

SÉMINAIRE DE PROBABILITÉS (STRASBOURG)

WILHELM VON WALDENFELS

Some remarks on Burkhardt's model for pressure broadening of spectral lines

Séminaire de probabilités (Strasbourg), tome 7 (1973), p. 301-317

http://www.numdam.org/item?id=SPS_1973__7__301_0

© Springer-Verlag, Berlin Heidelberg New York, 1973, tous droits réservés.

L'accès aux archives du séminaire de probabilités (Strasbourg) (<http://portail.mathdoc.fr/SemProba/>) implique l'accord avec les conditions générales d'utilisation (<http://www.numdam.org/conditions>). Toute utilisation commerciale ou impression systématique est constitutive d'une infraction pénale. Toute copie ou impression de ce fichier doit contenir la présente mention de copyright.

NUMDAM

Article numérisé dans le cadre du programme
Numérisation de documents anciens mathématiques

<http://www.numdam.org/>

SOME REMARKS ON BURKHARDT'S MODEL FOR
PRESSURE BROADENING OF SPECTRAL LINES

Wilhelm von Waldenfels

Abstract. In order to understand the connection between impact and quasistatic approximation, Burkhardt treated a simple model: At one moment at most one particle interacts with the radiator and causes a constant line shift during its impact time. The subject of this paper is to give an exact treatment of this model including all the mixed terms neglected by Burkhardt. As in Burkhardt's treatment the line shape is a sum of two terms. For frequencies near the unperturbed line the first one behaves like the impact approximation, whereas the second one can be neglected. For frequencies far the unperturbed line (at least at one side of the spectre) the first one can be neglected and the second one behaves but a factor like the quasistatic approximation. The second term is the same as in Burkhardt's paper. The first term includes all the correlations neglected by Burkhardt and gives the impact approximation in its complete form.

§ 1. Introduction and review of Burkhardt's treatment

The frequency distribution of a spectral line is given by a probability measure $J(\omega)d\omega$ on the real line, where $J(\omega)d\omega$ indicates the fraction of the total energy radiated into the frequency interval $\omega, \omega + d\omega$. If the light is emitted by an atom or ion placed in a gas the frequency distribution is no more a sharp line $J(\omega) = \delta(\omega - \omega_0)$, but $J(\omega)$ becomes a much broader profile. This line broadening has several reasons. Here we consider only pressure broadening, where the deformation of the line shape is due to stochastic fields produced by the neighbors of the emitting atom. For fixing our ideas let us assume van der Waals broadening, i.e., the frequency shift caused by a neighbor at distance r is $C \cdot r^{-6}$, $C > 0$. For the resulting line profile there are two basic approximations.

The quasistatic approximation assumes all molecules fixed in space. Let us assume that the broadening is caused only by the nearest atom. If r is not too big the probability that the nearest

neighbor at distance between r and $r + dr$ is equal to $n \cdot 4\pi r^2 dr$ where n is the mean density of perturbing particles. As $\Delta\omega = Cr^{-6}$ the probability for a frequency shift between $\Delta\omega$ and $\Delta\omega + d\Delta\omega$ is equal to

$$\frac{4\pi}{6} n \Delta\omega^{-\frac{3}{2}} d\Delta\omega$$

for $\Delta\omega$ large enough. So $J(\omega)$ is given by

$$\frac{4\pi}{6} n (\omega - \omega_0)^{-\frac{3}{2}}$$

for $\omega - \omega_0 > 0$ large enough and $J(\omega) = 0$ for $\omega < \omega_0$.

The other approximation is the impact approximation. There the movement of the particles is taken into account, but one assumes that the particles interact only in the time of nearest approach and then cause a sudden phase shift which is equal to the total phase shift of the particle during all the time. So a particle passing at distance ρ of the radiator with a velocity v makes at the time of its nearest approach the phase shift

$$\eta(\rho) = \int_{-\infty}^{+\infty} \frac{C dt}{(\rho^2 + v^2 t^2)^3} = \frac{3\pi}{8} \frac{C}{v\rho^5}$$

The line profile resulting from this approximation is due to Lindholm

$$J(\omega) = \frac{\text{Re } A / \pi}{(\omega - \omega_0 - \text{Im } A)^2 + (\text{Re } A)^2}$$

with

$$A = n v \int_0^{\infty} 2\pi \rho d\rho (1 - e^{i\eta(\rho)}).$$

The classical method of computation for the line profile is to use impact approximations in the middle of the line, i.e., near ω_0 and quasistatic approximations on the wings of the line. The problem remained why this should be in good agreement with reality. In 1940 Burkhardt proposed a simple model for pressure broadening and derived the range of validity of both approximations. The aim of this paper is to give a more thorough mathematical treatment and to include essential terms neglected by Burkhardt. This will be done by a method which is useful in much more general cases.

We review now Burkhardt's treatment.

