(1973)].
[16]P. C. Kepple and H. R. Griem, Phys. Rev. 173, 317 (1968); C. R. Vidal, J. Cooper and E. W. Smity, Astrophys. J. Suppl., 25, 37 (1973).
[17]A. V. Demura, V. S. Lisitsa and G. V. Sholin, Proc. XII ICPIG, Eindhoven, Holland, 1975, p. 37.
[18]H. R. Griem, Spectral Line Broadening by Plasmas, Academic Press, N. Y. 1974.
[19]G. V. Sholin and E. A. Oks, Dokl. Akad. Nauk SSSR 209, 1318 (1973) [Sov. Phys. Dokl. 18, 254 (1973)].

Translated by R. T. Beyer

Electron spectra from the autoionization of quasimolecules

A. Z. Devdariani, V. N. Ostrovskiĭ, and Yu. N. Sebyakin

Leningrad State University
(Submitted December 2, 1976)
Zh. Eksp. Teor. Fiz. 73, 412–421 (August 1977)

The energy spectra of the electrons emitted in collisions between heavy atomic particles, in which the molecule undergoes a transition to an autoionization state, are considered. The theory employed is a generalization of Fano's method to the case of the adiabatically time-dependent Hamiltonian. Spectrum features due to an extremum of the autoionization term are investigated. The spectra exhibit interference oscillations whose phase is numerically equal to the area of the figure bounded by the term and the horizontal line corresponding to the energy of the emitted electron. The shape of the atomic autoionization lines excited during the collisions and broadened as the atomic particles fly apart is determined. It is shown that the expressions usually employed in such cases are valid only for the line wing. The feasibility of an experimental observation of the spectral features is discussed.

PACS numbers: 32.80.Dz, 34.50.Hc

§1. INTRODUCTION

An effective autoionization mechanism in slow collisions between heavy atomic particles is the transition of the quasimolecule to an unstable autoionization state. Experimental and theoretical studies of the energy distributions (spectra) of electrons produced in such reactions can be used to obtain important information on the behavior of the states and on the physics of the process.

Transitions to the continuum of free states of the electron lead to autoionization, and it is important from the standpoint of a theoretical description of the spectra to determine the extent to which the continuum can be regarded as uniform. In fact, the uniformity of the continuum is violated by the presence of the autoionization state. However, we shall be concerned with the continuum states that are the initial states (for example, in the paper by Fano[1]) and correspond to the turning off of the interaction responsible for the decay of the autoionization state. For simplicity, such states will be referred to as diabatic. The uniformity of this type of continuum may be further violated by the presence of the limit of the continuous spectrum and a rapid variation in the wave functions with energy. The latter leads to a rapid change in the matrix elements, of which we shall be mainly concerned with that corresponding to the interaction with a discrete diabatic state lying against the background of the continuum. This matrix element will, in fact, determine the width of the adiabatic autoionization state.

The limit of the continuous spectrum of the quasimolecule will, in principle, always be present, and its correct inclusion in the theory presents an additional difficulty which has been considered in a number of papers (see Demkov[2] and Solov'ev,[3] and the references therein). However, if we are interested in the spectra of electrons at relatively low energies, the continuum can be assumed to be approximately uniform.[4–6] This results in a considerable simplification of the theoretical analysis of the spectra (§2) as compared with the case of the inhomogeneous continuum and, at the same time, yields an adequate description of a number of important physical effects responsible for the various spectrum features.

Although it is basically simple, a systematic analysis of the foregoing problems has not so far been made, and the theory formulated for the interpretation of particular experimental data has frequently been found to be subject to important inaccuracies and errors which will be noted below. In §§3 and 4 we consider the spectrum features that appear when the real part of the energy of the autoionization state has extrema for finite or infinite internuclear distances. The latter case corresponds to the inclusion of the broadening of atomic autoionization lines by the interaction between the atomic particles. In the important case of Coulomb interaction (the so-called Stark broadening of lines), it is possible to achieve an important improvement in the well-known formula of Berry[7] for the line shape, which is commonly used in the interpretation of experimental data.[8–11]

