THE DOPPLER WIDTH OF EMISSION AND ABSORPTION LINES

M. I. PODGORETSKII and A. V. STEPANOV

Joint Institute for Nuclear Research and P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor, August 3, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 561-566 (February, 1961)

We give a classical and quantum mechanical treatment of the influence of the Doppler effect on line shape. We consider the possibility of experimental observation of resonance absorption of γ rays in liquids.

THE purpose of the present work is to discuss certain features of the resonance absorption of γ rays and slow neutrons in liquids, where, since we have as our purpose only the formulation of the problems, we consider a highly idealized model of the liquid.

For a more pictorial description of the fundamental features of the phenomenon, it is logical to begin the treatment from the classical point of view. Let us assume that a certain system (an atom, nucleus, or other object) is part of a macroscopic system, and that it radiates electromagnetic waves of frequency ω_0. Then if the projection of its radius vector on the direction of emission changes as $x = x(t)$, the electromagnetic field can be written as

$$A \sim \exp\left[-i\omega_0 t - \lambda t/2 + i\varkappa x(t)\right], \qquad (1)$$

where $1/\lambda$ is the mean life, and κ is the wave number. Here it is assumed that a collision of the radiating atom with other atoms does not change its internal state, i.e., does not lead to collision broadening.

The corresponding Fourier component is

$$B \sim \int_0^\infty dt \exp\left[i\Omega t + i\varkappa x(t) - \frac{\lambda t}{2}\right],$$

where $\Omega = \omega - \omega_0$, and the spectral intensity is

$$J(\Omega) \sim \int_0^\infty \int_0^\infty dt\, dt' \exp\left\{i\Omega(t-t') - \frac{\lambda}{2}(t+t')\right\} \overline{\exp\{i\varkappa[x(t) - x(t')]\}}.$$

The quantity $\overline{\exp\{i\varkappa[x(t) - x(t')]\}}$ is given by

$$\overline{\exp\{i\varkappa[x(t)-x(t')]\}} = 1 + i\varkappa\overline{[x(t)-x(t')]} - \frac{\varkappa^2}{2!}\overline{[x(t)-x(t')]^2} - \frac{i\varkappa^3}{3!}\overline{[x(t)-x(t')]^3} + \cdots.$$

Assuming that the stochastic quantity $x(t) - x(t')$ has a Gaussian distribution, we obtain

$$\overline{\exp\{i\varkappa[x(t)-x(t')]\}} = 1 - \frac{\varkappa^2}{2!}\overline{[x(t)-x(t')]^2} + \frac{\varkappa^4}{4!}\overline{[x(t)-x(t')]^4} - \ldots = 1 - \left[\frac{\varkappa^2\sigma^2(|t-t'|)}{4}\right] + \frac{1}{2!}\left[\frac{\varkappa^2\sigma^2(|t-t'|)}{4}\right]^2 - \ldots = \exp\{-\varkappa^2\sigma^2(|t-t'|)/4\},$$

where

$$\sigma^2(|t-t'|)/2 = \overline{[x(t)-x(t')]^2}.$$

For the spectral intensity, we have the expression

$$J(\Omega) \sim \int_0^\infty \int_0^\infty dt\, dt' \exp\left\{i\Omega(t-t') - \frac{\lambda}{2}(t+t') - \frac{\varkappa^2}{4}\sigma^2(|t-t'|)\right\},$$

which, after some simple transformations, can be written as

$$J(\Omega) \sim \mathrm{Re}\int_0^\infty d\tau \exp\left\{-i\Omega\tau - \tfrac{1}{2}\lambda\tau - \tfrac{1}{4}\varkappa^2\sigma^2(\tau)\right\}. \qquad (2)$$

This relation describes the shape of the absorption line. In the classical case in which we are interested, it also follows immediately from Kirchhoff's theorem.* Relations like (2) can not only be used for the emission, absorption and scattering of photons, but also are applicable to particles, for example neutrons. However at this point it is more appropriate to go over to a quantum treatment, which we shall carry through for the case of absorption.†

It is well known[1] that the probability, per nucleus, for resonance absorption of a neutron (or γ quantum) can be written in the following form:

*In the quantum treatment one must take into account the fact that the emission of a photon, in general, results in a recoil which changes the state of motion of the radiating system and thus destroys the thermodynamic equilibrium (cf. later on p. 395). Under these conditions Kirschhoff's theorem is no longer valid.

