# On the Calculation of the Natural Width of the Spectral Lines of the Atom by the Methods of Nonequilibrium Statistical Mechanics.

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In the paper of ZUBAREV and the authors (1) the Schrödinger-type equation with damping for the dynamical system weakly coupled to a thermal bath was obtained on the basis of the method of the nonequilibrium statistical operator (2). The applicability of this general equation to the concrete problems was demonstrated in paper (1) on the examples of the calculation of the energy shift and width of the electron and exciton systems interacting with the phonon field. It was shown in (1) that these values of the shift and width coincide with the results of calculations by the other methods (3,4).

In this short note we present an additional important example of the application of the method of paper (1). We consider the problem of the natural width of spectral line of the atomic system and show that our result coincides with the result obtained earlier (see for example ref. (5,6)). This problem is an excellent example for elucidating the sense of the Schrödinger-type equation with damping.

It is well known that the excited levels of the isolated atomic system have a finite lifetime because there is a probability of emission of photons due to interaction with the self-electromagnetic field. This leads to the atomic levels becoming quasi-discrete and consequently acquiring a finite small width. It is just this width that is called the natural width of the spectral lines.

Let us consider an atom interacting with the self-electromagnetic field in the approximation when the atom is at rest. For simplicity, the atom is supposed to be in two states only, *i.e.* in a ground state $a$ and in an excited state $b$. The atomic system in the excited state $b$ is considered, in a certain sense, as a small « nonequilibrium » system, and the self-electromagnetic field as a thermostat or a thermal bath. The relaxation of the small system is then a decay of the excited level and occurs by radiative transitions.

We shall not discuss here the case when the electromagnetic field can be considered as an equilibrium system with infinitely many degrees of freedom, because it has been discussed completely in the literature (5,6).

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(1) D. N. ZUBAREV, A. L. KUZEMSKY and K. WALASEK: *Theor. Math. Phys.*, **5**, 280 (1970).
(2) D. N. ZUBAREV: *Nonequilibrium Statistical Thermodynamics* (Moscow, 1971).
(3) D. N. ZUBAREV: *Usp. Fis. Nauk*, **71**, 71 (1960).
(4) R. KNOX: *Theory of Excitons* (New York and London, 1963).
(5) W. HEITLER: *Quantum Theory of Radiation* (Oxford, 1954).
(6) M. L. GOLDBERGER and K. M. WATSON: *Collision Theory* (New York, London, Sydney, 1964).

Following the paper [1], we write the total Hamiltonian in the form

$$\mathscr{H} = \mathscr{H}_{\text{at}} + \mathscr{H}_f + V\,, \tag{1}$$

where

$$\mathscr{H}_{\text{at}} = \sum_{\alpha} E_\alpha a_\alpha^\dagger a_\alpha\,, \qquad \alpha = a, b\,, \tag{2}$$

is the Hamiltonian for the atomic system alone, $a_\alpha^\dagger$ and $a_\alpha$ are the creation and annihilation operators of the system in the state with energy $E_\alpha$. (For a detailed description of the algebra of second quantization for one system see, for example, ref. [7,8]).

$$\mathscr{H}_f = \sum_{k,\lambda} kc b_{k\lambda}^\dagger b_{k\lambda} \tag{3}$$

is the Hamiltonian of transverse electromagnetic field [5,6], $\lambda = 1{,}2$ is the polarization, $\hbar\boldsymbol{k}$ is the momentum of a photon, $b_{k\lambda}^\dagger$ and $b_{k\lambda}$ are the of creation and annihilation operators of the photon in the state $(\boldsymbol{k}\lambda)$, $c$ is the light velocity, $V$ is the interaction operator responsible for the radiative transitions and having the following form in the non-relativistic approximation:

$$V = -\frac{e}{mc}\boldsymbol{p}\cdot\boldsymbol{A}_{\text{tr}}(\boldsymbol{r})\,, \tag{4}$$

where $e$ and $m$ are the electron charge and mass, respectively, $\boldsymbol{A}_{\text{tr}}(\boldsymbol{r})$ is the vector potential of the transverse electromagnetic field at the point $\boldsymbol{r}$; $[\boldsymbol{p}\times\boldsymbol{A}_{\text{tr}}(\boldsymbol{r})] = 0$. For a finite system enclosed in a cubic box of volume $\Omega$ with periodic boundary conditions, one can write [5,6]

$$\boldsymbol{A}_{\text{tr}}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}}\sum_{k,\lambda}\left(\frac{2\pi\hbar^2 c}{k}\right)^{\frac{1}{2}}\boldsymbol{e}_{k\lambda}\left[b_{k\lambda}\exp\left[\frac{i\boldsymbol{k}\boldsymbol{r}}{\hbar}\right] + b_{\lambda k}^\dagger\exp\left[-\frac{i\boldsymbol{k}\boldsymbol{r}}{\hbar}\right]\right]. \tag{5}$$

