

ion. Transition to the higher electronically excited states is accompanied by an increase in the overlap which, in turn, is accompanied by the observed increase in  $\sigma_{ik}$ .

Associative processes may be characterized by effective cross sections  $\bar{\sigma}'_{ik} = \langle \sigma_{ik} v_0 \rangle / \bar{v}_0$ . Their values, determined from the present work and from previous data,<sup>6</sup> are given in the last column of the table for  $T \approx 500$  °K.

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## Higher-order perturbation theory effects in the shift and width of atomic levels in an optical field

N. L. Manakov, M. A. Preobrazhenskii, L. P. Rapoport, and A. G. Fainshtein

*Lenin Komsomol State University, Voronezh*

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The quasienergy method, developed earlier for the interaction of a system with a periodic field in which the level broadening effects are neglected, is reformulated for the calculation of quasistationary states in a strong optical field. The perturbation theory is developed for the real and imaginary parts of complex quasienergy and singularities which appear on allowance for corrections to the first nonvanishing order are considered. The cases of an isolated level and of a group of resonance levels are discussed separately. The shift and width of a level subjected to short-range and Coulomb potentials are analyzed in detail, including terms of the second and fourth orders in the field. At frequencies higher than the ionization potential the expressions obtained give, in particular, the corrections to the cross section of the classical photoelectric effect, proportional to the optical wave intensity. The exponential decay law of the system in a periodic field is considered. The possibility of experimental detection of the higher-order effects in the shift and width of levels is discussed.

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### §1. INTRODUCTION

In considering the processes of direct and resonance ionization of atoms in a strong field, and also the shifts and widths of atomic levels, it is usual to confine calculations to the first nonvanishing order in the perturbation theory of the interaction between a given system and the field. Inclusion of higher-order corrections makes it possible, on the one hand, to identify the range of validity of the results obtained in the first

nonvanishing approximation, and, on the other, to obtain a modified functional dependence of the shifts and widths on the field intensity. Calculations of the higher-order terms by the usual transient perturbation theory methods is fraught with difficulties typical of the higher orders of the perturbation theory in the case of finite level widths<sup>1</sup> and associated, in particular, with the need to allow for the contribution made to the width by the shift effects in lower order (and vice versa); there are also difficulties in integration of the singular ex-

pressions which arise in the calculations. If an optical field is considered classically and if the spontaneous level widths are ignored compared with the field broadening, the simplest and most effective method for including the higher-order corrections is the method of complex quasienergies. This approach is a direct generalization of the method of quasienergy states, first proposed to describe a system in a periodic field ignoring the decay effects,<sup>2,3</sup> to a class of problems in which the level broadening is important.

For a system with the periodic potential  $V(\xi, t) = V(\xi, t + T)$  the wave functions of the quasienergy states ( $\hbar = 1$ )

$$\psi_{\mathbf{E}}(\xi, t) = e^{-iEt} \Phi_{\mathbf{E}}(\xi, t), \quad \Phi(t+T) = \Phi(t), \quad T = 2\pi/\omega$$

satisfy the "steady-state" equation<sup>2,4</sup>

$$\mathcal{H}\Phi_{\mathbf{E}}(\xi, t) = E\Phi_{\mathbf{E}}(\xi, t), \quad \mathcal{H} = H_0(\xi) + V(\xi, t) - i\partial/\partial t, \quad (1)$$

and form a complete system of functions with a real spectrum of quasienergies  $E$ . If the unperturbed Hamiltonian  $H_0$  has a discrete, as well as a continuous, spectrum (this applies to an atom or a molecule), the application of a perturbation  $V$  may cause ionization and the spectrum  $E$  becomes purely continuous. Nevertheless, the quasienergy approach is still useful in an analysis of the spectral characteristics of a system in a field because it can easily be reformulated in terms of quasistationary quasienergy states and used to calculate the shifts and widths of the levels in a discrete spectrum  $H_0(\xi)$  on application of the field.

The problem of quasistationary quasienergy states corresponding to Eq. (1) is fully analogous to the problem of quasistationary states in a static potential: a solution of Eq. (1) satisfying the boundary condition on the radiation is sought; it is found that the function  $\Phi_{\mathbf{E}}$  rises exponentially in the limit  $\nu \rightarrow \infty$  and its corresponding eigenvalue  $E$  is complex. This approach is known to be equivalent to the solution of the Cauchy problem for the Schrödinger equation with the initial condition  $\psi(\xi, 0) = \Phi_0(\xi)$  in the exponential decay range. The real and imaginary parts of  $E$  determine the position and width of a quasistationary level which is formed from  $E_0$  on application of a field. It should be noted that scattering problems described by Eq. (1) may also be of physical interest. In this case the spectrum of  $E$  is continuous and the corresponding functions  $\Phi_{\mathbf{E}}$  are normalized to the  $\delta$  function of the solution of Eq. (1). As in the theory of scattering by a static potential, quasistationary levels correspond to scattering resonances and in this case the complex quasienergies and the functions of the states in question can be obtained as the poles and residues of  $\Phi_{\mathbf{E}}$  in the complex plane of  $E$ .

Since the exact solution of the decay problem is possible only in exceptional cases,<sup>1)</sup> the approximate methods of calculation of the parameters of quasistationary states are of practical importance. In alternating fields the situation differs from problems of the  $\alpha$ -decay type and from the ionization of atoms in a static field when the level width is associated with the tunneling of a particle across a barrier and cannot be found by the perturbation theory. In fact, for each

unperturbed state  $\Phi_n(\xi)e^{-iE_n t}$  of the operator  $H_0(\xi)$  there is an infinite set  $|n, k\rangle$  of quasienergy states in the zeroth approximation:

$$\Phi_{n,k}(\xi, t) = \Phi_n(\xi)e^{iE_n t}, \quad \tau = \omega t, \quad k = 0, \pm 1, \dots, \quad (2)$$

which are the eigenfunctions of the unperturbed Hamiltonian of quasienergy states

$$\mathcal{H}_0 = H_0(\xi) - i\omega \partial/\partial \tau$$

with quasienergies  $E_{n,k} = E_n + k\omega$ . Therefore, from the formal point of view, we find that in the zeroth approximation with respect to  $V$ , the operator  $\mathcal{H}$  in Eq. (1) has discrete quasienergy states against a continuous background. This problem is fully analogous to the cases of autoionization or predissociation, and the perturbation theory for  $V$  then gives the shift and width of levels.

We shall develop below (§ 2) the perturbation theory of quasistationary quasienergy states which can be used in dealing with decay when there is a discrete level against the continuum in the zeroth approximation. It should be noted that the first order of the perturbation theory applied to the problem of autoionization was obtained by Fano,<sup>6</sup> but the formalism employed by him cannot be used to obtain higher corrections. A calculation of the complex quasienergy of a particle associated with short-range and Coulomb forces is calculated in § 3, including terms of the second and fourth orders in the field. Since the interpretation of the imaginary part as the probability of ionization of the system is only approximate, the decay of a system in a periodic field is considered in § 4 and the limits of validity of the exponential decay law are established. The problem of possible experimental detection of the higher-order corrections and of the fundamental restrictions on the precision with which these quantities can be measured is considered in § 5.