If $r_k(t)$ is the distance of the k -th perturbator at time t , the total frequency shift $X(t)$ is given by

$$(1.1) \quad X(t) = \sum_k C \cdot r_k(t)^{-6} \quad (C > 0)$$

and the line profile by

$$(1.2) \quad J(\omega) = \left| \int_{-\infty}^{+\infty} e^{i(\omega_0 - \omega)t + i \int_0^t X(t') dt'} dt \right|^2$$

This formula is not correct, as the integral does not exist, but it gives a good idea of the situation. It can be replaced by an exact formula, as we shall see.

By shifting the frequency axis we shall assume that the frequency of the unperturbed line is $\omega_0 = 0$.

If the perturbators move on straight lines with constant velocities v , $X(t)$ becomes

$$(1.3) \quad X(t) = \sum_k C (\rho_k^2 + v(t - t_k)^2)^{-3}$$

where ρ_k is the impact parameter, i.e., the closest distance of the perturbator to the radiator, and t_k the corresponding time of closest approach. ρ_k and t_k are random parameters given by the gas conditions.

Burkhardt approximates the function

$$t \mapsto C(\rho^2 + v^2 t^2)^{-3}$$

by a rectangular profile

$$(1.4) \quad t \mapsto \begin{cases} \omega^s & \text{for } |t| < \tau/2 \\ 0 & \text{otherwise} \end{cases}$$

where ω^s and τ are determined by

$$(1.4') \quad \omega^s = C' \rho^{-6}, \quad C' = \frac{\pi}{4} C, \quad \tau = \frac{3}{2} \frac{\rho}{v}.$$

One has

$$(1.5) \quad \omega^s \tau = \eta(\rho) = \int \frac{C dt}{(\rho^2 + v^2 t^2)^3} = \frac{3\pi}{8} \frac{C}{v \rho^5}$$

So the k -th perturbator acts only in the time interval $[t_k - \tau_k/2, t_k + \tau_k/2]$ and then causes a constant frequency shift ω_k^s . On the assumption that at a given time only one particle interacts and that the perturbations do not overlap, (1.2) yields

$$(1.6) \quad \dot{J}(\omega) = \left| \sum_k \int_{I_k^s} e^{+i(\omega_k^s - \omega)t} dt + \sum_k \int_{I_k^f} e^{-i\omega t} dt \right|^2$$

where I_k^s are the perturbation intervals $[t_k - \tau_k/2, t_k + \tau_k/2]$ and I_k^f are the flight intervals $[t_{k-1} + \tau_{k-1}/2, t_k - \tau_k/2]$. Burkhardt assumes that the correlations of the different terms vanish and so $J(\omega)$ splits into

$$(1.7) \quad J(\omega) = \sum_k \left| \int_{I_k^s} e^{+i(\omega_k^s - \omega)t} dt \right|^2 + \sum_k \left| \int_{I_k^f} e^{-i\omega t} dt \right|^2$$

There is still a little mistake in the transition from (1.2) to (1.6) as any of the terms in (1.6) needs an additional factor of modulus 1, but this one cancels by the transition to (1.7).

Interpreting the sums in the right way and taking average Burkhardt finally gets

$$(1.8) \quad J(\omega) = \frac{1}{\pi} \frac{c}{c^2 + \omega^2} + \frac{n v}{2\pi} \int_0^{\rho_0} 2\pi \rho d\rho \frac{\sin^2(\omega - \omega^s)\tau/2}{(\omega - \omega^s)^2}$$

where ρ_0 is the maximal impact parameter taken into account, i.e., all perturbations with impact parameter $> \rho_0$ are neglected. c is the impact frequency

$$(1.9) \quad c = n \pi \rho_0^2 v$$

and n is the mean density of perturbators. In formula (1.8) we neglected the possibility that the perturbators may have different velocities. We assume that all of them have velocity v , their directions, however, may vary. ω^s and τ are considered as functions of ρ by (1.4').

The first term of (1.8) is Lorentz's expression for the line shape. The second term behaves like the quasistatic approximation, as Burkhardt showed by numerical methods.

If one takes all correlations into account and neglects the terms of order $c\tau \approx n\rho_0^3$, which is consistent to the assumption of non-overlapping perturbations, instead of (1.8) one gets

$$(1.10) \quad \mathcal{J}(\omega) = \frac{\operatorname{Re} A / \pi}{(\omega - \operatorname{Im} A)^2 + (\operatorname{Re} A)^2} + \frac{nv}{2\pi} \int_0^{\rho_0} 2\pi\rho d\rho \frac{\sin^2(\omega - \omega_s)\tau/2}{(\omega - \omega_s)^2}$$

where

$$(1.11) \quad A = nv \int_0^{\rho_0} 2\pi\rho d\rho (1 - e^{i\omega_s\tau - i\omega\tau})$$

The first term behaves for small frequencies $|\omega| \ll \frac{1}{\tau}$ like the well-known impact approximation in its complete form due to Lindholm

$$\mathcal{J}(\omega) = \frac{\operatorname{Re} A / \pi}{(\omega - \operatorname{Im} A)^2 + (\operatorname{Re} A)^2}, \quad A = nv \int_0^{\rho_0} 2\pi\rho d\rho (1 - e^{i\omega_s\tau})$$

The second term is the same as in (1.8). It behaves like

$$(1.12) \quad \sim \frac{\pi^{3/2}}{4} n C^{1/2} \omega^{-3/2}$$

for $\omega \rightarrow +\infty$. So it is superior to the impact term vanishing like ω^{-2} .

