THE CLASSICAL PATH APPROXIMATION IN THE THEORY OF LINE BROADENING BY FOREIGN GASES

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The problem of the atomic line broadening by foreign gases is investigated in the low pressure region in the classical path approximation. An extension of the impact theory is worked out. The general formulas are specified for the Lennard-Jones interatomic potentials.

1. Introduction

The present paper is devoted primarily to study the problem of the atomic lines broadening by foreign gases in the low density region. The stimulus has been given by the recent research on cesium lines broadening by inert gases performed by Ch'en and his coworkers [1, 2, 3, 4]. The most interesting experimental result is the non-linear dependence of the half-width and the line-shift on the density of the gas even in the low pressure region. We will attempt to show that it is possible to understand these results without introducing any new physical assumptions apart from those generally accepted in the papers based on the impact theory. Particularly, we will assume the binary collision approximation to be valid although in somewhat modified form as compared with the impact theory. We will limit ourselves to the investigation of an isolated atomic line perturbed by the collisions of the radiating atom with the perturbers, which are considered to be independent. We will also assume, that the interaction of the radiating atom with a perturber is realized through an interaction potential, which for a given atomic state, depends only on the relative distance. On this ground, the theory will be worked out along the lines putted on by Fano [5] and one of the present authors [6]. The general quantum-mechanical description of the theory is given in the second section, where the basic formulas are derived.

The essential features of the classical path approximation are discussed in the third section. The conclusion is, that we do not improve the accuracy of the calculations by taking the solutions of the Newtonian equation of motion instead of the straight lines trajectories. In the next two sections, the contributions of close and distant collisions are considered separately. As a by-product, the well-known formula of Anderson [7] for the line shift and half-width is rederived.

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In the last section, the formulas are specified by assuming the interaction potential to be one of the Lennard-Jones family. It seems remarkable, that we meet some difficulties in interpreting the experimental data in the very low pressure region when using those potentials.

2. *General treatment*

The intensity distribution function is, under the physical assumptions discussed in the introduction, given by the following formula

$$J_{if}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{\pm ixt}\, \bar{U}_{if}(t)\, dt, \tag{1}$$

where the indices i and f stand for the initial and final state, respectively, and where x denotes the deviation of the frequency of the emitted or absorbed light from the transition frequency of the unperturbed radiating atom, *i.e.*

$$x = \omega \mp \omega_{if}. \tag{2}$$

We have assumed here the transition frequency to be positive for the emission and negative for the absorption spectra. Besides, here and in the following, the upper plus or minus sign corresponds to the emission and the lower to the absorption spectra, whenever the choice in our formulas is required.

The Fourier conjugate of the intensity distribution function namely the function $\bar{U}(t)$, is given by

$$\bar{U}_{if}(t) = [\mathrm{Tr}\{\varrho(h_i) e^{ih_f t} e^{-ih_i t}\}]^N, \tag{3}$$

where the trace is to be taken over all states of the one-perturber motion and $\varrho(h_i)$ is the one-perturber density matrix. Quite obviously, we assume here the existence of some potentials, v_i and v_f, which represent the interaction between the radiating atom in its initial and final states and a perturber. To these potentials correspond the one-perturber Hamiltonians h_i and h_f, which are given by

$$h_i = h_0 + v_i \tag{4}$$

and

$$h_f = h_0 + v_f \tag{5}$$

with h_0 denoting the kinetic energy operator.

The intensity distribution function is most conveniently presented in the following form

$$J_{if}(x) = \frac{1}{\pi} \frac{\mathrm{Im}\, \Phi_{if}(x)}{[x \mp n V_{if} \pm \mathrm{Re}\, \Phi_{if}(x)]^2 + [\mathrm{Im}\, \Phi_{if}(x)]^2}, \tag{6}$$

where V_{if} is defined by

$$V_{if} = \Omega\, \mathrm{Tr}\, \{\varrho(h_i)(v_i - v_f)\}, \tag{7}$$

while the complex function $\Phi(x)$ is given by a rather complicated formula, namely

$$\Phi_{if}(x) = \frac{-n \int_0^\infty \frac{dV_{if}(t)}{dt} e^{\pm ixt} \int_0^\infty e^{\pm ixt'} \bar{U}_{if}(t'+t)\, dt'}{\int_0^\infty e^{-ixt} \bar{U}_{if}(t) dt}, \tag{8}$$

which will be, nevertheless, greatly simplified in the binary collision approximation. The function $V_{if}^{1}(t)$, which occurs here, is defined as follows

$$V_{if}(t) = \Omega \operatorname{Tr} \{\varrho(h_i) e^{ih_f t}(v_i - v_f) e^{-ih_i t}\}. \tag{9}$$

In these formulas we have denoted by n the perturbers density, *i.e.* the perturbers number N related to the volume Ω.

