\{\int_0^{t} dt'\,[\epsilon_f-\epsilon_i-U(r(t'))]\right\} , \qquad (4.1)$$

where $r(t)$ is the trajectory followed by the perturber. The spectrum is obtained by substituting the overlap integral (4.1) into (2.1); there results the classical spectrum[4,5] (constant factors are neglected)

$$J(\omega)=\int_0^{\infty} e^{-mv^2/2kT}\,v^2 dv\int_0^{\infty} 2\pi b\,db\left|\int_{-\infty}^{\infty} dt \times D(r(t\,;\,v\,,\,b))\exp\left\{i\int_0^{t} dt'\,[\omega-U(r(t'\,;\,v\,,\,b))]\right\}\right|^2 , \qquad (4.2)$$

where we have introduced the incident velocity $v=k_i/m$ and the collision impact parameter b defined by $l=mvb$; we have taken $\rho(\epsilon_i)\sim e^{-\epsilon_i/kT}$.

In order to interpret (4.2), we can, without changing the value of $J(\omega)$, rewrite the integral over the time t as

$$\lim_{T_1,T_2\to\infty}\int_{-T_1}^{T_2} dt\exp\left(-i\int_{-T_1}^{t} dt'E_f(t')\right)D(t) \times\exp\left(-i\int_{t}^{T_2} dt'\,E_i(t')\right) ,$$

where $E_i(t)$ is the total energy of the radiator plus radiation field before the radiative transition, and it depends on time through the influence of the perturber; $E_f(t)$ is the total energy after the transition, and it differs from $E_i(t)$ by the energy $-\omega$ of the absorbed photon in addition to the atomic energy difference $U(t)$. The first exponential in the integrand is the amplitude (time evolution operator in the adiabatic approximation) for the system to evolve from time $-T_1$ to t in the initial state, $D(t)$ is the amplitude for the radiative transition to occur at t, and the last exponential is the amplitude to evolve from t to time T_2 in the final state. Throughout the entire process, the perturber follows a trajectory determined by ϵ_i, l, and $U_i(r)$, so that the effect of the electronic transition on the perturber trajectories has been effectively neglected in deriving Eq. (4.2). Actually, the notion of a transition $i\to f$ is not really explicitly contained in (4.2), which can also be interpreted as the spectrum radiated by a classical charged oscillator of frequency $U(t)$ and amplitude of oscillation $D(t)$ which vary in time due to the influence of the perturber. The expression (4.2) may therefore be called the (fully) classical spectrum.

In general, the fundamental difference between semiclassical and classical transition probabilities, such as the scattering cross section for instance, is that in the former, the amplitudes corresponding to different paths are first added and the result is then squared; whereas in the latter, they are squared and then added; that is, the interference between different path amplitudes is neglected. The difference between the semiclassical and classical spectra is not of that fundamental character: In passing from the former to the latter, it is not the way of manipulating the amplitudes but the amplitudes themselves which are altered through dynamical approximations. This causes a quantitative change in the spectrum, but none of the qualitative features of the semiclassical spectrum, in particular the interference effects, are lost in the classical spectrum. The classical spectrum is not fundamentally more classical than the semiclassical one, but it so happens that it can be interpreted in purely classical terms; in particular it is not the analog of the classical differential scattering cross section: The analog of the latter is the statistical distribution of Margenau.[12]

V. INTERFERENCE AND RAINBOW EFFECTS

In the semiclassical spectrum and especially in the classical spectrum, the integral over paths (i.e., over r or t) is very similar in form to the integral over paths (i.e., over angular momenta or collision impact parameter) occurring in the semiclassical expression for the differential scattering cross section. In both cases, the path integral is of the form

$$\int dP e^{iA(P,\phi)} ,$$

where $A(P, \phi)$ is the action along the classical path P, and it depends on the observed quantity ϕ. Table I brings out the parallelism between the classical spectrum and the differential cross section. As a consequence of the above similarity, the two special features of the semiclassical cross section directly related to the integral over paths, namely, the interference and rainbow effects,[1] have analogs in the spectrum.