The formula (1.12) is not quite correct, as the true behaviour is

$$(1.13) \quad \sim \frac{4\pi}{6} n C^{1/2} \omega^{-3/2}$$

The factor is due to the deformation of the real interaction into a rectangular pulse.

§ 2. Formulation of the mathematical problem

We replace (1.2) by

$$(2.1) \quad \mathcal{J}(\omega) = \lim_{T \rightarrow \infty} \frac{1}{2\pi T} E \left| \int_0^T e^{-i\omega t + i \int_0^t X(t') dt'} dt \right|^2$$

E denotes the expectation operator taking the statistical average over the different functions $t \mapsto X(t)$. The normalization factor $(2\pi T)^{-1}$ makes sure that $\int \mathcal{J}(\omega) d\omega = 1$. The limit exists in the weak sense, if the quantity $E \exp i \int_{t'}^t X$ is a function $R(t-t')$ of the difference $t-t'$ and if

$$(2.2) \quad R(t) = E \exp i \int_0^t X$$

is continuous in t . The outcoming quantity $\mathcal{J}(\omega)$ is in most of the physically occurring cases a continuous function of ω , but in general a probability measure on the real line. As is common in physical papers measures will be denoted in the same way as functions.

$R(t)$ is related to $\mathcal{J}(\omega)$ by the formula

$$(2.3) \quad R(t) = \int e^{i\omega t} \mathcal{J}(\omega) d\omega$$

The connection between (2.1) and (2.3) is established by lemma 1, which is a bit more general.

Lemma 1: Be t_0 a real random variable, be T_0 and T_1, T_2, \dots random variables of finite expectations such that

$$E T_N \rightarrow +\infty$$

$$\frac{1}{E T_N} E |T_N - E T_N| \rightarrow 0$$

for $N \rightarrow \infty$. Then

$$(2.4) \quad \mathcal{J}(\omega) = \lim_{N \rightarrow \infty} \frac{1}{2\pi E T_N} E \left| \int_{T_0}^{T_N} e^{-i\omega t + i \int_{t_0}^t X} dt \right|^2$$

in the weak sense.

Proof. By virtue of Lévy's theorem it is sufficient to show that

$$R_N(t) = \int \mathcal{J}_N(\omega) e^{i\omega t} d\omega \rightarrow R(t)$$

for any t , calling $\mathcal{J}_N(\omega)$ the expression following the lim-sign. As $R(-t) = \overline{R(t)}$ and $R_N(-t) = \overline{R_N(t)}$, it is enough to prove the convergence for $t \geq 0$.

The integral $\int_{T_0}^{T_N} \exp(-i\omega t + i \int_{t_0}^t X) dt$ is the Fourier transform of

$$\varphi(t) = \chi_{T_0}^{T_N}(t) \exp i \int_{t_0}^t X$$

where $\chi_{T_0}^{T_N}$ is defined by

$$\chi_{T_0}^{T_N}(t) = \begin{cases} 1 & \text{for } T_0 \leq t < T_N \\ -1 & \text{for } T_N \leq t < T_0 \\ 0 & \text{otherwise.} \end{cases}$$

Using

$$\chi_{T_0}^{T_N} = \chi_0^{ET_N} - \chi_0^{T_0} + \chi_{ET_N}^{T_N}$$

one has

$$\begin{aligned} R_N(t) &= \frac{1}{ET_N} \int E \varphi(u) \bar{\varphi}(u-t) du \\ &= \frac{1}{ET_N} E \int e^{i \int_{u-t}^u X} \chi_{T_0}^{T_N}(u) \chi_{T_0}^{T_N}(u-t) du \\ &= \frac{1}{ET_N} R(t) \int du \chi_0^{ET_N}(u) \chi_0^{ET_N}(u-t) du + r_N(t). \end{aligned}$$

The first term is equal to

$$\frac{1}{ET_N} R(t) \int_0^{ET_N} \chi_0^{ET_N}(u-t) du \rightarrow R(t)$$

the second term may be estimated by

$$\begin{aligned} &\frac{2}{ET_N} E \int (\chi_0^{ET_N} + \chi_0^{T_N} + \chi_{ET_N}^{T_N})(u) (\chi_0^{T_0} + \chi_{ET_N}^{T_N})(u-t) du \\ &\leq \frac{6}{ET_N} (E|T_0| + E|T_N - ET_N|) \rightarrow 0 \end{aligned}$$

by hypothesis.