The formula (8) is useless as long as we do not assume that the density of the gas is low enough. Would it be the case, we may dissolve the function $\bar{U}(t'+t)$ into the following product

$$\bar{U}_{if}(t'+t) \approx \bar{U}_{if}(t') \bar{U}_{if}(t) \tag{10}$$

so that we arrive at

$$\Phi_{if}(x) \approx -n \int_0^\infty \frac{dV_{if}(t)}{dt} e^{\pm ixt} \bar{U}_{if}(t) dt. \tag{11}$$

Moreover, in the low density region the function $U_{if}(t)$ does not deviate appreciably from unity. Thus we obtain the following formula

$$\Phi_{if}(x) \approx -n \int_0^\infty \frac{dV_{if}(t)}{dt} e^{\pm ixt} dt \tag{12}$$

which has been already proposed by Fano [5] in a more general fashion. Still, detailed investigation indicates that we may improve the accuracy within the binary collision. In fact, we may replace the function $U_{if}(t)$ in (11) by some better approximation, namely the following one

$$U_{if}^{(1)}(t) = \exp\left\{\left(\mp i\Delta - \frac{1}{2}\Gamma\right) t\right\}, \tag{13}$$

where Δ and Γ are the line shift and half-width calculated in the impact approximation. The resulting expression

$$\Phi_{if}(x) \approx -n \int_0^\infty \frac{dV_{if}(t)}{dt} e^{\pm ixt} U_{if}^{(1)}(t)\, dt \tag{14}$$

requires the knowledge of the two-particles collision amplitudes only, although we have taken into account, to some extent, the influence of the whole gas on the colliding system.

The time derivative of $V_{if}(t)$, which is present in both (12) and (14), will be computed in the classical path approximation in the next section.

3. *Classical path approximation*

The so-called classical path approximation is neither defined uniquely nor it has to be connected with the classical paths, which are actually followed by the perturbers. In order to see the real meaning of this approximation, we shall consider two different formulas for the rate of change of $V_{if}(t)$. The first is the following one

$$\frac{dV_{if}(t)}{dt} = -i\Omega \operatorname{Tr}\{\varrho(h_i)\hat{V}S_f^+(t)\hat{V}'(t)S_i(t)\}, \tag{15}$$

where $\hat{V}$ is a shorthand for

$$\hat{V} = v_i - v_f \tag{16}$$

and $V'(t)$ is the corresponding Dirac operator, *i.e.*

$$\hat{V}'(t) = \exp\{ih_0t\}\hat{V}\exp\{-ih_0t\}, \tag{17}$$

and so are the potentials $v_i'(t)$ and $v_f'(t)$, which define the operators S_i or S_f with the help of the time-ordering operator P, in the following manner

$$S_{i(f)}(t) = P\exp\{-i\int_0^t v_{i(f)}'(t')dt'\}. \tag{18}$$

The second formula, which we wish to consider here, is the following one

$$\frac{dV_{if}(t)}{dt} = i\Omega \operatorname{Tr}\{\varrho(h_i)\hat{V}[v_f''(t)S_f^+(t)S_i(t) - S_f^+(t)S_i(t)v_i''(t)]\}, \tag{19}$$

with $v_i''(t)$ or $v_f''(t)$ defined as follows

$$v_{if}''(t) = \exp\{ih_{i(f)}t\}v_{i(f)}\exp\{-ih_{i(f)}t\} \tag{20}$$

while $S_i(t)$ or $S_f(t)$, which are already defined by (18), may be shown to be equal to