The main contribution to the path integral comes from those paths at which the action is stationary and which correspond, in the case of the spectrum, to the values of r or t at which the velocity of the perturber is unchanged by the electronic transition. Stationary phase integration is performed through the usual expansion of the phase, that is the action, in a Taylor series about the points of stationary phase, with only the first two terms kept:

TABLE I. Parallelism between the classical spectrum and the differential cross section.

	Classical spectrum	Cross section
Observed quantity ϕ	Frequency ω	Scattering angle θ
Variable parametrizing different paths P	Transition time t	Angular momentum l
"Path differential" dP	dt	$(l+1)^{1/2}\,dl$
Action $A(P,\ \phi)$	$\omega t - \int_0^t U(t')\,dt'$	$\theta l - \int_0^l \Theta(l')\,dl'$
	U = potential difference	Θ = classical deflection angle

$$A(r \text{ or } t,\ \omega) \simeq A_j(\omega) - \left[\tfrac{1}{2}(t-t_j)^2 \dot{U}(t_j) \text{ or } \tfrac{1}{2}(r-r_j)^2 U'(r_j)/\dot{r}(r_j)\right] ,$$

where $U' \equiv dU/dr$, $\dot{U} \equiv dU/dt = U'\dot{r}$, and $\dot{r} \equiv k_i(r)/m$ is the radial velocity; j labels the different values of r or t at which the velocities in the initial and final states are equal, that is, where $\omega - U(r \text{ or } t) = 0$; $A_j(\omega)$ is the corresponding value of the action. The resulting value of the path integral is

$$\textstyle\sum_j e^{i\eta_j} D_j \left|\dot{r}U'\right|_j^{-1/2}, \quad \eta_j = A_j \pm \tfrac{1}{4}\pi \tag{5.1}$$

where the sign in front of $\frac{1}{4}\pi$ is the sign of $-dU/dt$ at the point of stationary phase and D_j is the corresponding value of $D(r)$. The absolute square of (5.1) is [$D(r)$ is assumed real]

$$\sum_j |D_j|^2 \left|\dot{r}U'(r)\right|_j^{-1} + \sum_{i\neq j} D_i D_j \cos[\eta_j(\omega) - \eta_i(\omega)] \times \left|\dot{r}U'\right|_i^{-1/2} \left|\dot{r}U'\right|_j^{-1/2} . \tag{5.2}$$

The spectrum is obtained by averaging the above expression over angular momenta and initial energies. One may note that the semiclassical and classical expressions differ only by the values of the phases $\eta_j(\omega)$, which equal

$$\int_{b^*}^{r_j} dr \left[k_f(r;\ \epsilon_i + \omega,\ l) - k_i(r;\ \epsilon_i,\ l)\right]$$

in the first case, and $\int_0^{t_j} dt\,[\omega - U(t)]$ in the second.

A. Statistical Approximation and Rainbow Effect

The analog of the classical cross section is obtained by neglecting the second term in (5.2), which represents the interference between different paths. In that case, the average over angular momenta and over initial energies is easily performed, provided one takes $\rho(\epsilon_i) \sim e^{-\epsilon_i/kT}$; there results the statistical distribution of Margenau[12]:

$$J(\omega) = J_s(\omega) \equiv \textstyle\sum_j 4\pi r_j^2 e^{-U_i(r_j)/kT} \left|D(r_j)\right|^2 \left|U'(r_j)\right|^{-1} , \quad U(r_j) = \omega . \tag{5.3}$$

It is immediately apparent[6] that a local extremum in the slope dU/dr, at r_m for example, will result