## §2. GENERAL FORMALISM OF THE PERTURBATION THEORY FOR QUASISTATIONARY QUASIENERGY STATES

Since in the space of time-periodic functions  $\Phi(\xi, t)$  we can regard Eq. (1) as the eigenvalue problem, we shall develop the perturbation theory for quasistationary quasienergy states with the unperturbed basis (2) by applying the formal apparatus of the steady-state perturbation theory suitable for a discrete spectrum with zero level widths.<sup>7</sup>

### A. Isolated level

Let us assume that in the absence of a perturbation there is an isolated discrete level  $\Phi_0(\xi)$  with an energy  $E_0$ . We shall introduce the following Green function

$$\mathcal{G}_{\mathbf{E}} = \frac{1}{E - \mathcal{H}_0} = \sum_{n,k} \frac{|n, k\rangle \langle k, n|}{E - E_{n,k}} \quad (3)$$

and rewrite Eq. (1) in the form

$$|\Phi\rangle = |\Phi_0\rangle + G_{\mathbf{E}} V |\Phi\rangle, \quad (4a)$$

$$E = E_0 + \langle \Phi_0 | V | \Phi \rangle. \quad (4b)$$

Here,

$$G_E = (1 - |\Phi_0\rangle\langle\Phi_0|) \mathcal{G}_E$$

is the reduced Green function and

$$\langle\langle\Phi_1|\Phi_2\rangle\rangle = (2\pi)^{-1} \int_0^{2\pi} d\tau \langle\Phi_1(\tau)|\Phi_2(\tau)\rangle$$

is the scalar product in the space of periodic functions.

Iteration of the system (4) gives the Brillouin-Wigner series of quasienergies:

$$E = E_0 + \sum_{n=1}^{\infty} T_n(E), \quad T_n = \langle\langle\Phi_0|V(G_E V)^{n-1}|\Phi_0\rangle\rangle. \quad (5)$$

A series in powers of the perturbation (Rayleigh-Schrödinger series) is obtained by expanding  $T_n(E)$  as a series in  $E$  in the vicinity of  $E_0$ . For example, in the case when in the sum of Eq. (5) the only nonzero terms are those with even values of  $n$  (because of the selection rules), we obtain

$$E = E_0 + E_2 + E_4 + \dots,$$

where

$$E_2 = T_2(E_0), \quad E_4 = T_4(E_0) + E_2 \frac{\partial T_2}{\partial E} \Big|_{E_0}, \dots \quad (6a)$$

Since  $\partial G_E / \partial E = -G_E^2$ , the derivatives of  $T_n(E)$  can be represented in the form

$$\frac{\partial T_n}{\partial E} \Big|_{E_0} = -\langle\langle\Phi_0|V G_{E_0}^{2n} V|\Phi_0\rangle\rangle \quad (6b)$$

and so on.

In the case of a purely discrete spectrum of the quasienergy states the formulas (6) represent simply a different form of the perturbation theory for quasienergy states developed by Sambe<sup>4</sup> (see also Manakov *et al.*<sup>8</sup>). However, if  $H_0(\xi)$  has a continuous spectrum, the operator  $G_E$  is generally non-Hermitian and it is not single-valued. A quasistationary state is obtained by satisfying the radiation condition, i.e., by selecting the Green function with the diverging wave asymptote. In this case the consequence of the non-Hermitian nature of  $G_E$  is an imaginary part of the quasienergy:  $E = \text{Re}E - i\Gamma/2$ , where  $\Gamma > 0$  is the probability of decay of quasienergy states. Applying the formal solution of Eq. (4a),

$$|\Phi\rangle = (1 - G_E V)^{-1} |\Phi_0\rangle,$$

we obtain

$$E = E_0 + \langle\langle\Phi_0|R|\Phi_0\rangle\rangle, \quad R = V \frac{1}{1 - G_E V}.$$

Separating the Hermitian and anti-Hermitian parts of the operation  $R$

$$R = \frac{1}{2}(R+R^*) + \frac{1}{2}(R-R^*), \quad R^* = \frac{1}{1 - V G_E^*} V = V \frac{1}{1 - G_E^* V},$$

we obtain

$$\begin{aligned} \text{Re} E &= \langle\langle\Phi|V^{-1/2}V(G_E + G_E^*)V|\Phi\rangle\rangle, \\ \Gamma &= \langle\langle\Phi|V(G_E^* - G_E)V|\Phi\rangle\rangle. \end{aligned} \quad (7)$$

It should be pointed out that the exponential rise of  $\Phi$

and  $G_E$  at high values of  $r$  makes the integrals in Eqs. (4a) and (5) formally divergent, whereas the integrals in the system (6) have no divergences. This, the expansion of  $T_n$  and transition from (5) to (6) is in a sense analogous to the regularization of the integrals which appear in the theory of quasistationary states (see, for example, Zel'dovich and More<sup>9</sup>).

We shall now consider in greater detail the problem of a particle in a spherically symmetric potential  $U(r)$  in the presence of a monochromatic field:

$$\mathcal{H}_0 = -\frac{1}{2m} \Delta + U(r) - i\omega \frac{\partial}{\partial \tau}, \quad V(\mathbf{r}, \tau) = V^+(\mathbf{r}) e^{-i\tau} + V^-(\mathbf{r}) e^{i\tau}. \quad (8)$$

The Green function (3) can be expanded partially to give

$$\begin{aligned} \mathcal{G}_E(\mathbf{r}, \tau; \mathbf{r}', \tau') &= \sum_{k=-\infty}^{\infty} \sum_{LM} g_L(E - k\omega; r, r') Y_{LM}\left(\frac{\mathbf{r}}{r}\right) \\ &\times Y_{LM}^*\left(\frac{\mathbf{r}'}{r'}\right) e^{ik(\tau - \tau')}. \end{aligned} \quad (9)$$

Here,  $g_L(E; r, r')$  are the radial Green functions, whose spectral expansions have the usual form

$$g_L(E; r, r') = \sum_k \frac{\Phi_{kL}(r) \Phi_{kL}^*(r')}{E - E_{kL}} + \int_0^{\infty} dE' \frac{\Phi_{E'L}(r) \Phi_{E'L}^*(r')}{E - E'}. \quad (10)$$

To obtain  $g_E$  with the diverging wave asymptote, the integration contour in Eq. (10) for  $\text{Re}E > 0$  should be displaced in the complex plane in such a way as to pass a pole at  $E' = \text{Re}E - i\Gamma/2$  below. It should be noted that using the asymptote of  $g_L$  in the limit  $r \rightarrow \infty$ , we can obtain from Eq. (4a) the asymptote of the wave function of a quasistationary quasienergy state:

$$\Phi(r, \tau) \underset{r \rightarrow \infty}{\sim} \sum_k \sum_{LM} \frac{\pi}{(2E_k p_k)^{1/2}} \frac{1}{r} A_{kLM} Y_{LM}\left(\frac{\mathbf{r}}{r}\right) \cdot \exp\{i(p_k r + \eta_{EL} - k\tau)\}; \quad (11)$$

$$A_{kLM} = \langle\langle\Phi_{kL}(r) Y_{LM}(r/r) e^{-ik\tau} | V | \Phi\rangle\rangle,$$

$$E_k = E + k\omega, \quad p_k = (2mE_k)^{1/2}, \quad (12)$$

where the sum over  $k$  in Eq. (11) ( $k$  represents the number of the absorbed photons) includes only the "open" channels ( $\text{Re}E_k > 0$ ).