$$S_{i(f)}(t) = (P\exp\{i\int_0^t v_{i(f)}''(t')dt'\})^+. \tag{21}$$

It is remarkable that starting from the formula (15) we arrive in the classical limit at the straight line approximation, while in the second case we have to assume that the perturbers are moving along the trajectories resulting from the Newtonian equations of motion with the forces determined by the potentials v_i and v_f. The detailed analysis shows that an infinite variety of the classical path approximations may be reasonably justified. It is then clear that we do not improve the semi-classical calculations by introducing the solutions of the corresponding Newtonian equation of motion. Instead, we shall try to check the validity conditions of the straight line approximation as they are essentially equivalent to those of any other form of the classical path approximation. This problem is discussed in the Appendix, where the necessary mathematical framework is developed, Still, the physical picture involved here is very simple, for we require the de Broglie's wavelength of the pertuber to be, on the average, small compared to the dimensions of the effective range of the interaction.

This is the case when the long- and intermediate-range forces are weak enough. The contribution of the short range forces is given properly by the classical path approximation, if they increase in an evidently abrupt manner with the decreasing interatomic distance. In this case the detailed form of the short range interaction is namely unimportant and the quantum-mechanical result is essentially equivalent to the semiclassical one.

Under these assumptions we may evaluate the rate of change of $V_{if}(t)$ as follows

$$\frac{dV_{if}(t)}{dt} = -i \left\langle \int d^3\boldsymbol{R} \exp\left\{-\frac{v_i(\boldsymbol{R})}{k_B T}\right\} V(\boldsymbol{R}) S^{\mathrm{cl}}(t) V(\boldsymbol{R}_t) \right\rangle_{\mathrm{vel.av.}}, \tag{22}$$

where $S^{\mathrm{cl}}(t)$ is defined by

$$S^{\mathrm{cl}}(t) = \exp\{-i \int_0^t V(\boldsymbol{R}_{t'}) dt'\} \tag{23}$$

and the position vector of the perturber at time t is related to the initial position vector $\boldsymbol{R}$ by

$$\boldsymbol{R}_t = \boldsymbol{R} + \boldsymbol{v}t. \tag{24}$$

The bracket in (22) means that the average is to be taken over the Maxwellian distribution of velocities.

Let us now assume that the potentials v_i and v_f are central, *i.e.* they depend on the interatomic distance R only

$$v_{i(f)} = v_{i(f)}[R]. \tag{25}$$

Moreover, we shall consider R as a function of the impact parameter b and the time τ, namely

$$R(b, \tau) = (b^2 + v^2\tau^2)^{\frac{1}{2}}, \tag{26}$$

with the time τ defined as

$$\tau = -\boldsymbol{R}\boldsymbol{v}/v^2. \tag{27}$$

Substituting now (22) into (12) we arrive at the basic formula

$$\Phi_{if}(x) = i\pi n\bar{v} \int_0^\infty db^2 \int_{-\infty}^\infty d\tau \int_0^\infty dt \exp\{-\beta V[R(b, \tau)]\} \times$$
$$\times V[R(b, \tau)] S_1(\tau, \tau - t; b) V[R(b, \tau - t)] \exp\{-ixt\}, \tag{28}$$

where the function S_1 is defined as follows

$$S_1(t_1, t_2; b) = \exp\{-i \int_{t_2}^{t_1} V[R(b, t')] dt'\}. \tag{29}$$

Let us add that the formula (7) leads, in the classical path approximation, to the following result

$$\bar{V}_{if} = \pi\bar{v} \int_0^\infty db^2 \int_{-\infty}^\infty d\tau \exp\{-\beta V[R(b, \tau)]\} V[R(b, \tau)], \tag{30}$$

which, when combined with (28), completes the set of relations required for the numerical computation of the atomic line shape. These two formulas will be, for practical reasons, simplified by introducing the average velocity $\bar{v}$ instead of averaging over its distribution. We do not expect that this simplification, most commonly used in the pressure broadening calculations, may remarkably affect our results. However, we were not able to evaluate quantitatively the error introduced in this way.

The formula (28) has to be reconsidered in order to separate the close collision contribution, which results in the rapidly fluctuating terms in the integrand. This will be done in the next section.