Now, following [1], the interaction (4) is represented as a product, such that the atomic and field variables are factorized:

$$V = \sum_{\alpha,\beta}\varphi_{\alpha\beta}a_\alpha^\dagger a_\beta\,, \qquad \varphi_{\alpha\beta} = \varphi_{\beta\alpha}^\dagger\,, \tag{6}$$

where

$$\varphi_{\alpha\beta} = \frac{1}{\sqrt{\Omega}}\sum_{k,\lambda}\{G_{\alpha\beta}(k,\lambda)b_{k\lambda} + b_{k\lambda}^\dagger G_{\beta\alpha}^*(k,\lambda)\}\,, \tag{7}$$

$$G_{\alpha\beta}(k,\lambda) = -\frac{e}{mc}\left(\frac{2\pi\hbar^2 c}{k}\right)^{\frac{1}{2}}\boldsymbol{e}_{k\lambda}\left\langle\alpha\right|\exp\frac{i\boldsymbol{k}\boldsymbol{r}}{\hbar}\cdot\boldsymbol{p}\left|\beta\right\rangle\,, \tag{8}$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the eigenstates of energies and $E_\beta$ that of the Hamiltonian $\mathscr{H}_{\text{at}}$, and are given by

$$\mathscr{H}_{\text{at}}|\alpha\rangle = E_\alpha|\alpha\rangle\,, \qquad \alpha, \beta = a, b\,. \tag{9}$$

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(7) M. LAX: *Phys. Rev.*, **129**, 2342 (1963).
(8) M. LAX: *1966 Brandeis Lectures in Theoretical Physics* (New York, 1968).

In the electric-dipole approximation, from eqs. (7) and (8) we get

$$\varphi_{\alpha\beta} = -\frac{e}{mc}\langle\alpha|\boldsymbol{p}|\beta\rangle\cdot\sum_{k,\lambda}\left(\frac{2\pi c\hbar^2}{k}\right)^{\frac{1}{2}}\boldsymbol{e}_{k\lambda}(b_{k\lambda}+b^{\dagger}_{k\lambda})\,. \tag{10}$$

The matrix element of the dipole moment $\boldsymbol{d}=e\boldsymbol{r}$ between states $|\alpha\rangle$ and $|\beta\rangle$ is related to the matrix element of the momentum $\boldsymbol{p}$ in the following way:

$$\langle\alpha|\boldsymbol{p}|\beta\rangle = -\frac{m}{e\hbar}(E_\alpha - E_\beta)\,\boldsymbol{d}_{\alpha\beta}\,, \tag{11}$$

and we assume that $\langle\alpha|\boldsymbol{p}|\alpha\rangle = 0$.

As was already mentioned, we use the Schrödinger-type equation with damping ([1]) for the quantity $\langle a_\alpha\rangle$ which has the form

$$i\hbar\,\frac{\mathrm{d}\langle a_\alpha\rangle}{\mathrm{d}t} = E_\alpha\langle\alpha_\alpha\rangle + \sum_\beta K_{\alpha\beta}\langle a_\beta\rangle\,, \tag{12}$$

where

$$K_{\alpha\beta} = \frac{1}{i\hbar}\sum_\gamma\int\limits_{-\infty}^{0}\mathrm{d}t_1\exp[\varepsilon t_1]\langle\varphi_{\alpha\gamma}\tilde{\varphi}_{\gamma\beta}(t_1)\rangle_q\,, \tag{12a}$$

and $\langle\ldots\rangle_q$ denotes the statistical average with the quasi-equilibrium statistical operator ([2]), which has the form

$$\varrho_q(t,0) = Q_q^{-1}\exp\Big[-\sum_\alpha(f_\alpha(t)a_\alpha + f^*_\alpha(t)a^{\dagger}_\alpha + F_\alpha(t)a^{\dagger}_\alpha a_\alpha)\Big]\,, \tag{13}$$

$$Q_q = \mathrm{Sp}\exp\Big[-\sum_\alpha(f_\alpha(t)a_\alpha + f^*_\alpha(t)a^{\dagger}_\alpha + F_\alpha(t)a^{\dagger}_\alpha a_\alpha)\Big]\,, \tag{13a}$$

where $f_\alpha(t)$, $f^*_\alpha(t)$, $F_\alpha(t)$ are the parameters conjugated with quantities $\langle\alpha_\alpha\rangle$, $\langle\alpha^{\dagger}_\alpha\rangle$, $\langle a^{\dagger}_\alpha a_\alpha\rangle$ in the sense of nonequilibrium thermodynamics,

$$\tilde{\varphi}_{\alpha\beta}(t) = \varphi_{\alpha\beta}(t)\exp\left[\frac{i}{\hbar}(E_\alpha - E_\beta)\,t\right].$$