Lemma 2 shows a simple case in which the condition for T_N in lemma 1 is fulfilled.

Lemma 2: Let U_1, U_2, \dots be independent identically distributed random variables with

$$\mu = E U_k > 0$$

$$E U_k^2 < \infty$$

and put $T_N = U_1 + \dots + U_N$. Then

$$E T_N = N\mu$$

$$\frac{1}{E T_N} E |T_N - E T_N| \rightarrow 0$$

for $N \rightarrow \infty$.

Proof. By Schwarz's inequality there is

$$E |T_N - E T_N| \leq \left(E (T_N - E T_N)^2 \right)^{1/2} = \sqrt{N} \sigma$$

with $\sigma^2 = E U_k^2 - \mu^2$. This proves the lemma.

Recall Burkhardt's model. We call t_k' the moment of the beginning of the k -th interaction and t_k'' the moment of its end, $t_k'' - t_k' = \tau_k$, during the interval τ_k the perturbator causes the frequency shift ω_k^s and we assume that during that interval no other interaction takes place. We numerate the interactions in the way that $0 < t_0' < t_1' < t_2' \dots$. The differences $u_k = t_{k+1}' - t_k''$, $k = 0, 1, \dots$ are independent and they are all distributed with respect to the same exponential distribution

$$(2.5) \quad \text{Prob}\{u_k \in u, u + du\} = ce^{-cu} du$$

where c is given by (1.9). The condition of non-overlapping is (cf. 1.4')

$$(2.6) \quad c E \tau = n \pi \rho_0^3 \ll 1$$

and this quantity is the mean number of perturbators in a cylinder of radius and height \mathcal{P}_0 .

We apply lemma 1 and put into (2.4) $t_0 = T_0 = t_0'$, $T_N = t_N'$. The conditions of lemma 1 are fulfilled, as t_0' is again exponentially distributed with parameter c and has a finite expectation and $t_N' = t_0' + \tau_0 + u_0 + \tau_1 + \dots + \tau_{N-1} + u_{N-1}$. As all these quantities are independent and all τ_k and u_k are identically distributed, we almost have the case treated in lemma 2.

So we get

$$(2.7) \quad J(\omega) = \lim_{N \rightarrow \infty} E \frac{1}{2\pi N(E\tau + E\mu)} \left| \int_0^{t'_N - t'_0} \exp\left\{-i\omega t + i \int_0^{t' - t'_0} X(t' - t'_0) dt'\right\} dt \right|^2$$

This expression is completely determined by the quantities u_k, τ_k, ω_k^s as

$$t'_N - t'_0 = \tau_0 + \mu_0 + \dots + \tau_{N-1} + \mu_{N-1}$$

$$X(t - t'_0) = \begin{cases} \omega_k^s & \text{for } \tau_0 + \mu_0 + \dots + \tau_{k-1} + \mu_{k-1} \leq t \leq \\ & \tau_0 + \mu_0 + \dots + \tau_{k-1} + \mu_{k-1} + \tau_k \\ 0 & \text{otherwise.} \end{cases}$$

So (by slight modification of the meaning of the letters) we come to the following mathematical problem: Given are two independent sequences of random quantities. The first one consists of the independent random variables $u_k > 0, k = 0, 1, 2, \dots$, which are all distributed with respect to the same exponential distribution with parameter c : $\text{Prob}\{u_k \in u, u + du\} = c e^{-cu}$. The second one is formed out of independent identically distributed random pairs $(\tau_k, \omega_k^s), \tau_k > 0, E\tau_k < \infty$.

Put

$$(2.8) \quad T_N = \tau_0 + \mu_0 + \tau_1 + \mu_1 + \dots + \tau_{N-1} + \mu_{N-1}$$

and

$$(2.9) \quad X(t) = \begin{cases} \omega_k^s & \text{for } T_k < t < T_k + \tau_k \\ 0 & \text{otherwise.} \end{cases}$$

Then investigate the behaviour of

$$(2.10) \quad J_N(\omega) = \frac{1}{2\pi N(E\mu + E\tau)} E \left| \int_0^{T_N} \exp\left\{-i\omega t + i \int_0^t X\right\} dt \right|^2$$

for $N \rightarrow \infty$ and calculate the limit if it exists.

§ 3. Solution of the mathematical problem

According to the assumptions at the end of the last section we prove the following theorem.