4. *Close collision contribution*

We shall consider here the contribution to the integral over b in the equation (28) from the interval of the impact parameters smaller than a certain minimal value b_0, which will be defined later. Right now we only assume that the function $V[R]$ is, in this interval, very big compared to the values of x, which come into question. In this case we may reduce the contribution of close collisions (cc) in (28) to the following expression

$$\{\Phi_{if}(x)\}_{cc} = \pi n\bar{v}\int_0^{b_0^2} db^2 \int_{-\infty}^{\infty} d\tau \exp\{-\beta V[R(b,\tau)]\}\times$$
$$\times V[R(b,\tau)]\{1-S_1(\tau,-\infty;b)\}, \tag{31}$$

which follows from (28) when the exponential factor containing x is replaced by unity and use is made of the following differential equation

$$i\frac{\partial S_1(t_1,t_2;b)}{\partial t_2} = -S_1(t_1,t_2;b)V[R(b,t_2)]. \tag{32}$$

On the other hand, the close collision contribution to $n\overline{V}_{if}$ is, as it immediately follows from (30), given by

$$\{nV_{if}\}_{cc} = \pi n\bar{v}\int_0^{b_0^2} db^2 \int_{-\infty}^{\infty} d\tau \exp\{-\beta V[R(b,\tau)]\}V[R(b,\tau)]. \tag{33}$$

Thus the difference of (31) and (33), which enters into the line shape function (6), results in

$$\{\Phi_{if}(x)-n\overline{V}_{if}\}_{cc} = \pi n\bar{v}\int_0^{b_0^2} db^2 \int_{-\infty}^{\infty} d\tau \exp\{-\beta V[R(b,\tau)]\}\times$$
$$\times V[R(b,\tau)]S_1(\tau,-\infty;b). \tag{34}$$

The main contribution to this integral comes from the region of large negative times τ, since then the oscillations of the function S_1 are not too high. Therefore, we may omit the Boltzmann factor, thus getting

$$\{\Phi_{if}(x)-n\overline{V}_{if}\}_{cc} = -i\pi n\bar{v}\int_0^{b_0} db^2\{S_1(\infty,-\infty;b)-1\}, \tag{35}$$

when combining (34) and the following differential equation

$$i\frac{\partial S_1(t_1, t_1; b)}{\partial t_1} = V[R(b, t_1)]S_1(t_1, t_2; b). \tag{36}$$

Finally, omitting the highly oscillating first term in the curly bracket, we arrive at

$$\{\Phi_{if}(x) - n\overline{V}_{if}\}_{cc} = i\pi n\bar{v}b_0^2. \tag{37}$$

Thus we conclude, that the close collisions do not contribute to the line shift and their contribution to the half-width is correctly given by the impact theory.

5. *Distant collisions contribution*

The Boltzmann factor is not essential for the distant collisions (*dc*), for which we obtain from (28) and (30) the following formulas

$$\{\Phi_{if}(x)\}_{dc} = i\pi n\bar{v}\int_{b_0^2}^{\infty} db^2 \int_{-\infty}^{\infty} d\tau \int_0^{\infty} dt V[R(b, \tau)]\times$$
$$\times S_1(\tau, \tau - t; b)V[R(b, \tau - t)]\exp\{\pm ixt\} \tag{38}$$

and

$$\{n\overline{V}_{if}\}_{dc} = \pi n\bar{v}\int_{b_0^2}^{\infty} db^2 \int_{-\infty}^{\infty} d\tau V[R(b, \tau)]. \tag{39}$$

Using the relations

$$S_1(\tau, \tau - t; b) = S_1(\tau, 0; b)S_1(0, \tau - t; b) \tag{40}$$

and

$$S_1(0, \tau; b) = S_1^*(\tau, 0; b), \tag{41}$$

we may further simplify the formula (38) in the following way

$$\{\Phi_{if}(x)\}_{dc} = i\pi n\bar{v}\int_{b_0^2}^{\infty} db^2 \int_{-\infty}^{\infty} d\tau \int_{-\tau}^{\infty} F_x^*(\tau, b)F_x(t, b)dt \tag{42}$$