†Emission can be treated analogously.

$$W(E) \sim \sum_i q_i \sum_m \frac{|(m|V|i)|^2}{(E - E_0 + \varepsilon^i - \varepsilon^m)^2 + \Gamma^2/4}. \quad (3)$$

Here $E = p^2/2m$ is the energy of the incident neutron; E_0 and Γ are the energy and width of the resonance level of the absorbing nucleus; $V = V(\mathbf{r}_n - \mathbf{r}_N)$ is the operator for the interaction between the neutron and the nucleus, and depends on the difference $\mathbf{r}_n - \mathbf{r}_N$ between the radius vectors of the neutron and nucleus; ϵ^i and $E_0 + \epsilon^m$ are the initial and final energies of the absorbing system. The summation over i corresponds to an averaging over initial states, each of which is taken with weight q_i.

Assuming that the motion of the incident neutron is described by the plane wave

$$\Psi_n(\mathbf{r}_n) \sim \exp(i\mathbf{p}\mathbf{r}_n/\hbar)$$

and using the standard representation of the δ function

$$\delta(\rho) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\tau\rho}d\tau,$$

we can transform the expression for $W(E)$ as follows:

$$W(E) \sim |M_0|^2 \sum_i q_i \sum_m \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{d\rho}{(E - E_0 + \hbar\rho)^2 + \Gamma^2/4} \times \int_{-\infty}^{+\infty} d\tau \exp\left\{i\tau\left[\rho + \frac{\varepsilon^m - \varepsilon^i}{\hbar}\right]\right\} \left|\int d\mathbf{r}\varphi_i(\mathbf{r})\varphi_m^*(\mathbf{r})e^{i\varkappa\mathbf{r}}\right|^2,$$

where $\varkappa = \mathbf{p}/\hbar$, M_0 is the matrix element of the interaction of the neutron with an isolated nucleus, and the functions $\varphi_i(\mathbf{r})$ and $\varphi_m(\mathbf{r})$ determine the "molecular" states of the absorbing system.

Writing the operator for the coordinate of the nucleus in the Heisenberg representation, and carrying out the summation over m, we obtain

$$W(E) \sim \int_{-\infty}^{+\infty} d\tau \int_{-\infty}^{+\infty} \frac{e^{i\tau\rho}d\rho}{(E - E_0 + \hbar\rho)^2 + \Gamma^2/4} F_s(\varkappa, \tau),$$

where

$$F_s(\varkappa, \tau) = \sum_i q_i (i|\exp\{-i\varkappa\mathbf{R}_N(0)\}\exp\{i\varkappa\mathbf{R}_N(\tau)\}|i).$$

The quantity $F_S(\kappa, \tau)$ can be expressed in terms of the function introduced by Van Hove:[2]

$$G_s(\mathbf{r}, \tau) = \left\langle \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{R}_N(0) - \mathbf{r}')\delta(\mathbf{r}' - \mathbf{R}_N(\tau))\right\rangle,$$

which has the significance of a self-diffusion function.* Namely

$$F_s(\varkappa, \tau) = \int d\mathbf{r}\, e^{i\varkappa\mathbf{r}} G_s(\mathbf{r}, \tau).$$

For the majority of isotropic dynamical systems, the function $G_S(\mathbf{r}, \tau)$ has a Gaussian shape with a dispersion which depends on the time.[3] Then

$$F_s(\varkappa, \tau) = \pi^{-3/2}\sigma^{-3}(\tau)\int d\mathbf{r} \exp\left\{i\varkappa\mathbf{r} - \frac{r^2}{\sigma^2(\tau)}\right\} = \exp\left\{-\frac{\varkappa^2\sigma^2(\tau)}{4}\right\},$$

which gives

$$W(E) \sim \int_{-\infty}^{+\infty} \frac{d\rho}{(E - E_0 + \hbar\rho)^2 + \Gamma^2/4} \int_{-\infty}^{+\infty} d\tau \exp\left\{i\rho\tau - \frac{\varkappa^2\sigma^2(\tau)}{4}\right\}.$$

Calculating the integral over ρ, and using the relation[2] $\sigma^*(\tau) = \sigma(-\tau)$, which guarantees the reality of the expression for $W(E)$, we finally obtain

$$W(E) \sim \mathrm{Re}\int_0^{\infty} d\tau \exp\left\{i\frac{E_0 - E}{\hbar}\tau - \frac{\Gamma\tau}{2\hbar} - \varkappa^2\frac{\sigma^2(\tau)}{4}\right\}. \quad (4)$$

For $\Gamma = 0$, the expression analogous to (4) determines the angular and energy distribution of neutrons in incoherent scattering. Computing $W(E)$ in the semiclassical approximation, i.e., treating the motion of the atoms of the material classically, one can show that formula (4) is identical with the result (2) of the consistently classical computation.