It is clear from eq. (12$a$) that the $K_{aa}$ and $K_{ba}$ are equal to zero and thus (12) becomes

$$i\hbar\,\frac{\mathrm{d}\langle a_b\rangle}{\mathrm{d}t} = E_b\langle a_b\rangle + K_{bb}\langle a_b\rangle\,, \tag{14}$$

where

$$K_{bb} = \frac{2\pi\hbar^2 e^2}{m^2 c}\,\frac{1}{\Omega}\sum_k\int\limits_{-\infty}^{\infty}\mathrm{d}\omega\,\frac{1}{k}\,\frac{\mathscr{J}(k_1\omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}\,A^{ab}_{ab}\left(\frac{\boldsymbol{k}}{k}\right) \tag{15}$$

with $\hbar\omega_0 = E_b - E_a$,

$$\mathscr{I}(k, \omega) = \{(\langle n_k\rangle + 1)\,\delta(\omega + ck) + \langle n_k\rangle\,\delta(\omega - ck)\}\,, \tag{16}$$

$$\langle n_k\rangle = \sum_\lambda \langle n_{k\lambda}\rangle = \frac{1}{\exp[\beta ck] - 1} = n(k)\,, \tag{17}$$

$$A^{ab}_{ab}\left(\frac{\boldsymbol{k}}{k}\right) = |\langle a|\boldsymbol{p}|b\rangle|^2 - \left(\langle a|\boldsymbol{p}|b\rangle\,\frac{k}{k}\right)\left(\langle b|\boldsymbol{p}|a\rangle\,\frac{k}{\boldsymbol{k}}\right). \tag{18}$$

Next we have

$$\frac{1}{\Omega}\sum_k \int_{-\infty}^{\infty} \mathrm{d}\omega\,\frac{1}{k}\,\frac{\mathscr{I}(k, \omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}\,A^{ab}_{ab}\left(\frac{\boldsymbol{k}}{k}\right) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\mathrm{d}\omega\int_0^{\infty}\frac{\mathscr{I}(k, \omega)}{\hbar\omega_0 + \hbar\omega + i\varepsilon}\,k\,\mathrm{d}k\cdot\int A^{ab}_{ab}\left(\frac{\boldsymbol{k}}{k}\right)\mathrm{d}\mathcal{O}, \tag{19}$$

where $\mathrm{d}\mathcal{O}$ denotes the spherical angle element. It is easily verified that

$$\int A^{ab}_{ab}\left(\frac{\boldsymbol{k}}{k}\right)\mathrm{d}\mathcal{O} = \frac{8\pi}{3}\,|\langle a|\boldsymbol{p}|b\rangle|^2\,. \tag{20}$$

Substitution of (20) into (15) gives ($\nu = ck$)

$$K_{bb} = \frac{2}{3}\,\frac{e^2}{m^2c^3\hbar}\,|\langle a|\boldsymbol{p}|b\rangle|^2\cdot\int_0^{\infty}\nu\,\mathrm{d}\nu\left\{\frac{n(\nu) + 1}{\omega_0 - \nu + i\varepsilon} + \frac{n(\nu)}{\omega_0 + \nu + i\varepsilon}\right\}. \tag{21}$$

Finally, we obtain the formulae for width $\Gamma_b$ which we defined by $K_{bb} = \Delta E_b - (\hbar/2)i\Gamma_b$ from eq. (21) when the temperature tends to zero

$$\Gamma_b = \frac{4}{3}\,\frac{e^2\omega_0}{\hbar m^2c^3}\,|\langle a|\boldsymbol{p}|b\rangle|^2 = \frac{4}{3}\,\frac{\omega_0^3}{\hbar c^3}\,|\boldsymbol{d}_{ab}|^2\,. \tag{22}$$

This expression coincides with the well-known value for the natural width of spectral lines ([5]). We are not concerned with the calculation of the shift and the discussion of of its linear divergence because this is a usual example of the divergence of the self-energy in field theories.

Thus, with the aid of the Schrödinger-type equation with damping one can simply calculate the energy width and shift. This treatment can be used in a number of concrete problems of line broadening due to perturbations ([9]). In our paper we have calculated the width with the aid of the equation for the nonequilibrium averages. However, it is well known that the equations for nonequilibrium averages are equivalent to the equations for the appropriate Green's functions which are equivalent, in turn, to usual perturbation theory if the latter holds.

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([9]) J. COOPER: *Rev. Mod. Phys.*, **39**, 167 (1967).