where the function $F_x(t, b)$ is defined as

$$F_x(t, b) = V[R(b, t)]S_1(t, 0; b)\exp\{\pm ixt\}. \tag{43}$$

Therefore, the imaginary part of (38) is given by

$$\mathrm{Im}\,\{\Phi_{if}(x)\}_{dc} = \frac{1}{2}\pi n\bar{v}\int_{b_0^2}^{\infty} db^2\left|\int_{-\infty}^{\infty} d\tau F_x(\tau, b)\right|^2, \tag{44}$$

while its real part is readily be found from the Cauchy relation

$$\mathrm{Re}\,\{\Phi_{if}(x)\}_{dc} = \mp\frac{1}{\pi}\,\mathrm{p.v.}\int_{-\infty}^{\infty}\frac{\mathrm{Im}\,\{\Phi_{if}(x')\}dx'}{x - x'}. \tag{45}$$

The usefulness of these two relations consists in reducing the number of integrals which appear in the initial formula (42).

Let us stress, that the Boltzmann factor does not appear in the formula (37) of the precedent section nor in the formulas (39) and (42). In consequence, the line shape of the absorption spectra is identical with that of emission spectra.

In the limit of very low density we may neglect the x-dependence of Φ so that we do not need to treat separately the close collisions from the distant collisions contribution. In fact, in this case, the formula (35) holds in the whole range of the impact parameters, *i.e.*

$$\Phi_{if}(0)-n\overline{V}_{if} = -i\pi n\bar{v}\int_0^\infty db^2\{S_1(\infty, -\infty; b)-1), \tag{46}$$

which is the well-known formula of Anderson [7].

6. *Lennard–Jones potential calculation*

In order to get a more realistic description of the interatomic forces than that usually accepted, we have considered the potentials difference V of the Lennard–Jones family, namely

$$V[R] = \varepsilon\left\{\left(\frac{R_0}{R}\right)^6 - \left(\frac{R_0}{R}\right)^{2k}\right\}. \tag{47}$$

We have accepted here the opposite sign, with respect to the normal form of the L.–J. potentials, since we wish to restrict ourselves, from now on, to the absorption spectra only. We would also like to introduce a new set of dimensionless parameters

$$\zeta = \frac{\varepsilon R_0}{\bar{v}h}, \qquad \xi = \frac{xR_0}{\bar{v}}$$

$$s = \frac{\tau\bar{v}}{R_0}, \qquad \varrho = \frac{b}{R_0} \tag{48}$$

instead of the old ones*. The potential V will be replaced by a new function $u(\varrho, s)$ according to

$$V = \frac{\bar{v}h}{R_0}\,\zeta u(\varrho, s), \tag{49}$$

which is defined as follows

$$u(\varrho, s) = (\varrho^2+s^2)^{-3}-(\varrho^2+s^2)^{-k}. \tag{50}$$

Substituting now (34) combined with (38) and (39) into the formula (6) we obtain, after some simple calculations, the following expression for the intensity distribution function

$$J_{if}(x) = \frac{R_0}{\bar{v}}\,j_{if}(\xi, \zeta, N_0) \tag{51}$$

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* The Planck's constant divided by 2π is denoted by h.

with the function j_{if} given as

$$j_{if}(\xi, \zeta, N_0) = \frac{1}{\pi} \frac{N_0 w(\zeta, \xi)}{[\xi - N_0 d(\zeta, \xi)]^2 + [N_0 w(\zeta, \xi)]^2} \tag{52}$$

where $w(\zeta, \xi)$ and $d(\zeta, \xi)$ are defined by

$$w = \alpha^2 + \zeta^2 \int_{\alpha}^{\infty} d\varrho\varrho \Big| \int_{-\infty}^{\infty} ds u(\varrho, s) \exp\{-i\zeta \int_{0}^{s} u(\varrho, s')ds'\} \times$$
$$\times \exp\{-i\xi s\}\Big|^2 \tag{53}$$

and

$$d(\zeta, \xi) = \frac{1}{\pi} \text{ p. v.} \int_{-\infty}^{\infty} \frac{w(\zeta, \xi')d\xi'}{\xi - \xi'} - 2\zeta \int_{\varrho_0}^{\infty} d\varrho\varrho \int_{-\infty}^{\infty} ds u(\varrho, s), \tag{54}$$