Theorem. Put

$$(3.1) \quad \begin{aligned} \alpha(\omega) &= E e^{+i\omega^s \tau - i\omega \tau} \\ \beta(\omega) &= E \int_0^\tau e^{+i(\omega^s - \omega)t} dt \\ \tilde{\beta}(\omega) &= E \left| \int_0^\tau e^{i(\omega^s - \omega)t} dt \right|^2 \end{aligned}$$

and assume

$$(3.2) \quad |\alpha(\omega)| \leq a < 1$$

for all ω . The functions $J_N(\omega)$ are continuous, ≥ 0 and $\int J_N(\omega) d\omega = 1$. They converge for $N \rightarrow \infty$ uniformly in ω to a continuous function $J(\omega) \geq 0$ with $\int J(\omega) d\omega = 1$ and $J(\omega)$ is given by the formula

$$(3.3) \quad J(\omega) = \frac{1}{2\pi} \frac{1}{1+cE\tau} \left(c\tilde{\beta} + \frac{(1+c\beta)^2}{c+i\omega-c\alpha} + \frac{(1+c\bar{\beta})^2}{c-i\omega-c\bar{\alpha}} \right)$$

Proof: We arrange the proof in such a way that it holds in more general situations, too.

Put

$$C_k = \int_{T_k}^{T_k + \tau_k} e^{-i\omega t + i \int_0^t X} dt$$

$$D_k = \int_{T_k + \tau_k}^{T_{k+1}} e^{-i\omega t + i \int_0^t X} dt$$

Then the integral in (2.10) splits

$$\int_0^{T_N} = C_0 + D_0 + \dots + C_{N-1} + D_{N-1}.$$

Set

$$\begin{aligned} \alpha_k &= e^{-i\omega \tau_k + i\omega_k^s \tau_k} \\ \beta_k &= \int_0^{\tau_k} e^{-i\omega t + i\omega_k^s t} dt \\ \bar{\alpha}_k &= e^{-i\omega u_k} \\ \bar{\beta}_k &= \int_0^{u_k} e^{-i\omega t} dt \end{aligned}$$

Then

$$C_k = \beta_k \sigma_{k-1} \alpha_{k-1} \dots \sigma_0 \alpha_0$$

$$D_k = \xi_k \alpha_k \sigma_{k-1} \alpha_{k-1} \dots \sigma_0 \alpha_0.$$

We have

$$C_k \bar{C}_k = |\beta_k|^2$$

$$D_k \bar{D}_k = |\xi_k|^2$$

$$C_k \bar{D}_k = \beta_k \bar{\alpha}_k \bar{\xi}_k$$

$$D_k \bar{C}_k = \xi_k \alpha_k \bar{\beta}_k$$

and for $j > k$

$$C_j \bar{C}_k = \beta_j \sigma_{j-1} \alpha_{j-1} \dots \sigma_{k+1} \alpha_{k+1} \sigma_k \alpha_k \bar{\beta}_k$$

$$C_j \bar{D}_k = \beta_j \sigma_{j-1} \alpha_{j-1} \dots \sigma_{k+1} \alpha_{k+1} \sigma_k \bar{\xi}_k$$

$$D_j \bar{C}_k = \xi_j \alpha_j \sigma_{j-1} \alpha_{j-1} \dots \sigma_{k+1} \alpha_{k+1} \sigma_k \alpha_k \bar{\beta}_k$$

$$D_j \bar{D}_k = \xi_j \alpha_j \sigma_{j-1} \alpha_{j-1} \dots \sigma_{k+1} \alpha_{k+1} \sigma_k \bar{\xi}_k$$

We set

$$\alpha = E \alpha_k$$

$$\sigma = E \sigma_k$$

$$\beta = E \beta_k$$

$$\xi = E \xi_k$$

$$\tilde{\beta} = E \alpha_k \bar{\beta}_k$$

$$\tilde{\sigma} = E \sigma_k \bar{\xi}_k$$

$$\tilde{\beta} = E \beta_k \bar{\beta}_k$$

$$\tilde{\xi} = E \xi_k \bar{\xi}_k.$$

Using the assumptions on independence we get

$$J_N = \frac{1}{2\pi N (E u + E \tau)} \left[N \tilde{\beta} + N \tilde{\xi} + \right. \\ \left. + \left\{ \begin{aligned} &(N-1) \beta \sigma \tilde{\beta} + (N-2) \beta \sigma \alpha \sigma \tilde{\beta} + (N-3) \beta \sigma \alpha \sigma \alpha \sigma \tilde{\beta} + \dots \\ &+ (N-1) \beta \tilde{\xi} + (N-2) \beta \sigma \alpha \tilde{\xi} + (N-3) \beta \sigma \alpha \sigma \alpha \tilde{\xi} + \dots \\ &+ N \xi \tilde{\beta} + (N-1) \xi \alpha \sigma \tilde{\beta} + (N-2) \xi \alpha \sigma \alpha \sigma \tilde{\beta} + \dots \\ &+ (N-1) \xi \alpha \tilde{\xi} + (N-2) \xi \alpha \sigma \alpha \tilde{\xi} + (N-3) \xi \alpha \sigma \alpha \sigma \alpha \tilde{\xi} + \dots \end{aligned} \right\} \right. \\ \left. + \left[\begin{aligned} &\dots \\ &\dots \end{aligned} \right] \right]$$