According to the selection rules applying to  $k$ , the contribution to  $T_2$  in the calculation of  $E_2$  of Eq. (6) is made only by the partial terms in Eq. (9) with  $k = \pm 1$ . When the one-photon ionization channel ( $E_0 + \omega > 0$ ) is open, the integrand in Eq. (10) has a singularity of the type

$$1/(x+i0) = 1/x - i\pi\delta(x),$$

so that for  $\Gamma_2 = -2\text{Im}E_2$ , we obtain

$$\Gamma_2 = 2\pi \sum_{LM} |\langle\langle\Phi_{E_0+\omega,L}(r) Y_{LM}(r/r) | V^+ | \Phi_0\rangle\rangle|^2,$$

whereas in the calculation of  $\text{Re} E_2$  a singularity  $(E - E')^{-1}$  is integrated in the sense of its principal value. The photoionization probability  $\Gamma_2$  can also be calculated in terms of the flux determined by the function  $\Phi$  in Eq. (11) if we substitute in Eq. (12) the values  $E = E_0$  and  $\Phi = \Phi_0$ . Making the substitution  $G_E \rightarrow G_{\text{Re}E}$  in Eq. (7), we can also express the total width of a level in terms of the flux:

$$\Gamma = 2\pi \langle \Phi | V \delta(\text{Re } E - \mathcal{H}_0) V | \Phi \rangle = 2\pi \sum_k \sum_{LM} |A_{kLM}|^2. \quad (13)$$

The individual terms of the above sum represent partial widths corresponding to the ionization to states with quantum numbers  $LM$  and energies  $\text{Re } E + k\omega$ . The substitution  $E \rightarrow \text{Re } E$  in  $G_E$  makes Eq. (13) accurate to within  $\sim \Gamma/E_0$ . However, we shall show later (§ 4) that it is pointless to try for a higher precision in the distribution of the ionization probability between the channels.

In the calculation of  $E_4$  the integration in  $T_4(E)$  is carried out in the same way as in  $T_2$ . It should be noted that the correction  $\sim V^4$  to the one-photon ionization probability, governed only by the term  $T_4$ , includes a contribution which can be expressed in the following form with the aid of Eq. (7):

$$2\pi \sum_{LM} \{|A_{1,LM}|^2 + 2 \text{Re}(A_{1,LM}^{(1)*} \cdot A_{1,LM}^{(2)})\}, \quad (14)$$

where the one- and two-photon ionization amplitudes  $A_{1,LM}^{(1)}$  and  $A_{2,LM}$  are calculated in accordance with Eq. (12) in the first nonvanishing order, and

$$A_{1,LM}^{(2)} = \langle \varphi_{E_0+\omega, L} | Y_{LM} e^{-i\tau} | V G_{E_0} V G_{E_0} V | \Phi_0 \rangle$$

is the matrix element of the one-photon ionization accompanied by photon reemission. Thus, Eq. (14) is the sum of the two-photon ionization probabilities and of the terms corresponding to the interference between the amplitudes of the one- and two-photon processes. A similar physically clear interpretation is admissible in the case of the imaginary parts of the component matrix elements of  $T_{2n}(E_0)$  of any order. However, we must bear in mind that in addition of these "graph" terms, there is a contribution to the level width from the imaginary parts of the "nongraph" matrix elements corresponding to terms with derivatives in Eq. (6b). For real values of  $E$ , these contributions correspond to the secular and normalization terms in the transient perturbation theory.<sup>10</sup>

A calculation of the matrix elements (6b) is complicated compared with  $T_{2n}$  because of the presence of high-order singularities. For example, the integrand in  $\partial T_2/\partial E$  has a singularity of the  $(x+i0)^{-2}$  type when the spectral expansion is used for  $g_L$ . Similarly, for higher orders of the expansion (6), we encountered the singularities

$$\frac{1}{(x+i0)^n} = \frac{1}{x^n} + i\pi \frac{(-1)^n}{(n-1)!} \frac{d^{n-1}}{dx^{n-1}} \delta(x).$$

Since these singularities appear in Eq. (6) as a result of differentiation of the generalized function  $(x+i0)^{-1}$ , they are themselves generalized functions.<sup>11</sup> Integration of the expressions with the generalized functions

$$\frac{1}{x^n} = \frac{(-1)^{n-1}}{(n-1)!} \frac{d^{n-1}}{dx^{n-1}} \frac{1}{x} = \frac{1}{2} \lim_{\epsilon \rightarrow 0} \left[ \frac{1}{(x+i\epsilon)^n} + \frac{1}{(x-i\epsilon)^n} \right]$$

can be carried out using the standard formula

$$\int_a^b \frac{f(x)}{x^n} dx = F(b) - F(a), \quad \frac{dF(x)}{dx} = \frac{f(x)}{x^n}, \quad (15)$$

ignoring an infinite discontinuity of the integrand within the interval  $[a, b]$ .

## B. Adjacent quasienergy levels

In contrast to the steady-state problem, not only the degenerate (or almost degenerate) states  $H_0$  but also the resonant levels  $|n, 0\rangle$  and  $|m, k\rangle$ , for which we have  $E_n - E_m \approx k\omega$  are adjacent to an unperturbed quasienergy state of the Hamiltonian  $\mathcal{H}_0$ .

Modification of the perturbation theory of § 2.A to allow for adjacent levels is similar to the corresponding procedure in the steady-state perturbation theory. Let us assume that there is a set  $N$  of adjacent quasienergy states  $\{\Phi_i^{(0)}, E_i^{(0)}\}$ ; then, the solution (1) can be represented in the form

$$|\Phi\rangle = \sum_{i=1}^N a_i |\Phi_i^{(0)}\rangle + G_E^P V |\Phi\rangle, \quad G_E^P = \left(1 - \sum_{i=1}^N |\Phi_i^{(0)}\rangle \langle \Phi_i^{(0)}|\right) \mathcal{P}_N.$$

The quasienergy  $E$  and the coefficient  $a_i$  satisfy the system of equations

$$a_i (E_i - E_i^{(0)}) = \sum_{j=1}^N \langle \Phi_i^{(0)} | R(E) | \Phi_j^{(0)} \rangle a_j, \quad (16)$$

where

$$R(E) = V(1 - G_E^P V)^{-1} = V + V G_E^P V + \dots \quad (17)$$

To solve Eq. (16), we shall represent  $R$  as a sum of two terms:

$$R(E) = R_1 + R_2(E),$$

where  $R_1$  represents the first few terms of the expansion (17), whose inclusion results in mixing of the states  $\Phi_i^{(0)}$  in the first nonvanishing order. The eigenvalues of  $E_i$  of Eq. (16) corresponding to  $R_2 = 0$  are generally complex (because  $R$  is non-Hermitian). The corresponding eigenvectors  $|\varphi_i\rangle$  satisfy the following orthonormalization conditions:

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}, \quad \langle \varphi_i | = \langle \varphi_i | S^{-1}, \quad S = \sum_{i=1}^N |\varphi_i\rangle \langle \varphi_i|.$$

Applying these conditions, Eq. (16) can be represented in a form convenient for the calculations of corrections to  $|\varphi_i\rangle$  and  $E_i$  [compare with Eq. (4)]:

$$|\varphi\rangle = |\varphi_i\rangle + \sum_{j \neq i}^N \frac{|\varphi_j\rangle \langle \varphi_j | R_2(E) | \varphi_i \rangle}{E - E_j}, \quad (18)$$

$$E = E_i + \langle \varphi_i | R_2(E) | \varphi_i \rangle.$$

The iteration procedure of solution of Eq. (18) is analogous to that considered in § 2.A, except that in the present case the "perturbation operator"  $R_2$  depends on  $E$ .