The main initial propositions of the theory of spectra

 0038-5646/77/4602-0215$02.40

in the case of a homogeneous diabatic continuum have much in common with the well-developed theory of broadening of spectral lines. However, even in the analysis of the broadening of autoionization lines of atoms (§4), which is closest to this theory, there are a number of important differences between the two. They are physically related to the fact that the autoionization width is usually greater than the radiative width by several orders of magnitude. It follows that whereas the autoionization width proper can be neglected in comparison with the collisional width, in the case of radiative lines,[12] it can frequently not be neglected in the theory of autoionization line broadening. The lifetime of the autoionization states is relatively short, and the most interesting case is, therefore, the one in which the same collision event is accompanied by the formation of the autoionization state when the atoms come close together (impact parameters $\rho \lesssim r_a$, where r_a is the characteristic atomic size), whilst the broadening of the spectral lines is mainly due to distant encounters ($\rho \gg r_a$) between atoms already excited in another process and the atoms in the medium. Collision experiments can be used to exclude the effects of statistical averaging which is usually carried out in the theory of spectral-line broadening. Nevertheless, analyses of experimental data must take into account Doppler and instrumental broadening, but this problem will not be considered in this paper. It has been reviewed in detail by Gordeev and Ogurtsov[8] and by Gleizes *et al.*[11]

The above differences between the broadening of radiative and autoionization lines do not appear in the case of x-ray radiation emitted as a result of transitions to vacant molecular orbitals formed during collisions with small impact parameters. Many of the methods and results given in the present paper can, therefore, be extended to similar x-ray specta, the theory of which is being intensively developed at present.[13]

§2. BASIC EQUATIONS

Let us begin by formulating the general problem of finding the electron spectra in a form convenient for subsequent application. We shall consider the time-dependent quantum-mechanical problem which arises when the motion of the nuclei of the colliding atomic particles may be regarded as classical and given. In the orthonormal diabatic basis of discrete states $|\varphi_j\rangle$ ($j=1, 2, \ldots, N$) with energies $E_{0j}(t)$ and continuum states $|\omega\rangle$ with energies ω, the Hamiltonian $H(t)$ has the form

$$H(t)=H_0(t)+\hat{V}(t)=\sum_{j=1}^{N} E_{0j}(t)|\varphi_j\rangle\langle\varphi_j|+\int d\omega\,\omega|\omega\rangle\langle\omega|+\hat{V}(t),$$
$$\langle\varphi_i|\varphi_j\rangle=\delta_{ij}, \quad \langle\varphi_i|\omega\rangle=0, \quad \langle\omega|\omega'\rangle=\delta(\omega-\omega'), \qquad (2.1)$$

where $\hat{V}(t)$ is the interaction operator such that $\langle\omega|\hat{V}|\omega'\rangle=0$. The difference between (2.1) and the Hamiltonian used in the classic paper by Fano[1] is that the above expression contains an explicit dependence on time. The analysis given below corresponds to that given by Fano for the interaction of a number of discrete levels with a single, i.e., nondegenerate continuum.

We note that, in problems involving atomic collisions, the lower limit of the continuous spectrum is the energy $E_+(R)$ of the ionized quasimolecule. The position of the limit is, therefore, found to depend on the internuclear distance R, i.e., on the time t. In the time-dependent problem, the limit can always be made horizontal ($E\equiv 0$) through a phase transformation of the wave function with phase $-i\int E_+(t)dt$. We shall assume that this transformation has already been carried out in (2.1), so that $E_{0j}(t)$ is the energy of the molecular terms measured from the lower limit of the continuum; the energy ω of the emitted electrons is measured from it.

The solution of the time-dependent Schrödinger equa- equation will be taken in the form

$$|\psi\rangle=\sum_{j=1}^{N} a_j(t)|\varphi_j\rangle+\int d\omega\, b(\omega,t)e^{-i\omega t}|\omega\rangle, \qquad (2.2)$$

and the problem reduces to the determination of $a_j(t)$ and $b(\omega,t)$. In view of the aims of this analysis (§1), it will be sufficient to confine our attention to the simple approximation of a uniform diabatic continuum which has already been investigated in previous papers.[4-6] Assuming that the lower limit of the continuum lies well away from the energy region in which we are interested (so that the integral with respect to $d\omega$ can be evaluated between $-\infty$ and $+\infty$), and the matrix elements $\langle\varphi|V|\omega\rangle$ are slowly varying functions of ω (but, in general, are functions of t), we obtain, following Devdariani *et al.*,[6] the following set of equations involving only the amplitudes $a_j(t)$:

$$i\frac{d}{dt}a_j=\left(E_{0j}(t)-\frac{i}{2}\Gamma_j(t)\right)a_j+\sum_{\substack{k=1\\ k\neq j}}^{N}\left[V_{kj}(t)-\frac{i}{2}(\Gamma_k\Gamma_j)^{1/2}\right]a_k, \qquad (2.3)$$