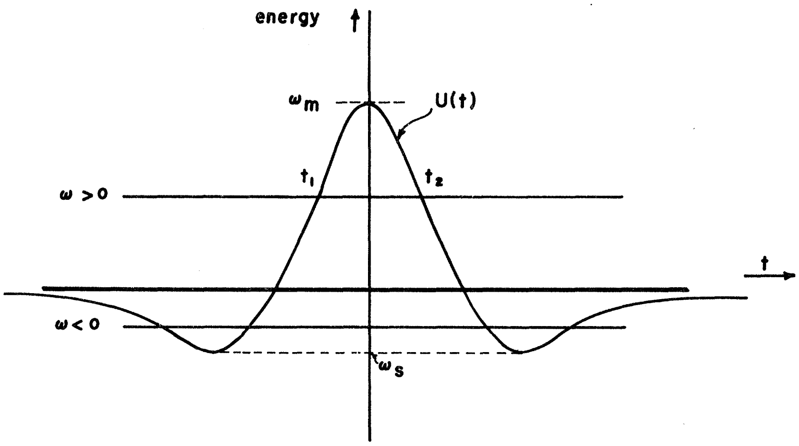

FIG. 1. Shape of $U(t)$ for a typical trajectory of the perturber, when $U(r)$ is a Lennard-Jones type of interaction.

in a local maximum in the spectrum at the frequency $\omega = U(r_m)$; for instance the minimum of a Lennard-Jones type of interaction will cause a sharp spike in the spectrum which is the analog of rainbow scattering. Actually, since in that case the slope $U'(r)$ vanishes at the potential minimum, the stationary phase integration in that region should be performed by including the third term in the Taylor expansion of the phase; the result is then expressed in terms of Airy functions and the spike is finite rather than infinite as according to (5.3). The mathematical procedure is exactly the same as in the treatment of rainbow scattering, and it has been given in detail by Ford and Wheeler[1] for that case. The spike associated with the minimum of a Lennard-Jones type of interaction is responsible for the red satellite observed in the spectrum of various gas mixtures.[7,8]

B. Interference Effect

Let us restrict ourselves to the classical spectrum for simplicity. In case the potential difference $U(r)$ is a Lennard-Jones type of interaction, the time-dependent frequency $U(r(t))$ for a typical trajectory of the perturber is of the general shape shown in Fig. 1. It is seen that for $\omega_m > \omega > 0$, there are two values of t at which $U(t) = \omega$, and for $\omega_s < \omega < 0$, there are four. The phase difference from t_i to t_j is

$$\eta_j(\omega) - \eta_i(\omega) = \omega[t_j(\omega) - t_i(\omega)] - \int_{t_i(\omega)}^{t_j(\omega)} U(t)\,dt + \tfrac{1}{4}n\pi ,$$

where n is the difference of the signs of $\dot{U}(t_j)$ and $\dot{U}(t_i)$; $\eta_j - \eta_i - \frac{1}{4}n\pi$ is the algebraic area between the curves $U(t)$ and ω in the interval t_i to t_j. The interference terms are proportional to $\cos[\eta_j(\omega) - \eta_i(\omega)]$; the wavelength of the oscillation, that is, the frequency increment $\Delta\omega$ separating two successive maxima of $\cos[\eta_j(\omega) - \eta_i(\omega)]$ in the vicinity of ω, is given by

$$2\pi = \left(\frac{d}{d\omega}(\eta_j - \eta_i)\right)\Delta\omega$$

$$= \left(\frac{\partial}{\partial\omega}(\eta_j - \eta_i) + \frac{\partial\eta_j}{\partial t_j}\frac{\partial t_j}{\partial\omega} + \frac{\partial\eta_i}{\partial t_i}\frac{\partial t_i}{\partial\omega}\right)\Delta\omega$$

$$= (t_j - t_i)\Delta\omega$$

[note that $\partial\eta_j/\partial t_j = \omega - U(t_j) = 0$ by definition of the times of stationary phase]. Thus the wavelength

$$\Delta\omega \sim 2\pi/|t_j - t_i| \tag{5.4}$$

is the inverse of the time separating the two velocity-conserving transition times.