while N_0 stands for

$$N_0 = \pi n R_0^3. \tag{55}$$

The numerical results based on these formulas will be presented in a subsequent paper. Some preliminary evaluations which has been published recently by the present authors [8] indicate, however, that we may expect a reasonable agreement of the theory with the experimental data on the argon and krypton broadening of cesium lines performed by Ch'en and others [1, 3]. However, we do not expect to approach very closely the experimental results using the Lennard–Jones potential. In fact, in the very low pressure region the ξ-dependence of w and d may be neglected so that we get the Lorentzian line shape, *i.e.*

$$j_{if}(\xi, \zeta, N_0) \approx \frac{1}{\pi} \frac{N_0 w(\zeta, 0)}{[\xi - N_0 d(\zeta, 0)]^2 + [N_0 w(\zeta, 0)]^2} \tag{56}$$

in accord with the orthodox impact theory. The values of $w(\zeta, 0)$ and $d(\zeta, 0)$ have been computed with ζ ranging from 1 to 8 as demonstrated in Fig. 1. The dependence of the line shift and half-width on the potential strength, *i.e.* on ζ, is much more conspicuos than one would expect from some intuitive predictions of Anderson [7]. An even more striking result is, that the ratio of the semi-half-width w to the line shift d has a broad minimum around the point $\zeta = 5.7$ (Fig. 2). The minimum value, of this ratio, which is equal to 0.71, is slightly above the experimental data, which are given in the quoted papers of Ch'en and others as being equal to 0.63 and 0.7 in the very low pressure region (the ratio of the "initial slopes") of the cesium resonance line broadening by argon and krypton, respectively. The computations with some others L.–J. potentials, with k higher than 4, diverge even strongly with experiment leading to the higher minimum value of this ratio. Moreover, the data on the helium and neon broadening of cesium lines [2, 4] cannot be explained with the use of any potentials from the Lennard–Jones family. Thus, the search of some more adequate potentials is clearly needed.