$$\Gamma_j(t)=2\pi|\langle\varphi_j|\hat{V}(t)|\omega\rangle|^2, \quad V_{kj}(t)=\langle\varphi_k|\hat{V}(t)|\varphi_j\rangle, \qquad (2.4)$$

and express $b(\omega,t)$ in terms of the $a_j(t)$:

$$b(\omega,t)=-i\sum_{j=1}^{N}\int_{t_0}^{t}\left[\frac{\Gamma_j(t')}{2\pi}\right]^{1/2}a_j(t')e^{i\omega t'}dt', \qquad (2.5)$$

where t_0 is the time at which the initial conditions are specified. We shall assume that only the discrete diabatic states are occupied for $t\leq t_0$.

We note that the inhomogeneity of the continuum can be partly taken into account by evaluating $\langle\varphi_j|V(t)|\omega\rangle$ for $\omega=E_{0j}(t)$ in the expression for $\Gamma_j(t)$ in (2.4) (compare this with the analysis given by Fano[1]), and by adding the appropriate shifts to the energies $E_{0j}(t)$ in (2.5) due to the interaction with the inhomogeneous continuum.[1,5] This correction to the energy will be unimportant in the problems with which we shall be concerned below because it simply shifts the terms by a constant amount without changing the shape of the spectra.

In the Hamiltonian given by (2.1), it may be assumed that not only are $E_{0j}(t)$ and $\hat{V}(t)$ functions of time but also the basis states $|\varphi_j\rangle$ and $|\omega\rangle$. Equations (2.3) and (2.5) are then obtained by neglecting the matrix elements of the operator $\partial/\partial t$. This is valid when the rate of change of the Hamiltonian is small, and the above matrix elements are of the order of this rate of change. In the lowest order of the adiabatic approximation with which we are concerned here, decay is connected only with the fact that the levels have a finite width $\Gamma(t)$, but a more general analysis of the adiabatic approximation in its lowest order, which does not assume the homogeneity of the continuum, has been given in a recent paper by Solov'ev.[3] The next order of the adiabatic expansion for the amplitudes contains in addition the dynamic effects connected with the fact that the matrix elements of the operator $\partial/\partial t$ are nonzero in the adiabatic basis. We note that the evaluation of the corrections to the simplest adiabatic approximation is a complicated problem which has not been solved even for the two-level system.

In the special case of a single discrete term placed in the continuum, Eq. (2.3) can be solved immediately[4]:

$$a(t)=a(t_0)\exp\left[-i\int_{t_0}^{t}E(t')\,dt'\right], \tag{2.6}$$

$$b(\omega,t)=-ia(t_0)\int_{t_0}^{t}\left[\frac{\Gamma(t')}{2\pi}\right]^{1/2}\exp\left[-i\int_{t_0}^{t'}E(t'')\,dt''+i\omega t'\right]dt'. \tag{2.7}$$

In these expressions, $E(t)=E_0(t)-i\Gamma(t)/2$ can be interpreted as the complex adiabatic autoionization energy.

§3. ADIABATIC CASE. STATE-ENERGY EXTREMUM

When the collisions are not too fast, the change in the Hamiltonian must be regarded as adiabatic and the initial condition is specified for adiabatic states. It is physically natural and mathematically convenient to extend the time t_0 at which the initial conditions are specified to $-\infty$. When this is done, the initial amplitude $a(t_0)$ must be increased so that the amplitudes $a(t)$ and $b(\omega,t)$ have finite values for finite t (see also Ostrovskii[4]). The amplitude $b(\omega,t)$ then acquires a common undetermined factor which we shall denote by G and which must be found from the normalization of the spectrum to the known total initial population of the quasistationary state or by matching near the limit of the continuous spectrum. The final result is that, instead of (2.5) and (2.7), we obtain the following expressions which are the basic formulas in the present paper:

$$b(\omega)=-iG\sum_{j=1}^{N}\int_{-\infty}^{\infty}\left[\frac{\Gamma_j(t)}{2\pi}\right]^{1/2}a_j(t)e^{i\omega t}\,dt, \tag{3.1}$$

$$b(\omega)=G\int_{-\infty}^{\infty}\left[\frac{\Gamma(t)}{2\pi}\right]^{1/2}\exp\left[-i\int_{t_0}^{t}E(t')\,dt'+i\omega t\right]dt, \tag{3.2}$$

where t_0 in the last expression is simply a parameter whose choice is unambiguously related to the choice of G.

