THEORY OF BROADENING OF SPECTRAL LINES

V. V. YAKIMETS

Moscow Engineering–Physical Institute

Submitted to JETP editor May 14, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 1469–1475 (November, 1966)

The Green function method is applied to the problem of the broadening of spectral lines which is caused by the interaction between the atom and the surrounding particles. We find the line shape caused by the pressure of foreign gases in the binary collision approximation.

ONE of the basic methods used for solving concrete problems in the theory of the broadening of spectral lines[1)] is the well-known Fourier analysis method which is based upon a consideration of the intensity of the radiation as the Fourier components of the correlation function. In the present paper we consider the correlation function as a particular case of the two-particle Green function which can be evaluated by diagram techniques. In such an approach one can, at least when using the binary collision approximation, sum an infinite number of important terms. (We note that this procedure to some extent corresponds to the method suggested by Anderson[2] for the calculation of the correlation function in the framework of the theory of collisions.) In this way we succeed in obtaining in the binary approximation from a consistent quantum-mechanical point of view a general solution of the problem of the broadening of lines by a foreign gas without making additional simplifying assumptions used in the impact or statistical theory.

1. We consider the transition between two degenerate states of an atom: an initial state a and a final state b with, respectively α and β as their degree of degeneracy. Using the general methods of perturbation theory we can show that the intensity distribution in the line corresponding to such a transition is determined by the expression (see [1], Sec. 37)

$$I(\omega)=\frac{2\pi}{\hbar}\sum_{\alpha\alpha'\beta\beta'}\mathbf{P}^{*}_{\beta'\alpha'}\mathbf{P}_{\beta\alpha}W_{\beta\alpha\alpha'\beta'}(\omega), \tag{1}$$

$$W_{\beta\alpha\alpha'\beta'}(\omega)=\int_{-\infty}^{\infty}\frac{dt}{2\pi}e^{-i\omega t}\,\mathrm{Sp}\Big\{\exp\Big[\beta\Big(\Omega+\sum_i\mu_iN_i-H\Big)\Big]\cdot$$
$$\times\sum_{\mathbf{pp}_1}a^{+}_{\alpha'\mathbf{p}_1+\mathbf{k}}(0)\,a_{\beta'\mathbf{p}_1}(0)\,a_{\beta\mathbf{p}}{}^{+}(-t)\,a_{\alpha\mathbf{p}+\mathbf{k}}(-t)\Big\}, \tag{2}$$

where $\mathbf{P}_{\alpha\beta}$ is the matrix element of the dipole moment of the atom evaluated using the unperturbed wave functions $\psi_\alpha(\mathbf{r})$ and $\psi_\beta(\mathbf{r})$; $a^{+}_{\alpha\mathbf{p}}(t)$ and $a_{\alpha\mathbf{p}}(t)$ the creation and annihilation operators of the atom (in the state α with c.m.s. momentum $\mathbf{p}$) in the Heisenberg representation; and H the total Hamiltonian of the system (atom and particles surrounding it). The averaging over the initial state is performed with the density matrix

$$\rho=\exp\Big[\beta\Big(\Omega+\sum_i\mu_iN_i-H\Big)\Big],\quad \beta=1/T.$$

One sees easily that W can be expressed in terms of the two-particle Green function with pairwise coinciding times

$$K_{\beta\alpha\alpha'\beta'}(\mathbf{k},t)=-i\,\mathrm{Sp}\Big\{\rho T_t$$
$$\times\sum_{\mathbf{pp}_1}a^{+}_{\alpha'\mathbf{p}_1-\mathbf{k}}(0)\,a_{\beta'\mathbf{p}_1}(0)\,a_{\beta\mathbf{p}}{}^{+}(-t)\,a_{\alpha\mathbf{p}-\mathbf{k}}(-t)\Big\} \tag{3}$$

as follows (we have omitted the indices for the sake of simplicity):

$$W(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^{\infty}dt\,e^{-i\omega t}iK(-\mathbf{k},t)$$
$$=\frac{1}{\pi}\mathrm{Re}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\frac{K(-\mathbf{k},\omega')}{\omega+\omega'-i\delta}. \tag{2'}$$