At room temperature, the velocity of the atoms (atomic weight between 2 and 200) is of the order 10^4–10^5 cm/sec; the range of the interatomic potentials is measured in angstroms; the time required to travel 10^{-8} cm is 10^{-12}–10^{-13} sec. Thus the order of magnitude of the wavelength $\Delta\omega$ is $2\pi(10^{12}$–$10^{13})$ cps, that is 200–2000 cm^{-1}. In the case of alkali-noble-gas mixtures, the depth of the potential well is of the order of[7] 5–50 cm^{-1}; the interference pattern therefore has no room to show up on the red side ($\omega < 0$) of the resonance line, and only the rainbow spike at $\omega = \omega_s$ appears (red satellite). On the violet side on the other hand, the interference structure can appear, and the order of magnitude of the wavelength $\Delta\omega$ agrees with the separation of the experimentally observed violet satellites.[8] The interference effect therefore constitutes a plausible explanation for violet satellites, provided the average over angular momenta and over velocities does not obliterate the interference structure.

In order to estimate the effect of the average over angular momenta, rectilinear trajectories $r(t) = (v^2t^2 + b^2)^{1/2}$ of uniform velocity v and impact parameter b are assumed. Only the case $\omega > 0$ is considered, so that there are two times of stationary phase t_1 and $t_2 = -t_1$; dU/dt has the same abso-

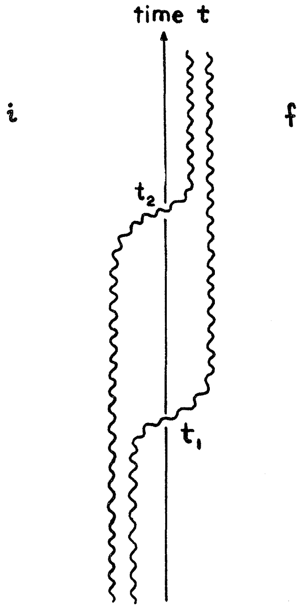

FIG. 2. Vertical time axis separates the plane into regions representing the initial and final states, respectively. The system can pass from one state to the other only at times t_1 and t_2 at which the velocity of the perturber is conserved in the transition. The wiggly lines represent the time evolution of the system, and show the two paths which cause the interference pattern.

lute value at these two times, but opposite signs, so that the phase difference $\eta_1 - \eta_2$ is

$$\eta_1 - \eta_2 = 2\int_0^{t_1} dt\{\omega - U[(v^2t^2+b^2)^{1/2}]\} + \tfrac{1}{2}\pi \ .$$

The integral over b in (4.2) ranges from $b=0$ to $b=B(\omega)$, where $B(\omega)$ is defined by $U(B)=\omega$. Because of the relation $r^2(t_1)=b^2+v^2t_1^2=B^2$, the integration variable b can be replaced by t_1: Noting that

$$\dot{r}(t_1)=v^2t_1/B \ , \quad b\,db=-v^2t_1\,dt_1 \ ,$$

we have

$$J(\omega)\sim \int_0^B 2\pi b\,db\,|\dot{U}(t_1(b))|^{-1}[2+2\cos(\eta_1-\eta_2)]$$

$$=4\pi B^2|U'(B)|^{-1}[1+\mathcal{T}(\omega)]$$

(averaged over velocities). The first term is the statistical distribution; the interference term is

$$\mathcal{T}(\omega)=B^{-1}\int_0^{B/v} dt_1$$

$$\times \ \sin(2\int_0^{t_1} dt\{\omega - U[(v^2t^2+B^2-v^2t_1^2)^{1/2}]\}) \ ;$$

it is clear that $\mathcal{T}(\omega)$ will, in general, be an oscillating function of $B(\omega)$ and therefore of the frequency ω. Thus the average over angular momenta does not, in general, destroy the interference structure. This is confirmed by Takeo's numerical calculation[11] of the classical spectrum with a Lennard-Jones interaction, in which two violet satellites appear (note that with a square well interaction, which has no repulsive branch as such, no violet satellites are obtained[11]). The effect of the thermal average is harder to estimate, but one may expect some structure to survive.