The information concerning the nature of the motion of the absorbing nuclei is contained in the quantity $\sigma^2(\tau)$, which can, in particular, be determined from experimental data on potential scattering of neutrons and from the shape of the resonance absorption line for neutrons and γ quanta. It is also not difficult to compute $\sigma^2(\tau)$ for certain simple models of the material.[3,4] Thus for an ideal gas,

$$\sigma^2(\tau) = v_0^2(\tau^2 - i\hbar\tau/kT), \quad (5)$$

where $v_0^2 = 2kT/M$, where M is the mass of the atom, k is the Boltzmann constant and T is the temperature.

For a harmonic oscillator of frequency Ω,

$$\sigma^2(\tau) = \frac{2\hbar}{M\Omega}\left\{\frac{\exp\{\hbar\Omega/kT\} + 1}{\exp\{\hbar\Omega/kT\} - 1}(1 - \cos\Omega\tau) - i\sin\Omega\tau\right\} \quad (6)$$

and finally, for an atom in a crystal lattice with cubic symmetry,

$$\sigma^2(\tau) = \frac{2\hbar}{M}\int_0^{\infty} \frac{\nu(\Omega)\,d\Omega}{\Omega}\left\{\frac{\exp\{\hbar\Omega/kT\} + 1}{\exp\{\hbar\Omega/kT\} - 1}(1 - \cos\Omega\tau) - i\sin\Omega\tau\right\}, \quad (7)$$

where $\nu(\Omega)$ is the normalized spectrum of eigenfrequencies of the crystal. Formulas (5) — (7) were obtained quantum mechanically.

The classical calculation[3] gives a somewhat different result in each of these cases:

*We should remind the reader that the argument of the δ function contains the quantum mechanical operator $\mathbf{R}_N(\tau)$ in the Heisenberg representation; since these are taken at different times, they do not commute with one another.

$$\sigma_{cl}^2(\tau) = v_0^2\tau^2, \quad (5')$$

$$\sigma_{cl}^2(\tau) = (2v_0^2/\Omega^2)(1 - \cos\Omega\tau), \quad (6')$$

$$\sigma_{cl}^2(\tau) = 2v_0^2\int_0^\infty \frac{\nu(\Omega)\,d\Omega}{\Omega^2}(1 - \cos\Omega\tau). \quad (7')$$

The main difference between the quantum mechanical and classical formulas is the appearance in the former of an imaginary part, which arises as a result of the noncommutativity of the operators. Physically, as it is not difficult to show for the example of the ideal gas, the imaginary part takes account of the recoil of the atom, i.e., the back reaction of the radiation on the matter. From their physical meaning, the classical expressions must be real ($\sigma_{cl}^2(\tau) \sim \overline{|\mathbf{r}(\tau) - \mathbf{r}(0)|^2}$).

It is not difficult to show that at high temperatures and after long times ($\tau \gg \hbar/kT$ in the case of a gas, and $\tau \gg 1/\Omega_{av}$ for the case of a crystal) the imaginary part is small. It should be mentioned that in the case of the oscillator and the crystal, the quantum effects do not disappear completely for $\tau \to \infty$, since formulas (6) and (7) contain the effective temperature

$$T_{eff}(\Omega) = \frac{\hbar\Omega}{2k}\frac{\exp\{\hbar\Omega/kT\} + 1}{\exp\{\hbar\Omega/kT\} - 1}.$$

At short times, the imaginary part dominates in $\sigma^2(\tau)$.

Substituting in (4) the values of $\sigma^2(\tau)$ for the gas and the crystal, we arrive at the well known expressions for the probability of absorption of slow neutrons which were obtained by Bethe and Placzek[5] and Lamb.[6] These same formulas are also suitable for describing the resonance absorption of γ quanta in gaseous and crystalline samples.[7,8]

Let us now consider an absorbing system which is diffusing inside a compressed gas or a liquid (which for simplicity we treat as a highly compressed gas). Because of the complexity of a consistent quantum mechanical approach, we shall compute the quantity $\sigma^2(\tau)$ classically, using the Langevin equation

$$\ddot{\mathbf{r}} + \eta\dot{\mathbf{r}} = \mathbf{f},$$

where $\mathbf{f}$ is the random force, $\eta = kT/MD$, and D is the diffusion coefficient. Then, as shown by Chandrasekhar,[9]

$$\sigma^2(\tau) = 4D[\tau - (1 - e^{-\eta\tau})/\eta]. \quad (8)$$

Substituting (8) in (2), we get

$$J(\Omega) \sim \mathrm{Re}\int_0^\infty d\tau \exp\left\{i\Omega\tau - \lambda\tau/2 - \varkappa^2 D\left[\tau - \frac{1 - e^{-\eta\tau}}{\eta}\right]\right\}. \quad (9)$$