Bearing in mind that K is connected with the retarded Green function[3, 4] K^R, which is analytical in the upper ω-halfplane, by the relation*

[1)]An exposition of the basic theory and references to a number of surveys and original papers can be found in Sobel'man's book.[1]

*cth ≡ coth.

$$K(\omega) = -\operatorname{Re} K^R(\omega) - i \operatorname{cth} \frac{\beta(\omega + \mu_a - \mu_b)}{2} \operatorname{Im} K^R(\omega),$$

we get

$$W(\omega) = \frac{1}{\pi} \frac{\operatorname{Im} K^R(-\mathbf{k}, -\omega)}{1 - \exp[\beta(\omega + \mu_b - \mu_a)]}, \tag{4}$$

where μ_a and μ_b are the chemical potentials of the atoms in the initial and final states. Equations (1) and (4) solve the problem considered in a general form.

2. The solution of the problem of the broadening of a line by the pressure of a foreign gas can be reduced to finding the following temperature-dependent Green function:[2)]

$$\mathcal{K}_{\beta\alpha\alpha'\beta'}(\mathbf{k}, \omega_m) = -\frac{1}{\beta} \sum_n \int d\mathbf{p}\, G_{\beta\beta'}(\mathbf{p}, \varepsilon_n) G_{\alpha\alpha'}(\mathbf{p} - \mathbf{k}, \varepsilon_n - \omega_m),$$

$$d\mathbf{p} = \frac{d^3p}{(2\pi\hbar)^3}, \tag{5}$$

where, for instance, $G_{\alpha\alpha'}(\mathbf{p}, \epsilon_n)$ is the exact single-particle Green function characterizing the transition of an atom from the state α to the state α' under the influence of the interaction with the medium. To fix the ideas we shall consider the atoms to be a Fermi gas, i.e., we shall put $\epsilon_n = \pi i(2n+1)/\beta$.

It is well known that the function $K^R(\omega)$ is defined as the analytical continuation into the upper halfplane with an infinite set of points on the real axis where its value is given by the relations

$$K^R(\omega_m + \mu_b - \mu_a) = \mathcal{K}(\omega_m), \qquad \omega_m = 2\pi i m / \beta. \tag{6}$$

Calculations, using Eq. (5), are in the general case a very complicated problem. They can be performed appreciably more easily only in the binary collision approximation (the conditions for its applicability will be elucidated later). In that approximation the expressions for the G-functions can be obtained in a way similar to the one used, for instance, by Galitskiĭ[5] for the zero-temperature case. To simplify the subsequent calculations we neglect the perturbation of the final level so that

$$G_{\beta\beta'}(p) = \frac{\delta_{\beta\beta'}}{\varepsilon_n - \xi_b(\mathbf{p})},$$

$$\xi_b(\mathbf{p}) = \frac{\mathbf{p}^2}{2m_1} - \mu_b, \quad p = (\mathbf{p}, \varepsilon_n), \tag{7}$$

where m_1 is the mass of the emitting atom. It is convenient to consider the functions $G_{\alpha\alpha'}$ as the matrix elements of the operator G_a acting on the variable state of the atom. This operator has the form

$$G_a(p) = [\varepsilon_n - \xi_a(\mathbf{p}) - \Sigma(p)]^{-1},$$

$$\xi_a(\mathbf{p}) = \frac{\mathbf{p}^2}{2m_1} + \omega_0 - \mu_a, \tag{8}$$

where ω_0 is the energy of the excited state of the atom. The self-energy part Σ is equal to

$$\Sigma(p) = \int d\mathbf{p}_1 n_{\mathbf{p}_1} \operatorname{Re} f(\mathbf{p}_c, \mathbf{p}_c) + \oint d\mathbf{p}_1\, d\mathbf{k} \frac{n_{\mathbf{p}_1} |f(\mathbf{p}_c, \mathbf{k})|^2}{k^2/2\mu - p^2/2\mu}$$
$$+ \int d\mathbf{p}_1\, d\mathbf{k} \frac{n_{\mathbf{p}_1} |f(\mathbf{p}_c, \mathbf{k})|^2}{\varepsilon_n - \xi_a(g m_1/m + \mathbf{k}) - \varepsilon(g m_2/m - \mathbf{k}) + \varepsilon(\mathbf{p}_1)}. \tag{9}$$