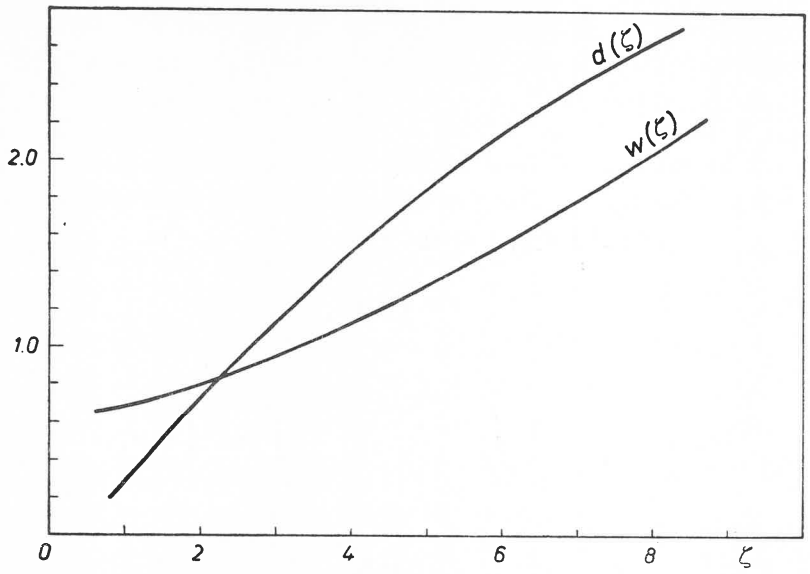

Fig. 1

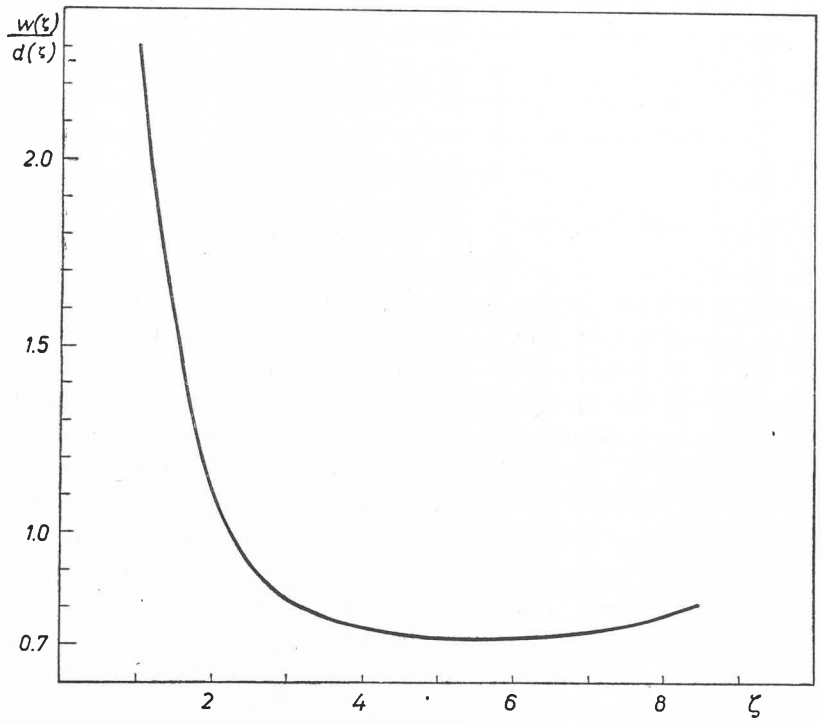

Fig. 2

APPENDIX

The straight line approximation

The connection between the quantum-mechanical and the corresponding classical expressions will be established here with the help of the displacement operator in the momentum space which is generated by the position vector $\boldsymbol{R}$ according to the following rule

$$|\boldsymbol{k}\rangle = \exp\{i\boldsymbol{k}\boldsymbol{R}\}|0\rangle \tag{A1}$$

where $|\boldsymbol{k}\rangle$ stands for the eigenstate of the momentum with the eigenvalue k/h. Using the last relation we may transform the quantum-mechanical expressions, like the following one

$$V_{if}(t) = \Omega \int d^3\boldsymbol{k}\langle\boldsymbol{k}|\varrho(h_i)\hat{V}S_f^+(t)S_i^-(t)|\boldsymbol{k}\rangle, \tag{A2}$$

coming closer to the corresponding classical path expressions. In fact, one can easily see that

$$V_{if}(t) = \Omega \int d^3\boldsymbol{k}\langle 0|[\varrho(h_i)]_{\boldsymbol{k}}\hat{V}[S_f^+(t)]_{\boldsymbol{k}}[S_i(t)]_{\boldsymbol{k}}|0\rangle, \tag{A3}$$

where we have related the following operator

$$[O]_{\boldsymbol{k}} = \exp\{-i\boldsymbol{k}\boldsymbol{R}\}O\exp\{i\boldsymbol{k}\boldsymbol{R}\} \tag{A4}$$

to an operator O. In particular, using the notation of the 3rd section, we arrive at

$$[S_{i(f)}]_{\boldsymbol{k}} = P\exp\{-i\int_0^t v'_{i(f)}(\boldsymbol{R}+\boldsymbol{v}t';\, t')dt'\}, \tag{A5}$$

where the time-dependent potential v' is given by

$$v'_{i(f)}(\boldsymbol{R}+\boldsymbol{v}t';\, t') = \exp\{ih_0t'\}v_{i(f)}\exp\{-ih_0t'\} \tag{A6}$$

and the velocity $\boldsymbol{v}$ is defined as the ratio of the corresponding eigenvalue of the momentum $h\boldsymbol{k}$ to the reduced mass of the colliding particles. The classical path approximation is valid whenever the angular momentum of the relative motion is, on the average very large, *i.e.*

$$kR_0 \gg 1 \tag{A7}$$

where R_0 is, in general, the characteristic length of the interaction potential. In this case we may replace the operators v' by the corresponding "straight lines" time-dependent potentials getting

$$[S_f^+]_{\boldsymbol{k}}[S_i]_{\boldsymbol{k}}|0\rangle \approx S^{\mathrm{cl}}|0\rangle. \tag{A8}$$

Moreover, the density matrix in (A2) should be replaced by the classical distribution function. Finally, we arrive at the formula (22) of the text for the rate of change of (A2).

The present approach may be extended by the methods of perturbation theory producing some quantum corrections to the classical path approximation.

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