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Abstract

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THE NATURAL CONTOUR OF ENERGY LEVELS

In quantum mechanics, the broadening of spectral lines is associated with the broadening of energy levels. The application of the uncertainty relation makes it possible to find the mean width of the levels. The question of the contour of levels corresponding to the contour of the natural broadening of spectral lines is generally not considered. The usual methods of quantum electrodynamics ($^{1-3}$), based on the solution of the time equation, give the correct expression for the contour of a spectral line, but do not touch upon the question of the broadening of energy levels. In some cases it is assumed that the contour of a spectral line completely repeats the contour of the excited energy level (^{2}), but the meaning of this concept is not clarified. In the present work an expression is obtained that can be interpreted as the natural contour of energy levels.

Let us consider an isolated system consisting of two interacting subsystems: an atom and an electromagnetic field. The Schrödinger equation for the stationary states of such a system has the form:

$$(\dot{H}_a + H_\mathrm{p} + U)\Psi = E\Psi. \tag{1}$$

Here H_a and H_p are the Hamiltonians of the free atom and of the electromagnetic field, respectively. The interaction operator has the form (^{1})

$$U = -\frac{e}{mc}\mathbf{p}\mathbf{A}, \tag{2}$$

where $\mathbf{p}$ is the momentum operator of the optical electron of the atom; $\mathbf{A}$ is the vector potential of the electromagnetic field:

$$\mathbf{A} = \sum_{\mathbf{k},l}(q_{\mathbf{k}l}e^{i\mathbf{kr}} + q^{+}_{\mathbf{k}l}e^{-i\mathbf{kr}})\mathbf{e}_{\mathbf{k}l}. \tag{3}$$

In expression (3) the summation is carried out over two values of the polarization l and all values of the wave vector $\mathbf{k}$, determined by the dimensions of the periodicity cube V. In what follows the summation over l and $\mathbf{k}$ is denoted by a single index.

The matrix elements of the operators q_x and q_x^+ are equal to

$$(q_x)_{m_x,n_x} = \sqrt{\frac{2\pi c^2 h}{V\omega_x}}\sqrt{n_x}\,\delta_{n_x-1,m_x}, \qquad (q_x^+)_{m_x,n_x} = \sqrt{\frac{2\pi c^2 h}{V\omega_x}}\sqrt{n_x+1}\,\delta_{n_x+1,m_x}. \tag{4}$$

Here n_x and m_x are the quantum numbers of the states of the x-th oscillator; ω_x is the frequency; $\mathbf{e}_x$ is the polarization vector.

We seek the solution of (1) in the form

$$\Psi = \sum_{i,\,(n_x)} C_{i\,(n_x)}\psi_{i\,(n_x)}, \tag{5}$$

where $\psi_{i\,(n_x)}$ is the product of the eigenfunction of the free atom in the i-th

state and of the eigenfunction of the field in the state (n_x). The symbol (n_x) denotes the totality of all symbols $n_1, n_2, \dots, n_x, \dots$, which determine the state of all oscillators of the field. Substituting (2) and (5) into (1) and carrying out the well-known transformations, we obtain a system of equations for determining $C_{i(n_x)}$:

$$(E_{i(n_x)}-E)C_{i(n_x)}-\sum_{j,x'}(p_{ij})_{x'}\sqrt{n_{x'}+1}\,C_{j(n_x+\delta_{xx'})}-\sum_{j,x'}(p_{ij})_{x'}\sqrt{n_{x'}}\,C_{j(n_x-\delta_{xx'})}=0, \tag{6}$$

where

$$E_{i(n_x)} = E_i + \sum_x h\omega_x(n_x+1/2), \tag{7}$$

$$(p_{ij})_x = -ie\sqrt{\frac{2\pi h}{V\omega_x}}\omega_{ij}(\mathbf{r}\mathbf{e}_x)_{ij}. \tag{8}$$

In (6) and (8) it has been taken into account that, within the limits of the atom, $\mathbf{kr} \ll 1$ (^{4}). The notation of the indices is borrowed from (5) and has the following meaning: $(n_x+\delta_{xx'})$ differs from (n_x) only in that the oscillator x' is in the state $n_{x'}+1$, and not $n_{x'}$. To simplify the calculations, let us assume that the atom has only two energy levels: $E_1 = 0$ and E_2.