The selection of the operator  $R_1$  depends on the actual problem. For example, in the case of a  $k$ -photon ( $k > 2$ ) resonance between the ground state  $\Phi_0$  with  $E_0^{(0)}$  and a multiplet  $N$  of adjacent levels  $\{\Phi_i^{(0)} \exp(-ik\tau), E_i^{(0)} - k\omega\}$ , from which one-photon ionization can take place, we can assume that

$$R_1 = V + V G_{E_0}^P V.$$

This operator does not mix the states  $\Phi_i^{(0)}$  with  $\Phi_0$ ,

but the quasienergies  $E_i$  ( $i = 1, 2, \dots, N$ ) become complex and the denominators in Eq. (18) remain fairly large for all values of  $\omega$ . Inclusion of the remaining terms in  $R(E)$  is made in accordance with Eq. (18). The ground-state quasienergy is then

$$E = E_0 + \langle \Phi_0 | R_2(E) | \Phi_0 \rangle + \sum_{j=1}^N \frac{\langle \Phi_0 | R_2(E) | \Phi_j \rangle \langle \Phi_j | R_2(E) | \Phi_0 \rangle}{E - E_j + k\omega} + \dots \approx E_0 + \sum_{j=1}^N \frac{B_j}{E_0 - E_j + k\omega}, \quad (19)$$

where

$$E_0 = E_0^{(0)} + \langle \Phi_0 | V G_{E_0}^P V | \Phi_0 \rangle, \quad (19a)$$

$$B_j = \langle \Phi_0 | M_k | \Phi_j \rangle \langle \Phi_j | M_k | \Phi_0 \rangle, \quad M_k = V (G_{E_0}^P V)^{k-1}.$$

The imaginary part of Eq. (19) represents the probability of resonance ionization of the ground state. In the first nonvanishing order with

$$\Gamma^{(0)} = \sum_{j=1}^N \frac{\Gamma_j \operatorname{Re} B_j + 2\Delta_j \operatorname{Im} B_j}{\Delta_j^2 + \Gamma_j^2/4}, \quad \Delta_j - \frac{i}{2} \Gamma_j = E_j - k\omega - E_0, \quad (20)$$

Eq. (19a) assumes the same form as the resonance scattering cross section in the presence of nearby poles of the  $S$  matrix [see Eq. (5.7.24) in Ref. 12].

As in the nonresonance ionization case,  $\Gamma$  can be represented also in the form of a sum of partial widths. In particular, substituting in Eq. (12) the expression

$$|\Phi\rangle = |\Phi_0\rangle + \sum_{j=1}^N \frac{|\Phi_j\rangle \langle \Phi_j | M_k | \Phi_0 \rangle}{E_0 - E_j + k\omega},$$

we find that  $\Gamma^{(0)}$  is given by

$$\Gamma^{(0)} = 2\pi \sum_{L, M} |A_{k+1, L, M}|^2 = 2\pi \sum_{L, M} \left| \sum_{j=1}^N \frac{\langle \Phi_{E_0 + (k+1)\omega, L} | Y_{LM} e^{-i(k+1)\tau} V | \Phi_j \rangle \langle \Phi_j | M_k | \Phi_0 \rangle}{\Delta_j - i\Gamma_j/2} \right|^2. \quad (21)$$

This expression has the form of the usual probability of  $(k+1)$ -photon ionization in the first nonvanishing order, except that in summation over the intermediate states the unperturbed levels of the multiplets  $\Phi_i^{(0)}$  are replaced with states modified by the field and with corresponding complex quasienergies. The same considerations were used by Zon and Katsnel'son to obtain the above expression.<sup>13</sup> It is clear from Eqs. (20) and (21) that the frequency dependence  $\Gamma(\omega)$  is not a superposition of pure Lorentzian curves but is affected by interference between the ionization amplitudes via the various states of the modified multiplet.

### § 3. HYPERPOLARIZABILITY AND NONLINEAR CORRECTIONS TO THE PHOTOELECTRIC EFFECT TO ALLOW FOR SHORT-RANGE AND COULOMB POTENTIALS

We shall now consider the interaction of a bound particle with a monochromatic field in the dipole approximation:

$$V(\mathbf{r}, \tau) = -e\mathbf{r}\mathbf{F}(\tau), \quad \mathbf{F}(\tau) = \frac{F}{\sqrt{1+\varepsilon^2}} \{\cos \tau, \varepsilon \sin \tau, 0\}, \quad (22)$$

where  $-1 \leq \varepsilon \leq 1$  is the degree of ellipticity of the polarized radiation. The complex quasienergy  $E$ , corresponding to the energy  $E_0$  of an unperturbed isolated level, can be represented as a series in terms of  $F$ :

$$E = E_0 - \sum_{n=1}^{\infty} \frac{1}{(2n)!} \gamma_{2n}(\varepsilon, \omega) F^{2n}. \quad (23)$$

Here,  $2\gamma_2(\varepsilon, \omega) \equiv \alpha$  is the dynamic polarizability. The coefficients  $\gamma_{2n}$  with  $n > 1$  are analogous to the hyperpolarizabilities in a static field. We shall use the results of § 2 to calculate the complex dynamic hyperpolarizability  $\gamma_4(\varepsilon, \omega) \equiv \gamma$  for a particle experiencing short-range and Coulomb forces. In particular, this quantity should allow us to find an important quantity which is the field intensity  $F$  limiting the range in which we can use the results of the first nonvanishing order ( $-\frac{1}{4}\alpha F^2$ ) and the associated concepts of the Stark shift and ionization broadening in describing the field perturbation of a spectrum.

#### A. Short-range potential<sup>21</sup> $U(r) = (1/r^2)\delta(r)[1 + r(2/2r)]$

Integrating Eq. (6a) with respect to angular variables and  $\tau$ , we can represent  $T_4$  as a combination of radial integrals

$$M_{L_1, L_2, L_3}(\omega_1, \omega_2, \omega_3) = \langle \Phi_0 | r g_{L_1}(E_0 + \omega_1) r g_{L_2}(E_0 + \omega_2) r g_{L_3}(E_0 + \omega_3) r | \Phi_0 \rangle.$$

The radial Green functions  $g_L(E; r, r')$  can be described by the spectral expansion of Eq. (10) and for  $L_2 = \omega_2 = 0$  the sum over  $\lambda$  does not include the term corresponding to the state  $\varphi_0(r)$ . Application of the formulas for the point potentials<sup>15</sup> makes it possible to obtain easily the matrix elements  $r$  needed in the calculation of  $M$ . In view of singularities of the  $(E_1 - E_2 \pm i0)^{-2}$  type in the matrix elements  $r$  between the states in the continuous spectrum, the integrals in  $M_{L_1, L_2, L_3}$ , representing the intermediate states, in fact, contain singularities of the  $(x + i0)^{-k}$  type where  $k > 1$  and these are integrated on the basis of the theory of residues. The above treatment simplifies greatly if the perturbation  $V$  is selected, in contrast to Eq. (22), in the form

$$V(\mathbf{r}, \tau) = -\frac{e}{mc} \mathbf{A} \hat{\mathbf{p}}, \quad \mathbf{F}(\tau) = -\frac{1}{c\omega} \frac{\partial \mathbf{A}(\tau)}{\partial \tau}. \quad (24)$$