Here m_2 is the mass of the foreign particles, $m = m_1 + m_2$,

$$\mu = \frac{m_1 m_2}{m}, \quad \varepsilon(\mathbf{p}) = \frac{p^2}{2m_2}, \quad \mathbf{p}_c = \frac{m_2 \mathbf{p} - m_1 \mathbf{p}_1}{m},$$
$$\mathbf{g} = \mathbf{p} + \mathbf{p}_1, \quad n_{\mathbf{p}} = \{\exp[\beta(\varepsilon_{\mathbf{p}} - \mu)] + 1\}^{-1};$$

the scattering amplitude of two particles in vacuo is

$$f(\mathbf{p}, \mathbf{k}) = \int d^3r e^{-i\mathbf{p}\mathbf{r}} V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}), \tag{10}$$

$V(\mathbf{r})$ is the interaction potential, $\psi_{\mathbf{k}}(\mathbf{r})$ the wavefunction of the relative motion of the particles, and $\mathbf{k}$ their relative momentum at infinity.[3)]

If we now in Eq. (5) sum over n in the usual manner,[6] we find

$$\mathcal{K}(k) = \int \frac{d\mathbf{p}}{\exp[-\beta\xi_b(\mathbf{p})] + 1}$$
$$\times \int_{-\infty}^{\infty} \frac{dx}{e^{\beta x} + 1} \frac{1}{\pi} \operatorname{Im} G_a(\mathbf{p} - \mathbf{k}; x - i\delta)$$
$$\times \frac{\exp[\beta(-\xi_b(\mathbf{p}) + x)] - 1}{\omega_m - \xi_b(\mathbf{p}) + x}. \tag{11}$$

Using this to determine the function K^R and substituting its value into (4) we get an expression for the line shape which describes at the same time the influence of Doppler broadening and pressure effects,

[2)] See, for instance, [3,4] for a definition and for the diagram technique for temperature-dependent Green functions and their connection with retarded Green functions.

[3)] The function V (see Eq. (28)) and the functions ψ and f connected with it are operators in the same sense as G_a. To simplify the formulae we omit here and henceforth the appropriate indices.

$$W(\omega)=\int d\mathbf{p}\frac{1-n_b(\mathbf{p})}{\exp[\beta(\Delta\omega+\xi_a(\mathbf{p}))]+1}$$
$$\times\frac{1}{\pi}\operatorname{Im}G_a(\mathbf{p}+\mathbf{k};\ \Delta\omega+\xi_a(\mathbf{p})-i\delta),$$
$$\Delta\omega\equiv\omega-\omega_0. \quad (12)$$

If there is no interaction

$$\pi^{-1}\operatorname{Im}G_a\to\delta(\Delta\omega+\xi_\mathbf{p}-\xi_{\mathbf{p}+\mathbf{k}}),$$

and (12) changes to

$$W(\omega)=\int d\mathbf{p}[1-n_b(\mathbf{p})]n_a(\mathbf{p}+\mathbf{k})\delta(\Delta\omega+\xi_\mathbf{p}-\xi_{\mathbf{p}+\mathbf{k}}), \quad (13)$$

which determines the Doppler contour of the line (at any temperature). In accordance with the problem considered we shall be interested in the opposite limiting case when the line width is caused mainly by the interaction between the atom at the particles surrounding it. In that case we can neglect $\mathbf{k}$ in the argument of the G-function and take it at the point $p = p_0$ outside the integral sign and we find