If collisions are not important, formula (9) leads to the usual formula, which is valid for an ideal gas. In the opposite limiting case, the condition

$$kT/MD^2\varkappa^2 \approx (\Lambda/2\pi L)^2 \gg 1 \quad (10)$$

is satisfied, where Λ is the wave length and L is the mean free path. Then (9) goes over into

$$J(\Omega) \sim \mathrm{Re}\int_0^\infty d\tau \exp\left\{i\Omega\tau - \left(\frac{\lambda}{2} + \varkappa^2 D\right)\tau\right\},$$

which leads to*

$$J(\Omega) \sim [\Omega^2 + (\lambda/2 + \varkappa^2 D)^2]^{-1}. \quad (11)$$

If the damping is weak, the width of the line is of the order of $\varkappa^2 D$, which differs from the usual Doppler width $\varkappa(kT/M)$ by the small factor L/Λ.

Under conditions where collisions are unimportant, the absorbing atom can be assumed to be free, and the absorption of the γ quantum is accompanied by a recoil

$$\Delta\omega = \hbar\omega_0^2/2Mc^2. \quad (12)$$

If the absorption takes place in the presence of an interaction between the absorbing system and some other body, the recoil momentum is distributed over the two bodies, which results in an increase of the effective mass and a consequent reduction of the shift $\Delta\omega$.

As the ratio L/Λ decreases, the collisions become more important, and the absorbed photon interacts effectively with more and more of the atoms in the material, which results in a further increase in the effective mass M_{eff}. The latter in turn is associated with a reduction in the Doppler width, which is of order $M_{eff}^{1/2}$, and with a much more rapid drop in the shift due to recoil, which is of order M_{eff}^{-1}. One may therefore expect that when condition (10) is satisfied the recoil leads to practically no shift of the center of the line.

For soft γ rays, condition (10) may be satisfied in liquids, if we assume that the diffusion model of the liquid gives any sort of description of the situation.[12] It then follows that it may be possible to observe resonance absorption of γ rays when working with a liquid source and absorber. We may expect that the conditions for observing resonance absorption in this case will be much more favorable than in a gas, disregarding for the moment the fact that it will be possible to use much stronger sources. First of all, in working with gases one must somehow compensate the recoil,

*For the case of $\lambda = 0$ this formula was given in the paper of Wittke and Dicke,[10] A more detailed analysis of the limiting cases of formula (9) was given by Podgoretskiĭ and Stepanov.[11]

which makes the experiment more difficult. This is not necessary in liquids. Secondly the intensity of resonance absorption in liquids should be considerably stronger than in gases, since the line width is much smaller.

The resonance absorption of γ quanta and neutrons can be used to study the mechanism of transfer in the liquid. Of particular interest in this connection are experiments of the type of resonance absorption of γ quanta in Kr^{83} ($E_\gamma = 9.3$ kev, $N_e/N_\gamma \sim 10$, $T_b = -151°C$, $T_m = -157°C$). The fact that the boiling point is close to the melting point enables us to eliminate temperature effects and to investigate the dependence of resonance absorption on the state of aggregation.

The authors thank F. L. Shapiro for many stimulating discussions, and also M. V. Kazarnovskii and I. I. Sobel'man for help in this work.

Note added in proof (January 16, 1961). After this paper was sent to press, we saw a preprint of the paper of Singwi and Sjölander, which contains similar results. [See Phys. Rev. **120**, 1093 (1960); transl. note.]

[1] W. Heitler, The Quantum Theory of Radiation, Oxford University Press, 1954.

[2] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[3] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

[4] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956).

[5] H. Bethe and G. Placzek, Phys. Rev. **51**, 450 (1937).

[6] W. Lamb, Phys. Rev. **55**, 190 (1939).

[7] R. L. Mössbauer, Z. Physik **151**, 124 (1958).

[8] R. L. Mössbauer, Z. Naturforsch. **14a**, 211 (1959).

[9] S. Chandrasekhar, Stochastic Problems in Physics and Astronomy, Revs. Modern Phys. **15**, 1 (1943).

[10] J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

[11] M. I. Podgoretskii and A. V. Stepanov, Preprint, Joint Institute for Nuclear Research.

[12] K. S. Singwi and A. Sjölander, Bull. Am. Phys. Soc. **5**, 168 (1960).

Translated by M. Hamermesh
87