The final expressions for  $\alpha$  and  $\gamma$  in Eq. (23) are in the form<sup>3)</sup>

$$\alpha(\omega) = 8 \left\{ -\frac{1}{\omega^2} - \frac{8}{3\omega^4} + \frac{4}{3\omega^4} [(\omega+1)^k + i(\omega-1)^k] \right\}, \quad (25)$$

$$\gamma(\varepsilon, \omega) = \frac{128}{15\omega^4} \{ [f_l(\omega) + f_l(-\omega)] l^2 + [f_A(\omega) + f_A(-\omega)] A^4 \},$$

where  $l = (1 - \varepsilon^2)/(1 + \varepsilon^2)$  and  $A = 2\varepsilon/(1 + \varepsilon^2)$  are the degrees of the linear and circular polarizations related by  $A^2 + l^2 = 1$  (Ref. 14):

$$f_A(\omega) = 45\omega^2 + 96 + 5i(\omega^2 - 1)^k (\omega^2 - 7) - 4i(\omega - 1)^k \times (3\omega^2 + 14\omega - 32) + 3i(2\omega - 1)^k,$$

$$f_l(\omega) = 60\omega^2 + 124 + 5i(\omega^2 - 1)^k (\omega^2 - 7) - \frac{4}{\omega} [10(\omega - 1)^k (2\omega - 1)^k - i(2\omega - 1)^k (3\omega^2 + 12\omega^2 - 23\omega + 10) - 2i(\omega - 1)^k (\omega^3 - 42\omega^2 + 76\omega - 5)].$$

The values  $(\omega - 1)^{1/2}$  and  $(2\omega - 1)^{1/2}$  corresponding to the negative range of the radicand are selected on the upper imaginary semiaxis. The singularities in the

amplitudes of the  $A_{LM}^{(3)}$  type in Eq. (14), which appear when calculations are made by the methods of the conventional transient perturbation theory, have a much more complex structure and cannot be interpreted unambiguously. The correct result can be obtained by introducing a cutoff factor in the operator (22). Some of the singularities are not integrable at all and cancel out only in the calculation of the sum in Eq. (14). All this complicates greatly the calculations of the higher-order corrections compared with the quasistationary quasienergy states.

If  $\omega < \frac{1}{2}$ , the quantity  $\gamma$  is real and it governs the correction  $\sim F_4$  to the Stark shift. If  $\omega > \frac{1}{2}$ , the quantity  $\gamma$  has an imaginary part which governs the two-photon ionization probability and can be represented as a sum of the moduli of the squares of the partial amplitudes  $A_{20}$  and  $A_{22}$  in Eq. (14):

$$W_1(\omega) = \frac{32}{45} \left(\frac{F}{\omega^2}\right)^4 (2\omega-1)^{1/2} \left\{ 3(2\omega-1)^2 A^2 + \left[ 2(2\omega-1)^2 + \frac{5}{\omega}(\omega-1)^2 |1+i(\omega-1)^{1/2}|^2 \right] l^2 \right\}. \quad (26)$$

If  $\omega > 1$ , the one-photon ionization channel is also open and then  $\gamma$  has an imaginary part corresponding to the corrections to the photoelectric effect, which allow for the processes involving photon reemission [the second term on the right-hand side of Eq. (14)], and also the secular term  $\text{Im}(E_2 \partial T_2 / \partial E_0)$ . The final expression for the probability of ionization producing photoelectrons of momentum  $p = (\omega - 1)^{1/2}$  is

$$W_1(\omega) = \frac{16}{3} \left(\frac{F}{\omega^2}\right)^2 (\omega-1)^{1/2} + \frac{64}{9} \left(\frac{F}{\omega^2}\right)^4 (\omega-1)^{1/2} \left\{ (1+\omega)^{1/2} (\omega^2-7) - \frac{2}{5} (3\omega^2+14\omega-32) + \frac{\omega-1}{5\omega} (7\omega^2-7\omega+5) l^2 \right\}. \quad (27)$$

Moreover, there are corrections to the photoelectric effect from the two-photon ionization [ $W_2(\omega)$ ], which alters the photoelectron momentum distribution. It follows from Eq. (26) that  $W_2$  is a nonanalytic function of  $\omega$  (threshold singularities), so that the frequency dependences  $W_2(\omega)$  are very different for  $\omega < 1$  and  $\omega > 1$ .

At high frequencies ( $\omega \gg 1$ ) the real and imaginary parts of  $\gamma(\omega)$  decrease rapidly:

$$\gamma(\omega \gg 1) \approx \frac{128}{15\omega^5} \left\{ -\frac{12(\sqrt{2}-1)}{\omega^{1/2}} + \frac{90}{\omega} + 10i + i \frac{12(\sqrt{2}-1)}{\omega^{1/2}} \right\} + \left[ \frac{14-9\sqrt{2}}{\omega^{1/2}} (i-1) + \frac{30-20\sqrt{2}}{\omega} \right] l^2,$$

and the asymptote of the imaginary part is governed by the value of  $W_1$ .

The frequency dependences of the real and imaginary parts of  $\alpha(\omega)$  and  $\gamma(\omega)$  are plotted in Figs. 1 and 2. It is clear from these figures that  $\gamma(\omega)$  has threshold singularities of different types, typical of the reaction cross sections in the case of finite-radius potentials.<sup>15</sup> The strong frequency dependence of  $\gamma$  makes it impossible to determine accurately the critical field  $F_{cr}$  in which  $E_2(F_{cr}) \approx E_4(F_{cr})$  and the perturbation theory becomes invalid:  $F_{cr} = F_{cr}(\omega)$ . Since for  $\omega \sim 1$  we have  $F_{cr} \sim \frac{1}{2}$ , whereas in the case of  $\omega \gg 1$ , we have  $F_{cr} \propto \omega^{1.75}$

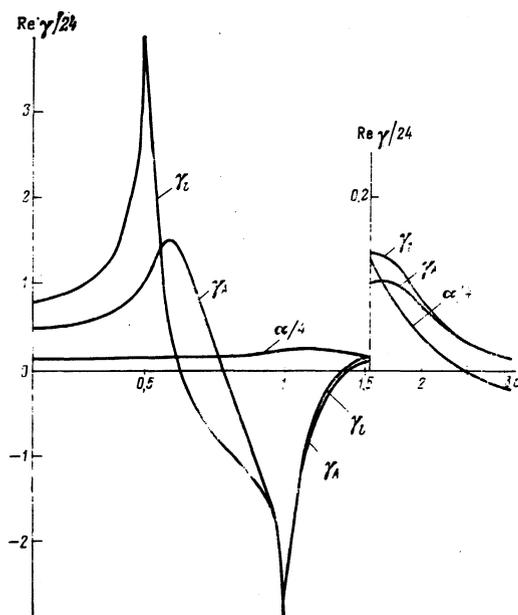


FIG. 1. Frequency dependences of  $\text{Re}\alpha$  and  $\text{Re}\gamma$  for a short-range potential. The values of  $\gamma_L$  and  $\gamma_A$  correspond to the linear and circular polarization of the incident radiation.

for  $\text{Re}E$  and  $F_{cr} \propto \omega^{1.25}$  for  $\Gamma$ . Thus, as in the case of one-photon ionization, the perturbation theory of the width of levels becomes invalid in weaker fields than the theory of the shift. An increase in the number of photons taking part in a given event increases this difference.<sup>5</sup>

The above formulas can be applied to negative ions if the bound-state function is multiplied by a numerical coefficient which allows for the difference between the asymptote of the wave function of an ion and the function in a  $\delta$  well (see, for example, Smirnov's monograph<sup>16</sup>). The probability of two-photon ionization of an  $H^-$  ion calculated using Eq. (26) is in good agreement with the results of numerical calculations<sup>17</sup> carried out using exact asymptotes of the wave functions of  $H^-$  for the discrete and continuous spectra.