The system of equations (6) can be solved by the method of successive approximations. As the zeroth approximation we take the state in which the atom is in the excited state and there are no photons in the field, i.e. only $C_{2(0)}(E)$ is nonzero. The equations (6) for the first approximation have the form

$$(E_2 - E)C_{2(0)} - \sum_{x'} (p_{21})_{x'} C_{1(\delta_{xx'})} = 0,$$

$$(h\omega_{x'} - E)C_{1(\delta_{xx'})} - (p_{12})_{x'} C_{2(0)} = 0. \tag{9}$$

The system (9) describes the interaction of the excited level of the atom with the practically continuous spectrum of possible states of the field. An analogous system of equations has already been solved in the works of Rice (^{6}) and Stepanov (^{7}) on the theory of predissociation. In contrast to (9), in those works it was assumed that the matrix elements do not depend on the energy and that the energy spectrum is homogeneous. In our case these conditions are not fulfilled, since the matrix elements $(p_{12})_{x'}$ and the density of energy levels of the electromagnetic field

$$\rho_\omega = \frac{\omega^2}{\pi^2 c^3} V \tag{10}$$

depend on ω. Nevertheless, the solution obtained in (^{6,7}) is also applicable to the present problem. Indeed, from the form of equations (9) it follows that the interaction of the two subsystems has a resonant character; the values of $C_{2(0)}(E)$ are large only for those energies E of the whole system which are close to E_2, and for $E \sim E_2$ the change in the matrix elements and in the density of energy levels is small and may be neglected. Therefore, according to (7), $|C_{2(0)}(E)|^2$, i.e. the probability of finding the atom on the second level if the energy of the whole system is equal to E (E is close to E_2), is given by the expression

$$|C_{2(0)}(E)|^2 = \frac{|p_{21}|^2_{x'}}{\frac{\pi^2 \left(|p_{21}|^2_{x'}\right)^2}{\varepsilon^2} + (E_2 - E)^2}, \tag{11}$$

where ε is the distance between neighboring energy levels of the field, equal to $h/\rho\omega_{21}$, and the bar over the matrix element denotes averaging over all directions $\mathbf{e}_{\chi'}$:

$$\overline{|p_{21}|^2} = \frac{2\pi\hbar\omega_{21}e^2}{V} \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta \, d\vartheta \, |(\mathbf{r}\mathbf{e}_{\chi'})_{21}|^2 = \frac{2}{3} \frac{\pi\hbar\omega_{21}}{V} |r_{21}|^2. \tag{12}$$

Introducing the notation

$$\beta = \frac{\pi \overline{|p_{21}|^2_{\chi'}}}{\varepsilon} = \frac{2}{3} \frac{e^2\omega_{21}^3}{c^3} |r_{21}|^2, \tag{13}$$

formula (11) may be written in the form

$$|C_{2(0)}(E)|^2 = \frac{\beta\varepsilon}{\pi} \frac{1}{\beta^2 + (E_2 - E)^2}. \tag{14}$$

Expression (14) determines the probability referred to one level of the field state. In order to obtain the probability density, i.e., the probability referred to a unit energy interval, it is necessary to multiply expression (14) by the number of levels in a unit energy interval, $1/\varepsilon$. As a result we have

$$|C_{2(0)}(E)|_E^2 = \frac{\beta}{\pi} \frac{1}{\beta^2 + (E_2 - E)^2}. \tag{15}$$

Solving the problem of transitions, quantum electrodynamics ([1,3]) gives the following expression for the contour of a spectral line:

$$I(\omega) = I_0 \frac{\gamma}{\pi} \frac{1}{\gamma^2 + (\omega_{21} - \omega)^2}, \tag{16}$$

where γ is the half-width of the spectral line,

$$\gamma = \frac{2}{3} \frac{e^2 \omega_{21}^3}{c^3 \hbar} |r_{21}|^2 = \frac{\beta}{\hbar}. \tag{17}$$

It is seen from this that the parameter β coincides with the half-width of the spectral line on the energy scale. The similarity of (15) and (16) suggests that expression (15) may be interpreted as the contour of an atomic energy level, caused by interaction with the zero electromagnetic field.

In nature there is no absolutely isolated atom. The simplest real system is not an isolated atom, but an atom in the zero electromagnetic field, from which one cannot in principle abstract. Therefore the simplest atomic system is described by the Hamiltonian $H_a + U$, where U is the operator of interaction with the electromagnetic field. Such a system possesses a practically continuous energy spectrum E and eigenfunctions $\Psi(E)$. In its physical meaning, the quantity $|C_{2(0)}(E)|_E^2$ gives the probability of manifestation, in the total state of the system $\Psi(E)$, of the properties of the atom, i.e., of the state ψ_2. According to (15), different energy levels E of the complete system correspond to different degrees of manifestation of the properties of the atom. The dependence of the quantities $|C_{2(0)}(E)|_E^2$ on E gives the natural contour of the energy levels of the atom, which appears under the most varied experimental conditions, in particular in the contour of spectral absorption and emission lines.

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Note: Figure translations are in progress. See original paper for figures.

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