$$W(\omega)=n_a\pi^{-1}\operatorname{Im}G_a(p_0;\ \Delta\omega+\xi_a(p_0)-i\delta), \quad (14)$$

where n_a is the number density of the excited atoms. We have assumed here that in the whole range which is practically accessible

$$|\Delta\omega|\ll 1/\beta. \quad (15)$$

If we introduce special symbols for the real and the imaginary parts of Σ

$$\Sigma=\Delta+i\gamma,$$

we can write for W referred to one atom the characteristic expression

$$W(\omega)=\frac{1}{\pi}\frac{\gamma(\Delta\omega)}{(\Delta\omega-\Delta)^2+\gamma^2(\Delta\omega)}. \quad (16)$$

We have thus reached the interesting conclusion that in the binary approximation the line shape is completely described by the dispersion formula in the usual form but with a width γ depending on the frequency.

3. If we bear in mind in what follows the application of the results obtained to the broadening due to electrons we can put $m_1 \gg m_2$, i.e., assume the atom to be at rest, when we evaluate Σ. The equations for Δ (bearing (15) in mind) and γ then become

$$\Delta=\int d\mathbf{p}\,n_\mathbf{p}\operatorname{Re}f(\mathbf{p},\mathbf{p});$$
$$\gamma=\pi\int d\mathbf{q}\,d\mathbf{p}\,|f(\mathbf{p},\mathbf{p}-\mathbf{q})|^2 n_\mathbf{p}\delta(\Delta\omega+\varepsilon_\mathbf{p}-\varepsilon_{\mathbf{p}-\mathbf{q}}). \quad (17)$$

We shall see below that because of the inequality (15) the effective interaction potential V_0 is always much less than the average energy, $\epsilon_0 \approx \beta^{-1}$ of the thermal motion of the perturbing particles. This fact makes it possible to use high-energy perturbation theory[7] to find the functions $\psi_\mathbf{k}(\mathbf{r})$. If the particle moves along the x-axis

$$\psi_\mathbf{k}(\mathbf{r})=\exp\left\{ikx-\frac{i}{k}\int^x \tilde{V}(x')dx'\right\},\quad \mathbf{r}=(\rho,x),$$
$$\tilde{V}(x)=\exp\left\{\frac{i}{k}H_a x\right\}V(\mathbf{r})\exp\left\{-\frac{i}{k}H_a x\right\}, \quad (18)$$

where H_a is the Hamiltonian of the free atom. If we use this expression to evaluate the scattering amplitude (10) and substitute the result into (7) we find after straightforward transformations ($x = vt$)

$$\gamma=\frac{1}{2}\int v\,d\mathbf{p}\,n_\mathbf{p}\int d^2\rho$$
$$\times\left|\int_{-\infty}^{\infty}dt\,\tilde{V}(t)\exp\left\{i\Delta\omega t-i\int^t\tilde{V}(t')dt'\right\}\right|^2, \quad (19)$$
$$\Delta=\int v\,d\mathbf{p}\,n_\mathbf{p}\int d^2\rho\sin\left\{\int_{-\infty}^{\infty}\tilde{V}(t)dt\right\}. \quad (19')$$

We see easily that the collision theory formula is obtained from this in the limit $\Delta\omega\to 0$.

The result of a study of the relations obtained shows the following (in the adiabatic approximation $V\propto C_s r^{-s}$). When $s\geq 3$ the short-range character of the potential has as consequence that we can put $\Delta\omega = 0$ in (19) in the whole interval

$$\Delta\omega\ll\Omega\equiv C_s\rho_0^{-s},\quad \rho_0=\left(\frac{C_s}{v_0}\right)^{1/(s-1)},\quad v_0=\left(\frac{2}{m_2\beta}\right)^{1/2} \quad (20)$$