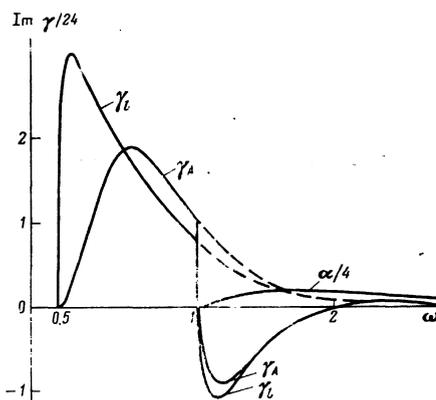


FIG. 2. Frequency dependences of  $\text{Im}\alpha$  and  $\text{Im}\gamma$  for a short-range potential. The dashed parts represent the contribution made to  $\text{Im}\gamma$  by the probability of two-photon ionization.

## B. Coulomb potential $U(r) = -2/r$

The polarizability and hyperpolarizability of the hydrogen atom were calculated by Manakov *et al.*<sup>8</sup> for the frequency range  $\omega \leq \frac{1}{2}$ . Therefore, we shall consider the range of frequencies in which the ionization of an atom is possible and  $\gamma$  has an imaginary part. The question of those corrections to the probability of the photoelectric effect which are nonlinear in respect of the intensity becomes important in investigations of multiphoton resonance ionization in strong fields since in practically all the experiments carried out so far the upper resonance level is one-photon wide. The expression for  $T_4$  in terms of radial matrix elements is then of the same form as for the  $\delta$  potential but  $M_{L_1, L_2, L_3}$  cannot be calculated completely by analytic methods. The radial Coulomb Green functions  $g_L(E; r, r')$  for  $E < 0$  have been calculated employing the Sturm expansion<sup>18</sup> and those for  $E > 0$  have been found employing the spectral expansion (10). The matrix elements  $r$  of the Sturm and Coulomb functions can be expressed in terms of the hypergeometric functions  ${}_2F_1$  and they do not have singularities for bound-bound and bound-free transitions; the matrix elements of the free-free transitions, which have singularities of the  $(x \pm i0)^{-2}$  and  $\ln(x \pm i0)/(x \pm i0)$  type, can be calculated by making the substitution  $V \rightarrow Ve^{-6r}$  and going to the limit  $\delta \rightarrow 0$ .

Summation and integration over the intermediate states are carried out numerically and singularities are separated and then integrated analytically in accordance with Eq. (15). In contrast to the short-range potential, the contribution of singularities to  $M_{L_1, L_2, L_3}$  is extremely small because the main contribution is that of a sum over the discrete spectrum in Eq. (10).

The frequency dependences of the shift and width of the ground state of hydrogen in the  $\omega > \frac{1}{2}$  case are plotted in Figs. 3 and 4. For  $\omega < \frac{1}{2}$  (we recall that  $\omega$  is measured in units of the ionization potential) the one- and two-photon ionization channels are closed ( $\text{Im } E = 0$ ), the polarizability  $\alpha(\omega)$  rises monotonically, and  $\gamma(\omega)$  has pole singularities at the points  $\omega_n^{(2)} = \frac{1}{2}(1 - 1/n^2)$  corresponding to two-photon resonances of excited  $ns$  states with the principal quantum number  $n$ . For  $1 > \omega > \frac{1}{2}$ , the value of  $\gamma$  has pole singularities of the second order at the points defined by  $\omega_n^{(1)} = 1 - 1/n^2$

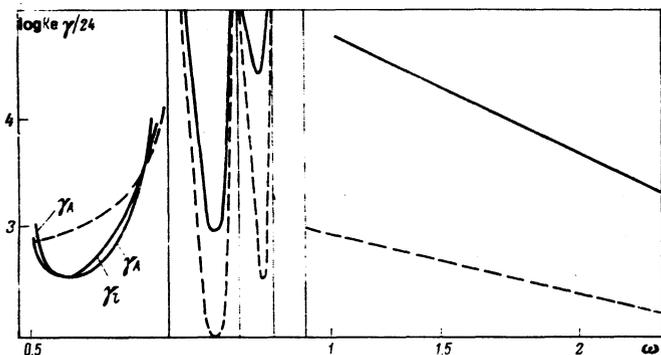


FIG. 3. Frequency dependence of  $100(\text{Re } \alpha)$  (dashed curves) and  $\text{Re } \gamma$  for a Coulomb potential.

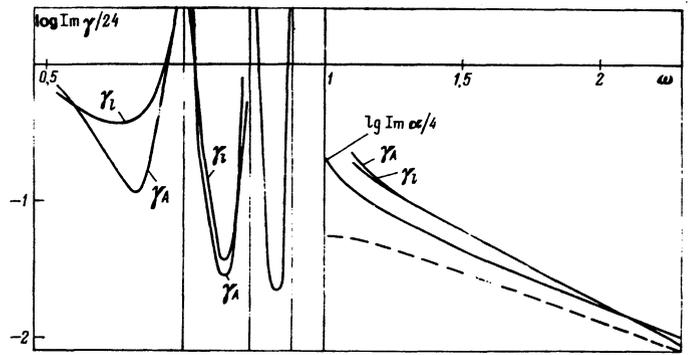


FIG. 4. Frequency dependences of  $\text{Im } \alpha$  and  $\text{Im } \gamma$  for a Coulomb potential. The dashed curve represents the contribution made to  $\text{Im } \gamma$  by the probability of two-photon ionization (based on the results of Klarsfeld<sup>19</sup>).

(one-photon resonances involving the  $np$  states). Then,  $\text{Re } \gamma$  remains always positive and rises rapidly on approach of  $\omega$  to the limit of the continuous spectrum. The high value of  $\text{Re } \gamma$  in the frequency range  $\omega \sim 1$  has the result that in the case of the potential with the Coulomb asymptote the critical field  $F_{cr}$  up to which the perturbation theory is valid decreases rapidly on increase of the frequency and can be several orders of magnitude lower than for  $\omega = 0$ . The width of a level has threshold singularities typical of the Coulomb potential<sup>15</sup> and remains finite at the one- and two-photon ionization thresholds. For  $\omega > 1$ , the value of  $\text{Im } \gamma$  governs the corrections to the cross section of the conventional photoelectric effect and these cross sections are proportional to the wave intensity<sup>41</sup>:

$$\sigma(F, \omega) = \sigma_0(\omega) \left\{ 1 + \frac{1}{6} F^2 \frac{\text{Im } \gamma(\omega)}{\text{Im } \alpha(\omega)} \right\}.$$

## §4. DECAY OF A SYSTEM UNDER THE ACTION OF A PERIODIC PERTURBATION

In the presence of a static potential the imaginary part of the complex energy  $E = \text{Re } E - i\Gamma/2$  governs the probability of decay of the system and the exponential decay law

$$W(t) = 1 - e^{-\Gamma t} \quad (28)$$

is valid for time intervals

$$\frac{1}{E_a} < t < \frac{1}{\Gamma} \ln \left( \frac{E_a}{\Gamma} \right) \quad (29)$$

( $E_a$  is the characteristic energy parameter of the system) and it is satisfied with the relative precision of  $\sim \Gamma/E_a$  (see, for example, Refs. 7 and 15). An expression of the same type as Eq. (28) and the limits of its validity will now be obtained for the case of decay under the action of a periodic perturbation.