By virtue of (3.2) this expression converges for $N \rightarrow \infty$ uniformly in ω to

$$(3.4) \quad \mathcal{J} = \frac{1}{2\pi \left(\frac{1}{c} + E\tau\right)} \left[\tilde{\beta} + \tilde{\xi} + \left\{ \beta \delta \tilde{\beta} + \beta \delta \alpha \delta \tilde{\beta} + \beta \delta \alpha \delta \alpha \delta \tilde{\beta} + \dots \right. \right. \\ \left. \left. + \beta \tilde{\xi} + \beta \delta \alpha \tilde{\xi} + \beta \delta \alpha \delta \alpha \tilde{\xi} + \dots \right. \right. \\ \left. \left. + \xi \tilde{\beta} + \xi \alpha \delta \tilde{\beta} + \xi \alpha \delta \alpha \delta \tilde{\beta} + \dots \right. \right. \\ \left. \left. + \xi \alpha \tilde{\xi} + \xi \alpha \delta \alpha \tilde{\xi} + \xi \alpha \delta \alpha \delta \alpha \tilde{\xi} + \dots \right\} \right. \\ \left. + \overline{\{ \}} \right]$$

Now

$$\delta = E e^{-i\omega u} = c \int_0^\infty e^{-i\omega u - cu} du = \frac{c}{c+i\omega}$$

$$\xi = \tilde{\xi} = \frac{1}{c+i\omega} = \frac{\delta}{c}$$

$$\tilde{\xi} = \frac{2}{c^2 + \omega^2} = \frac{1}{c} \left(\frac{1}{c+i\omega} + \frac{1}{c-i\omega} \right) = \frac{\delta}{c^2} + \overline{\frac{\delta}{c^2}}$$

So

$$\mathcal{J} = \frac{1}{2\pi} \frac{c}{1+cE\tau} \left[\tilde{\beta} + \left\{ \left(\beta + \frac{1}{c}\right) (\delta + \delta \alpha \delta + \delta \alpha \delta \alpha \delta + \dots) \left(\tilde{\beta} + \frac{1}{c}\right) \right\} \right. \\ \left. + \overline{\{ \}} \right]$$

and finally

$$(3.5) \quad \mathcal{J} = \frac{1}{2\pi} \frac{1}{1+cE\tau} \left[c \tilde{\beta} + \left\{ (1+c\beta) \frac{1}{c+i\omega-c\alpha} (1+c\tilde{\beta}) \right\} + \overline{\{ \}} \right]$$

As $\tilde{\beta} = \beta$, the formula stated in the theorem follows at once.

If in (3.4) we had dropped all the terms in $\{ \}$, as Burkhardt did, we should have come to

$$\mathcal{J} = \frac{1}{2\pi} \frac{c}{1+cE\tau} \left[\tilde{\beta} + \frac{2}{c^2 + \omega^2} \right]$$

and this is exactly Burkhardt's formula.

The fact that \mathcal{J} is ≥ 0 and continuous is obvious. We have still to show that $\int \mathcal{J}(\omega) d\omega = 1$.

We go back to the equation (3.4). By Parseval's equality

$$\frac{1}{2\pi} \int \tilde{\beta}(\omega) d\omega = \frac{1}{2\pi} E \int |\beta(\omega)|^2 d\omega = E \int |\mathbb{1}[0, \tau] e^{i\omega s t}|^2 dt = E\tau$$

as $\beta(\omega)$ is the Fourier transform of $\mathbb{1}[0, \tau](t) e^{i\omega s t}$ and $\mathbb{1}[0, \tau](t) = 1$ for $t \in [0, \tau]$ and $= 0$ for t outside that interval.

As

$$\int \tilde{\xi}(\omega) d\omega = \int \frac{2 d\omega}{c^2 + \omega^2} = 2\pi/c,$$

we still have to check that

$$\int \{ \} d\omega = 0$$

By using

$$|\alpha \delta| \leq \alpha \sqrt{\frac{c^2}{c^2 + \omega^2}}$$

one immediately sees that $\int \{ \}$ may be split up into single terms.

Each term, however, vanishes. This follows from the following remarks:

- (i) $\hat{\alpha}$ is the Fourier transform of the function $ce^{-ct} \mathbb{1}_{\geq 0}(t)$, which is in $L^1 \cap L^2$.
- (ii) $\hat{\alpha}$ is the Fourier transform of the integrable measure $\hat{\alpha} = E e^{i\omega s \tau} d\tau$,
 $\langle \hat{\alpha}, f \rangle = E e^{+i\omega s \tau} f(\tau)$
 The support of $\hat{\alpha}$ is contained in \mathbb{R}_+

- (iii) $\hat{\beta}$ is the Fourier transform of the $L^1 \cap L^2$ -function $\hat{\beta}$
 $\hat{\beta}(t) = E \mathbb{1}[0, \tau](t) e^{i\omega s t}$, $|\hat{\beta}(t)| \leq 1$.