Because the integrals are so complicated, not much, in general, can be deduced concerning the shape of the violet satellites, outside of numerical computations such as that of Takeo.[11] Nevertheless, some general properties may be inferred from formula (5.4) according to which the separation of the violet satellites from their parent line should be roughly inversely proportional to the transit time of the perturber through the repulsive core of the potential difference $U(r)$. One may then write

$$\Delta\omega \sim |t_1-t_2|^{-1} \sim R^{-1}(T/m)^{1/2} \ , \tag{5.5}$$

where R is the radius of the repulsive core of $U(r)$, T is the temperature, and m is the reduced mass of the radiator-perturber couple.

There is no sufficient experimental data to verify the temperature dependence. In the case of alkali–noble-gas mixtures, the separation of the violet satellite decreases with increase of both the mass of the alkali and that of the noble atom; at constant reduced mass, the satellite separation decreases as the mass of the alkali increases, indicating that the repulsive radius R increases with the mass of the alkali, which seems reasonable. When the ordinal number of the member of the series, n, increases, the radius of the alkali increases roughly as n^2, so that the same may be expected of the repulsive radius R, with the result that $\Delta\omega \sim n^{-2}$; according to the data of Ch'en and Wilson,[18] the violet satellite separation goes roughly as n^{-p} with p between 2 and 3. The above qualitative agreement of the very simple formula (5.5) with the experimental data tends to confirm the interpretation of the violet satellites as an interference structure.

In the special case that the initial interatomic potential has a deep attractive well above the repulsive part of the final potential curve, the shape of the interference structure can be deduced in a fairly simple manner. This has been considered by Coolidge *et al.*[9] for bound-continuum emission, and by Mies and Smith[10] for continuum-continuum emission in relation with the collision-induced spectrum of metastable helium. In these cases, the interference structure somewhat reflects the nodal structure of the wave function above the well, and for this reason it appeared to be a purely quantum-mechanical effect not to be expected in classical pressure-broadening theory.[10]

VI. DISCUSSION

When interpreted in terms of Feynman amplitudes, the semiclassical and classical expressions of the spectrum become more meaningful and their mutual relation appears more clearly. The interference structure discussed by Coolidge *et al.*[9] and by Mies and Smith,[10] and the seemingly unrelated one obtained numerically by Takeo[11] appear to belong to a very general type of effect, namely, the interference resulting from the existence of several paths, in this case two, connecting initial and final states. This "two path interference," the archetype of which is met in the diffraction of particles (or waves) through two slits, is also responsible for the nodal structure of the wave function, as seen in Sec. II, and for interference fringes in the differential scattering cross section.[1] What is perhaps particular to the case of the spectrum is that the different paths are distinguished by a temporal parameter rather than by a spatial one as is more common, and one might speak of a "two slits in time" interference effect, as is suggested by the pictorial representation of Fig. 2.

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K-Shell-Fluorescence Yield for Carbon and Other Light Elements

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By recording the absolute number of K x-ray quanta emitted from a thin graphite target bombarded with electrons of energy E between 2 and 30 keV, the quantity $\omega_K \cdot Q_K(E)$ for carbon has been measured, where ω_K is the K-shell-fluorescence yield and $Q_K(E)$ the ionization cross section for the K shell. $Q_K(E)$ was calculated with the formula of Gryzinski, and the fluorescence yield of carbon was obtained as $\omega_K = 0.0035$. This value is much higher than the two other experimental values, but in agreement with a semiempirical formula of Byrne and Howarth and in near agreement with a recent calculation of McGuire. It is shown that this formula and this calculation seem to be valid for elements with atomic numbers down to $Z \approx 6$.

I. INTRODUCTION

The K-shell-fluorescence yield ω_K is defined as the number of radiation transitions per vacancy in the K shell of an atom. The method of production of this vacancy is of no significance. Measurements of ω_K for elements of atomic numbers $Z \gtrsim 15$ give a uniform picture,[1] but for low-Z elements the measured values in part differ greatly from one another (by a factor of 5 for Ne and Al). The recent tabulation of ω_K data for elements with $Z \leq 13$ is given by Dick and Lucas.[2]

Formulas for the evaluation of ω_K are always fitted to experimental values,[1,3,4] and therefore they cannot give additional information. We note that these formulas contain parameters which low-