The amplitude of the probability of finding the investigated system in an initial state  $\Phi_0$  after a time  $t$  from the application of the field can be written in the form

$$A(t, t_0) = \langle \Phi_0 | \Psi(t_0 + t) \rangle = \sum_c \int dE e^{-iEt} \langle \Phi_0 | \Phi_{E,c}(t + t_0) \rangle \langle \Phi_{E,c}(t_0) | \Phi_0 \rangle, \quad (30)$$

where  $\exp(-iEt)\Phi_{E,c}(r,t)$  is the complete system of quasienergy solutions of the Schrödinger equation with a continuous spectrum of quasienergies  $E$ ;  $c$  are the other quantum numbers of quasienergy states;  $\psi(t)$  is the solution of the Cauchy problem subject to the initial condition  $\psi(t_0) = \Phi_0$ . In view of the periodicity of  $\Phi_{E,c}(t)$ , the amplitude (30) depends periodically on  $t_0$ . Physically this is due to the fact that a sudden application of a perturbation produces a situation in which different values of  $t_0$  correspond to different initial values of the field intensity. Averaging Eq. (30) with respect to  $t_0$  over a period  $T$  and applying the relationship

$$\sum_{k=-\infty}^{\infty} \exp\{ik(\tau - \tau' + \omega t)\} = 2\pi\delta(\tau - \tau' + \omega t),$$

we can represent the expression for

$$\bar{A} = \frac{1}{T} \int_0^T A(t, t_0) dt,$$

in the form<sup>5)</sup>

$$\bar{A}(t) = \sum_{k=-\infty}^{\infty} \sum_{c,h} \int dE e^{-i(E+\hbar\omega)t} \langle \Phi_0 | \Phi_{E,c,h} \rangle \langle \Phi_{E,c,h} | \Phi_0 \rangle, \quad (31)$$

where  $\Phi_{E,c,h} = \Phi_{E,c} e^{i\hbar\omega t}$  is the complete set of the quasienergy states of Eq. (1). We can easily see that the right-hand side of Eq. (31) is identical with the amplitude  $\langle \langle \Phi_0 | \tilde{\psi}(t) \rangle \rangle$ , where  $\tilde{\psi}(t)$  is the solution of the Cauchy problem for the equation

$$i \frac{\partial \tilde{\psi}}{\partial t} = \left[ H \left( \frac{\tau}{\omega} \right) - i\omega \frac{\partial}{\partial \tau} \right] \tilde{\psi}(t), \quad \tilde{\psi}(0) = \Phi_0. \quad (32)$$

Since the "Hamiltonian" in Eq. (32) is independent of  $t$ , we can use the familiar results of the theory of the decay of a "prepared" state<sup>7</sup> and rewrite  $\bar{A}(t)$  in the form

$$\bar{A}(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \frac{e^{-iEt}}{E - E_0 - \langle \Phi_0 | V | \Phi_E \rangle}, \quad (33)$$

where  $\Phi_E$  is given by Eq. (4a) with real values of  $E$ . The integrand in Eq. (33) has a pole in the complex plane of  $E$  at  $E = E_p$ , where  $E_p = \text{Re}E - i\Gamma/2$  is clearly given by Eq. (4b). When  $E_0 t \gg 1$  ( $E_0 \sim |E_0 + N\omega|$ , where  $N$  is the threshold number of photons), the main contribution to Eq. (33) is due to the residue at that pole so that the probability of ionization of the system in a time  $t$  is

$$W(t) = 1 - 2\kappa - |\bar{A}(t)|^2 = 1 - 2\kappa - \frac{e^{-\Gamma t}}{|1 + \beta|^2}, \quad (34)$$

$$\beta = -\frac{\partial}{\partial E} \langle \Phi_0 | V | \Phi_E \rangle \Big|_{E=E_p}.$$

In the first nonvanishing order of the perturbation theory the quantities  $\beta$  and  $\kappa$  are of the second order in the field:

$$\beta^{(2)} = -\frac{\partial T_2(E)}{\partial E} \Big|_{E_0} = \langle \Phi_0 | V G_{E_0}^2 V | \Phi_0 \rangle, \quad (35)$$

and  $\kappa^{(2)}$  is again given by Eq. (35), where the Green function is replaced only with the part corresponding to a sum over the discrete states. It is clear from Eq. (35) that for  $\omega < |E_0|$  the quantities  $\beta^{(2)}$  and  $\kappa^{(2)}$  are real and positive. For the hydrogen atom we can express  $\beta^{(2)}$  in terms of the hypergeometric function  ${}_3F_2$ ,

whereas in the case of the short-range potential, this quantity is

$$\beta^{(2)} = \frac{1}{3} \left( \frac{F}{\omega^2} \right)^2 \left\{ \omega^2 - 72 - 12[(1+\omega)^{3/2} + (1-\omega)^{3/2}] + \frac{32}{\omega} [(1+\omega)^{3/2} - (1-\omega)^{3/2}] \right\}, \quad \kappa^{(2)} = 0,$$

and when  $\omega$  is increased from 0 to 1, it increases from  $F^2/16$  to  $0.8F^2$  (in rydbergs—see § 3). It should be noted that the correct value of  $\beta^{(2)}$  in Eq. (35) is obtained if  $V$  is described by Eq. (22) and not Eq. (24). This is due to the fact that in the calculation of the complex quasienergy the representations (22) and (24) are equivalent but a sudden application of Eq. (24) does not correspond to a sudden application of an electric field  $F(t)$ .

It follows from Eq. (34) that the linear regime  $W(t) = \Gamma t$  is attained after a time

$$t \gg \beta/\Gamma \quad (36)$$

(we then naturally have  $t \ll 1/\Gamma$ ). In the problems of decay in the presence of a static potential it is usually assumed that  $\beta$  is of the order of  $\Gamma/E_0$  (Ref. 7) so that Eq. (36) is identical with the inequality (29) on the left-hand side. However, in our case

$$\beta \sim (V/E_0)^2, \quad \Gamma \sim E_0 (V/E_0)^{2N},$$

and, therefore, for  $N > 1$  the time taken to attain the linear regime increases considerably to

$$t \gg \frac{1}{E_0} \left( \frac{E_0}{V} \right)^{2N-2}.$$

This produces a wide "plateau" of the time dependence  $W(t)$ . The existence of such a plateau has been established for the one-dimensional  $\delta$ -potential model by numerical solution of the Cauchy problem.<sup>20</sup> From the physical point of view the height of the plateau  $2(\beta - \kappa)$  is governed by the probability  $W_B$  of ionization of an atom as a result of a "shock" delivered by the application of the field. In fact, if we calculate  $W_B(t, t_0)$  in the first order of the secular perturbation theory and average over the fast oscillations, we find that in the limit  $E_0 t \gg 1$  this probability is

$$W_B = 2(\beta^{(2)} - \kappa^{(2)}) \approx 1 - 2\kappa^{(2)} - \frac{1}{|1 + \beta^{(2)}|^2}$$

where  $\beta^{(2)}$  is the total probability of the loss of an atom from its initial state and  $\kappa^{(2)}$  is the probability of a transition to other discrete levels as a result of this shock.

An anomalously high value of  $\beta$  obtained in our case is explained by the fact that in the static potential the total Hamiltonian can always be divided into  $H_0$  and  $V$  in such a way that the application of  $V$  has a minimal effect on the unperturbed wave function and simply causes decay of the state, whereas on application of a time-dependent perturbation the separation of  $\mathcal{H}$  into  $\mathcal{H}_0$  and  $V$  is governed by the formulation of the problem. Therefore, in experimental investigations it is usual to switch on a perturbation adiabatically and there is no shock due to a sudden application of the field so that we can expect  $\beta$  to have the value  $\sim \Gamma/E_0$ .