The support of $\hat{\beta}(t)$ is contained in \mathbb{R}_+

- (iv) By the convolution theorems the functions $\hat{\beta} \hat{\alpha}, \dots$ occurring in $\{ \}$ are Fourier transforms of continuous L^1 -functions with support in \mathbb{R}_+ , hence of functions which vanish in the origin.

As the value at the origin of a function is equal to the integral of its Fourier transform, there follows $\int \hat{\beta} \hat{\alpha} = 0, \dots$

§ 4. Discussion

We now want to discuss (3.3) in the case of van der Waals broadening. Then ω^s and τ are random quantities depending on the impact parameter ρ by equation (1.4'). The distribution of ρ is given by

$$(4.1) \quad E f(\rho) = \frac{1}{\pi \rho_0^2} \int_0^{\rho_0} 2\pi \rho' d\rho' f(\rho').$$

So

$$(4.2) \quad E\tau = \frac{1}{\pi \rho_0^2} \int_0^{\rho_0} \frac{3\rho'}{2v} 2\pi \rho' d\rho' = \rho_0/v.$$

Recall that the condition of non-overlapping perturbations is equivalent (2.6) to $cE\tau = n\pi\rho_0^3 \ll 1$. As (by (3.1)) the quantity $|\tilde{\beta}(\omega)|$ is bounded by $E\tau$ equation (3.3) may be simplified to

$$\tilde{J}(\omega) = \frac{1}{2\pi} \left(c\tilde{\beta} + \frac{1}{c+i\omega-c\alpha} + \frac{1}{c-i\omega-c\bar{\alpha}} \right)$$

or

$$(4.3) \quad \tilde{J}(\omega) = \frac{c}{2\pi} \tilde{\beta} + \frac{1}{\pi} \frac{c(1-\operatorname{Re}\alpha)}{(\omega-c\operatorname{Im}\alpha)^2 + c^2(1-\operatorname{Re}\alpha)^2}.$$

As $|\tilde{\beta}(\omega)| \leq E\tau^2$ and for frequencies $\omega \approx c$ the second term behaves like $1/c$, the ratio between the first and the second term is $\approx c^2 E\tau^2$, so the first term can be neglected for $\omega \approx c$. For these frequencies $\alpha = E e^{i\omega_s\tau - i\omega\tau}$ may be approximated by $E e^{i\omega_s\tau}$ and $c(1-\alpha)$ by

$$(4.4) \quad A = n v \int_0^{\infty} \left(1 - \exp\left(\frac{3\pi i}{8} \frac{c}{v\rho^5}\right) \right) 2\pi \rho d\rho,$$

replacing the upper limit ρ_0 of the integral by $+\infty$. So for small frequencies of magnitude $\leq c$ the impact approximation holds.

For large frequencies, $\omega \approx \frac{1}{E\tau}$, both terms of (4.3) are of order $c(E\tau)^2$, so the first term cannot be neglected. A detailed discussion shows that $\frac{c}{2\pi} \tilde{\beta}$ behaves for $\omega \rightarrow +\infty$ like $\frac{\pi^{3/2}}{4} n c^{1/2} \omega^{-3/2}$, so at least for $\omega > 0$ for large ω the term $\frac{c}{2\pi} \tilde{\beta}$ is larger than

the second term in (4.3) which behaves like c/ω^2 .

Proposition. For $\omega \rightarrow \infty$ one has

$$(4.5) \quad \frac{c\tilde{\beta}}{2\pi} = \frac{\pi^{3/2}}{4} n C^{1/2} \omega^{-3/2} + O(\omega^{-\frac{16}{9}}).$$

Proof: One has

$$(4.6) \quad \frac{c}{2\pi} \tilde{\beta} = \frac{nv}{2\pi} \int_0^{\rho_0} 2\pi \rho d\rho \frac{\sin^2(\omega - \omega^s) \tau/2}{(\omega - \omega^s)^2}$$

with $\omega^s = \frac{\pi}{4} C \rho^{-6} = C' \rho^{-6}$, $\tau = \frac{3\rho}{2v}$. Putting $x = C' \rho^{-6}$ one gets

$$(4.7) \quad \frac{c}{2\pi} \tilde{\beta} = \frac{nv}{2\pi} \int_{\omega_0}^{\infty} 2\pi \frac{1}{6} C^{12/6} x^{-8/6} dx \frac{\sin^2[(\omega-x) 3C^{1/6}/4v x^{1/6}]}{(\omega-x)^2}$$

with $\omega_0 = C' \rho_0^{-6}$

The key to the following proof is the observation that

$$(4.8) \quad \frac{\sin^2 \alpha x/2}{x^2} \approx 2\pi \alpha \delta(x)$$

So

$$(4.9) \quad \frac{c\tilde{\beta}}{2\pi} \approx nv \int_{\omega_0}^{\infty} 2\pi C^{12/6} x^{-8/6} dx \frac{3C^{1/6}}{6} \frac{\delta(x-\omega)}{2v x^{1/6}} = \frac{\pi}{2} n \sqrt{C'} \omega^{-3/2}$$