(ρ_0 is the so-called Weisskopf radius) and hence in the given interval

$$\gamma=nv_0\int d^2\rho\,\{1-\cos\eta(\rho)\},$$
$$\eta(\rho)=B\left(\frac{1}{2},\frac{s-1}{2}\right)\frac{C_s}{v_0\rho^{s-1}}, \quad (21)$$

where $B(x, y)$ is a β-function. The characteristic impact parameter can be determined from $\eta(\rho)\approx 1$ and as to order of magnitude is equal to ρ_0. In the opposite limiting case of high frequencies $\Delta\omega\gg\Omega$ we find by applying the method of steepest descent on the real axis

$$\gamma=|\Delta\omega|^{2\cdot 4\pi^2 nC_s^{3/s}/s}|\Delta\omega|^{1+3/s}, \quad (22)$$

where now the role of the characteristic impact parameter is played by the quantity $\rho_0(\Omega/\Delta\omega)^{1/s} < \rho_0$. Substituting (22) into Eq. (16) and neglecting in the denominator of the latter the shift and width as compared to $\Delta\omega$ we find a statistical distribution in the wings of the line.

It is clear from Eq. (19) that for large $\Delta\omega$ we have $V_0 \sim \Delta\omega$ and because of condition (15) the above-mentioned inequality $V_0 \ll \epsilon_0$ is clearly satisfied. Moreover, since ρ_0 is the effective impact parameter in the problem we conclude that the calculations given here which are based upon the binary collision approximation are valid provided ρ_0 is much less than the average distance between the particles $n^{-1/3}$. In that case $\gamma \ll \Omega$ and the main part of the integral intensity is concentrated in the collision region. The dependence of γ on $\Delta\omega$ is thus unimportant if $s \geq 3$.

The case $s = 2$ (broadening of a hydrogen-like spectrum in a plasma by the linear Stark effect) has specific peculiarities, which make it necessary to take the dependence $\gamma(\Delta\omega)$ into account in the region $\Delta\omega \ll \Omega$. We note first of all that if $\Delta\omega$ is sufficiently small it follows from (21) that the width γ for $s = 2$ is determined by an integral which at large ρ has a logarithmic divergence (the divergence in (19′) for the line shift is unimportant as it completely vanishes when we take the non-adiabaticity of the interaction Δ into account). This divergence occurs in the case of a high-temperature plasma because the screening of the charge in the system of perturbing particles has not been taken into account and it can be removed by cutting off the integral at the Debye radius $\rho_D = (4\pi ne^2\beta)^{-1/2} \gg \rho_0$.[4)]

On the other hand, for impact parameters

$$\rho \gg \rho_0 = C_2 / v_0 \tag{23}$$

we can use the Born approximation to evaluate the scattering amplitude (16). Indeed, $V \propto C_2\rho^{-2}$ and the condition for the applicability of perturbation theory $|V| \ll v/\rho$ leads immediately to the inequality (23). Moreover, in the region where perturbation theory is valid (when the interactions between the particles and the atom are completely additive) and for not too large $\Delta\omega$ the most important contribution to the intensity $I(\Delta\omega)$ must be given by collisions with impact parameters

$$\rho \lesssim v_0\tau_0 = v_0 / \Delta\omega \equiv \rho_\omega. \tag{24}$$

The frequency range in which the Born approximation is applicable is thus determined by conditions (23) and (24) in conjunction: $\Delta\omega \ll \Omega$ which is exactly the same as the interval (20). Noting that then $\rho_0 \ll \rho_\omega, \rho_D$ we get (in the adiabatic approximation) from (19)

$$\gamma = \frac{n\pi^3 C_2^2}{v_0}\int_{\rho_0}^{\rho_D}\frac{d\rho}{\rho}\exp\left(-\frac{2\rho}{\rho_\omega}\right) \cong \frac{n\pi^3 C_2^2}{v_0}\left[\ln\frac{\rho_\omega}{2\rho_0} + \mathrm{Ei}\left(-\frac{2\rho_D}{\rho_\omega}\right)\right], \tag{25}$$

where $\mathrm{Ei}(x)$ is the exponential-integral. The collision theory relation

$$\gamma = \frac{n\pi^3 C_2^2}{v_0}\ln\frac{\rho_D}{\rho_0} \tag{26}$$

is valid provided $\rho_\omega \gg \rho_D$ which corresponds to $\Delta\omega \ll v_0/\rho_D \equiv \Omega_D$.