In the derivation of the decay probability (34) of the state  $\Phi_0$  we have simplified the integral (33) by omitting the terms representing the contribution of the poles corresponding to other quasistationary states and also the nonexponential terms governing the asymptote of  $W(t)$  in the limit  $\Gamma t \gg 1$ . An estimate of these terms can be made as described earlier<sup>7</sup> and it shows that for times  $t \lesssim 1/\Gamma$  they have a higher order of smallness in respect of  $V$  than  $\beta$  (moreover, there may be terms which are proportional to  $\beta$  but which oscillate at atomic frequencies). In the resonance ionization case we normally have to include in Eq. (33) the contribution of all the poles corresponding to resonance levels. Then,  $\bar{A}(t)$  represents a sum of several exponential functions and the ionization probability is identical, in the first nonvanishing order, with the results reported by Kazakov *et al.*<sup>21</sup>

## § 5. POSSIBILITY OF EXPERIMENTAL OBSERVATION OF HIGHER-ORDER EFFECTS

In investigations of the processes occurring in fairly high fields when the perturbation theory is still applicable but the corrections to the results of the first nonvanishing order in respect of the width and positions of the levels are significant, it is important to consider the possibility of experimental detection of new effects resulting from inclusion of these corrections. An analysis of this problem depends largely on the conditions under which a given experiment is carried out and, therefore, we shall confine ourselves to a brief review of several typical situations.

The simplest case is the observation of those corrections to the level shifts which are nonlinear in respect of the intensity. Although direct observations of this effect in optical fields have not yet been made, calculations of the hyperpolarizabilities of alkali atoms<sup>8</sup> show that nonlinear effects are important even in fields of  $5 \times 10^6$  V/cm, typical of experimental studies of the ionization of alkali atoms.<sup>22</sup> The effects proportional to  $V^4$  can be detected directly by determining the nonlinear intensity dependence of the ion yield maximum under resonance ionization conditions or by employing modifications of other methods for experimental investigation of nonresonance perturbations of the spectra.<sup>22</sup> We recall that in the case of the hydrogen atom in a static electric field we can observe not only the linear but also the quadratic and cubic Stark effects.<sup>23</sup>

Determination of corrections to the width of a resonance level from the experimentally determined frequency dependence of the ion yield is very difficult in the most interesting case when the one-photon ionization of the upper level is possible. Even a formal analysis of the expansion (19) shows that these corrections make a contribution to the ionization probability which are of the same order as the nonresonance ("potential") terms dropped in the derivation of Eq. (20) which applies to the resonance case. Therefore, an unambiguous separation of the probability into the resonance and nonresonance parts (like the separation of the potential and resonance amplitudes in the scat-

tering theory<sup>12</sup>) is impossible if precision exceeding  $\Gamma/E_a \propto (V/E_a)^2$  is required.<sup>6)</sup> Consequently, in determining the higher-order effects in the resonance ionization experiments it is desirable to establish a situation in which the one-photon ionization of the upper level is impossible.

Allowance for corrections to the level width in the nonresonance ionization case makes the functional dependence of the ionization probability  $\Gamma(I)$  different from the usual power law  $\Gamma \propto I^N$ . In the experiments these effects may be masked by corrections to the ionization probability per unit time, due to a deviation of the time dependence  $W(t)$  from the exponential law (28). It follows from the results of § 4 that in the optimal case a determination of the ionization probability  $W(t)$  makes it possible to find  $\Gamma$  with a precision<sup>7)</sup> of the order of  $\Gamma/E_a$ . Therefore, the corrections to the width of levels can be determined in the  $N > 1$  case also in nonresonance ionization experiments.

<sup>1)</sup>The exact solution in the quasistationary approach has been obtained so far only in the problem of the decay of a particle bound by short-range forces in a circularly polarized field.<sup>5</sup>

<sup>2)</sup>We shall use the Rydberg system of units:  $e = m = \hbar = 1$ ;  $E$  is measured in units of  $|E_0|$  and  $F$  in units of  $F_0 = |E_0|^3/2/8m/e\hbar$ .

<sup>3)</sup>The expression for  $\gamma$  in the case of a circular field obtained by Manakov and Rapoport<sup>5</sup> is marred by misprints.

<sup>4)</sup>We note that the corrections to the cross section of the photoelectric effect calculated by Klarsfeld<sup>19</sup> allow only for the two-photon ionization and, therefore, are incorrect.

<sup>5)</sup>We note that in a circular field the amplitude (30) is independent of  $t_0$  because in this case the field intensity does not vary with time and the averaging procedure is unnecessary.

<sup>6)</sup>Clearly, this relationship limits also the precision of the determination of the shift of levels.

<sup>7)</sup>This applies also to the determination of the partial widths and, therefore, separation between channels with a precision better than that in Eq. (13) is pointless.

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## Adiabatic invariants and the problem of quasiclassical quantization of many-dimensional systems

E. A. Solov'ev

*Zhdanov State University, Leningrad*

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A method for calculating spectra of complicated systems in the quasiclassical approximation is proposed, which is based on the adiabatic invariance of quantum numbers; this enables one to avoid the basic calculational difficulties involved in finding caustics and fixing initial data for the quantized classical trajectories. The validity of this method is verified with the example of a two-dimensional anharmonic oscillator. The results of the adiabatic calculation are identical with those obtained previously by an exact direct quasiclassical calculation for this case. Some general questions connected with the application of the method are discussed.

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### 1. INTRODUCTION

Much attention has been given to the development of the quasiclassical method for many-dimensional systems that do not permit separation of the variables (see, for example, Refs. 1-3 and references given there). Progress in this field is of great importance for the theoretical study of the spectra of such physically important objects as closed and open resonators, excitons, hydrogenlike atoms in strong magnetic fields, polyatomic molecules (vibrational spectra), and so on. Nevertheless we know of only two papers<sup>2,3</sup> devoted to the quasiclassically exact calculation of the discrete spectrum; the cases considered were the nondegenerate and the degenerate two-dimensional anharmonic oscillator. This situation is due to the lack of a practical recipe for finding the quantized classical trajectories. The only way at present is to choose initial data directly and then check the quantum conditions for the resulting trajectories. For systems with several degrees of freedom this method requires an excessive amount of computer time, mainly spent in rejecting unsuitable trajectories. Furthermore, the checking of the quantum conditions requires the calculation of caustics,<sup>1)</sup> which are integral characteristics of trajectories, so that it is hard to find an algorithm for them. These difficulties naturally arise in the case of many-dimensional systems that do not admit separation of variables. Pre-

cisely this sort of situation is discussed in what follows.

In the present paper an approach is proposed which is different in principle, and which allows the removal of the main obstacles in the path of the quasiclassical calculation of spectra—those of fixing the initial data of trajectories and finding caustics. This approach is based on the adiabatic invariance of the quantum numbers. According to the adiabatic principle, the contracted action calculated over a closed path is conserved during a slow change of the potential; i.e., it is an adiabatic invariant.<sup>4</sup> Consequently, in a slow change of the potential the Bohr-Sommerfeld quantization conditions are not violated and the trajectory of a particle will continue throughout to be a quantized one. The adiabatic principle can be used to calculate the spectrum of a Hamiltonian  $H$  in the quasiclassical approximation in the following obvious way: First one chooses a reference Hamiltonian  $H_0$  for which the classical trajectories that satisfy the quantization conditions are known, and then calculates with the classical equations of motion the development in time of these quantized trajectories during a slow change of the interaction  $V = H - H_0$ . When the interaction has been fully turned on, one obtains the quantized trajectory for the Hamiltonian  $H$  and the corresponding eigenvalue of the energy. The more slowly the interaction is turned on, the