and this is but a factor the true asymptotic behaviour as it has been pointed out in § 1. We proceed now to the actual proof. Assume

$$(4.10) \quad 0 < \lambda < 1$$

Then for ω large enough the integral in (4.7) splits

$$(4.11) \quad \int_{\omega_0}^{\infty} = \int_{\omega_0}^{\omega - \omega^\lambda} + \int_{\omega + \omega^\lambda}^{\infty} + \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} = \underline{I} + \underline{II} + \underline{III}.$$

Now

$$(4.12) \quad |\underline{I}| \leq \text{const } \omega^{-4/3} \int_{\omega^\lambda}^{\infty} \frac{dx}{x^2} = O(\omega^{-4/3 - \lambda})$$

and

$$\begin{aligned}
 |\underline{\text{II}}| &\leq \text{const} \int_{\omega_0}^{\omega - \omega^\lambda} x^{-4/3} (x - \omega)^{-2} dx \\
 &= \text{const} \omega^{-10/3} \int_{\omega_0/\omega}^{1 - \omega^{\lambda-1}} \frac{x^{-4/3}}{(1-x)^2} dx \\
 &= \text{const} \omega^{-\frac{10}{3}} \left(\int_{\omega_0/\omega}^{1/2} + \int_{1/2}^{1 - \omega^{\lambda-1}} \right)
 \end{aligned}$$

so

$$(4.13) \quad \underline{\text{II}} = O(\omega^{-3}) + O(\omega^{-\frac{7}{3} - \lambda})$$

Put $3C^{1/6}/2v = c$. Then

$$\underline{\text{III}} = \omega^{-\frac{4}{3}} \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} \frac{\sin^2(c x^{-\frac{1}{6}}(x - \omega)/2)}{(x - \omega)^2} dx + O(\omega^{-8/3 + 2\lambda})$$

as

$$\begin{aligned}
 &\left| \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} \frac{\sin^2(c x^{-\frac{1}{6}}(x - \omega)/2)}{(x - \omega)^2} (x^{-\frac{4}{3}} - \omega^{-\frac{4}{3}}) dx \right| \\
 &\leq \frac{c^2}{4} (\omega - \omega^\lambda)^{-2/6} \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} \left| \frac{4}{3} \int_{\omega}^x \xi^{-\frac{7}{3}} d\xi \right| dx.
 \end{aligned}$$

Furthermore,

$$\begin{aligned}
 &\left| \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} dx \frac{\sin^2[c x^{-\frac{1}{6}}(x - \omega)/2] - \sin^2[c \omega^{-\frac{1}{6}}(x - \omega)/2]}{(x - \omega)^2} \right| \\
 &\leq \int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} dx \left| \frac{1}{6} \int_{\omega}^x d\xi \frac{c \xi^{-7/6}(x - \omega) \sin(c \xi^{-1/6}(x - \omega))}{(x - \omega)^2} \right| \\
 &= O(\omega^{2\lambda - 8/6})
 \end{aligned}$$

and

$$\int_{\omega - \omega^\lambda}^{\omega + \omega^\lambda} \frac{\sin^2[c \omega^{-\frac{1}{6}}(x - \omega)/2]}{(x - \omega)^2} dx = 2\pi c \omega^{-1/6} + O(\omega^{-\lambda}).$$

So finally,

$$(4.14) \quad \underline{\text{III}} = 2\pi \omega^{-3/2} c + O(\omega^{2\lambda-8/3}) + O(\omega^{-\frac{4}{3}-\lambda})$$

and combining (4.12) - (4.14) one obtains

$$(4.15) \quad \frac{c\tilde{\beta}}{2\pi} = \frac{3}{6} n v C' \frac{2}{6} + \frac{1}{6} / 2v \quad 2\pi \omega^{-\frac{3}{2}} \\ + O(\omega^{-\frac{4}{3}-\lambda}) + O(\omega^{2\lambda-8/3})$$

In order to obtain a minimum choose $\lambda = \frac{4}{9}$. Then (4.5) results.

L i t e r a t u r e

- |1| Burkhardt, G.
Über die Stoßverbreiterung und Statistische Verbreiterung von Spektrallinien. Z. Physik 115, 592 (1940).
- |2| Traving, G.
Über die Theorie der Druckverbreiterung von Spektrallinien. G. Braun, Karlsruhe, 1960.
- |3| Waldenfels, W. von
An Approach to the Theory of Pressure Broadening of Spectral Lines. To appear in Probability and Information Theory II, Lecture Notes in Math., Springer.

Universität Heidelberg
Institut für Angewandte Mathematik
69 Heidelberg / BRD
Im Neuenheimer Feld 5