In the opposite limiting case ρ_ω plays the role of the cut-off parameter, as expected, and γ becomes

$$\gamma = \frac{n\pi^3 C_2^2}{v_0}\ln\frac{\Omega}{2\Delta\omega}, \quad \Omega_D \ll \Delta\omega \ll \Omega. \tag{27}$$

This expression is the same as the result obtained by Lewis[8] by a different method. One can easily show that for the densities of practical interest, for the case $n\rho_0^3 \ll 1$ the inequality $\Omega_D > \gamma$ is always valid so that the exact definition of the line shape (27) refers only to the wings of the line. For instance, in the temperature range 0.5 to 4.10^4 °K which is of practical interest and for densities of 10^{15} to 10^{18} cm^{-3}, when $\ln(\rho_D/\rho_0) \cong \ln(n^{-1/3}/\rho_0)$ we can approximately write

$$\Omega : \Omega_D : \gamma \cong 1 : h^{1/3} : h, \quad h \equiv n\rho_0^3 \ll 1.$$

In conclusion we give an expression for the operator γ taking the non-adiabatic perturbation into account. If we follow Griem et al.[9] and put in (25)

$$\hbar V(t) = e^2\mathbf{r}_a\frac{\boldsymbol{\rho} + \mathbf{v}t}{(\rho^2 + v^2t^2)^{3/2}}, \tag{28}$$

where $\mathbf{r}_a$ is the radius vector of the atomic electron and if we perform the necessary operations we find

$$\gamma = \frac{16ne^4}{3v_0\hbar^2}\left\{\ln\frac{2\rho_\omega}{\rho_0} - \frac{\rho_D}{\rho_\omega}K_1\left(\frac{\rho_D}{\rho_\omega}\right)K_0\left(\frac{\rho_D}{\rho_\omega}\right)\right\}\mathbf{r}_a\cdot\mathbf{r}_a, \tag{29}$$

where $K_\nu(x)$ is a Macdonald function. In the interior region $\Delta\omega \ll \Omega_D$ (29) is the same as the expression given in [9].

---

4)A consistent account of the screening influence of the medium leads, generally speaking, to a $\Delta\omega$-dependence in the potential of the interaction between the atom and the particles in the plasma. However, in the interval $\Delta\omega \ll \Omega_D$ (see below) where this influence is important it turns out to be possible to put $\Delta\omega = 0$ in $V(r, \Delta\omega)$ which corresponds to the usual Debye screening of the charge.

The author expresses his great gratitude to V. M. Galitskiĭ and V. I. Kogan for valuable advice and discussions.

[1] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, 1963; English translation to be published by Pergamon Press.

[2] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[3] A. I. Larkin, JETP **37**, 264 (1959), Soviet Phys. JETP **10**, 186 (1960).

[4] Abrikosov, Gor'kov, and Dzyaloshinskiĭ, Metody kvantovoĭ teorii v statisticheskoĭ fiziki (Quantum Field Theoretical Methods in Statistical Physics), Fizmatgiz, 1962; English translation published by Pergamon Press.

[5] V. M. Galitskiĭ, JETP **34**, 151 (1958), Soviet Phys. JETP **7**, 104 (1958).

[6] E. S. Fradkin, Nucl. Phys. **12**, 465 (1959).

[7] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963; English translation published by Pergamon Press.

[8] M. Lewis, Phys. Rev. **121**, 501 (1961).

[9] Griem, Kolb, and Shen, Phys. Rev. **116**, 4 (1959).

Translated by D. ter Haar
177