Let us begin by considering (3.2) which describes the case of a single autoionization state. The functions $E(t)$ will be assumed to be analytic (their analytic properties are discussed by Demkov *et al.*[2]). The integral (3.2) can be evaluated approximately by the method of stationary phase:

$$b(\omega)=G\sum_{n}\frac{1}{2}\left[-\Gamma(t)\Big/\frac{dE}{dt}\right]^{1/2}\Big|_{t=t_n}\exp\left[-i\int_{t_0}^{t_n(\omega)}E(t')\,dt'+i\omega t_n(\omega)\right] \tag{3.3}$$

where $t_n(\omega)$ is a stationary phase point, i.e., the root of the equation

$$E(t_n)=E_0(t_n)-\frac{1}{2}i\Gamma(t_n)=\omega. \tag{3.4}$$

Summation is carried out over all points t_n on the contour of integration after it has been deformed in accordance with the method of stationary phase. This approximation will, in general, correspond to a slow variation of the Hamiltonian with time. Its validity will be discussed in detail below for a number of special cases. The approximation is, in fact, consistent with the general adiabatic theory of transitions to the continuum when the latter is not homogeneous,[2,3] and this allows us, for example, to carry out the above matching with the results obtained near the limit of the continuous spectrum (see Ostrovskii[4] for further details).

Among the points $t_n(\omega)$, we can choose those that are close to the real axis of t, and reach the real axis as $\Gamma\to 0$. This can be described qualitatively by saying that the corresponding terms in (3.3) describe classically the allowed population of continuum states in accordance with the Franck-Condon principle. This population occurs in a resonant fashion at the instant of time when the real part of the autoionization term becomes equal to ω (to within Γ). In general, there are several such instants of time [when $E_0(t)$ is nonmonotonic] and the arguments in (3.3) describe different phases assumed by the emitted electron. These phases are complex, and this takes into account the reduction in the population of the autoionization state due to decay. Coherent emission of electrons with the same energy at different instants of time produces interference. Since the phase difference is a function of ω, the spectrum is found to contain oscillations.

There are also other points $t_n(\omega)$ that remain complex as $\Gamma\to 0$. This corresponds to the classically forbidden subbarrier transition to the continuum, and usually produces a fast (exponential) decrease in the spectrum with ω.

Let us illustrate this picture by considering the example of a parabolic energy term[1)] $E_0(t)=-\alpha t^2+\omega_0(\alpha>0)$. In this case, the spectrum can be expressed in a closed form in terms of the Airy function Ai(z):

$$b(\omega)=G\mathrm{Ai}\left[\alpha^{-1/3}\left(\Delta\omega+\frac{1}{2}i\Gamma\right)\right],\quad \Delta\omega=\omega-\omega_0. \tag{3.5}$$

When $\omega \gg \omega_0$, the continuum states are populated by the subbarrier mechanism (the root of (3.4) is near the imaginary axis):

$$b(\omega)=-\frac{1}{2}GA^{1/2}(\omega)\exp\left(-\frac{2}{3}A(\omega)\right)$$
$$A(\omega)=\alpha^{-1/2}\left(\Delta\omega+\frac{1}{2}i\Gamma\right)^{1/2} \quad (\mathrm{Re}\,A(\omega)>0). \tag{3.6}$$

The form of the leading exponential which describes the fast fall in the spectrum in this region [$|b| \sim \exp(-\frac{2}{3}\alpha^{-1/2}\times\Delta\omega^{3/2})$] does not depend on Γ. States with $\omega \ll \omega_0$ are populated in a classically allowed fashion at two different instants of time [roots of (3.4) near the real axis: $t \approx \pm\alpha^{1/2}|\Delta\omega|^{1/2}$]

$$b(\omega)=GB^{-1/4}(\omega)\sin\left[\frac{2}{3}B(\omega)+\frac{1}{4}\pi\right],$$
$$B(\omega)=\alpha^{-1/2}\left(-\Delta\omega+\frac{1}{2}i\Gamma\right)^{1/2}, \quad (\mathrm{Re}\,B(\omega)>0). \tag{3.7}$$

The phase of the resulting oscillations is $\sim\frac{2}{3}\alpha^{-1/2}(\Delta\omega^{3/2})$ and is numerically equal to the area of the figure between the $E_0(t)$ curve (in our case, a parabola) and the horizontal line $E = \omega$. The amplitude of the oscillations decreases exponentially with $\Delta\omega(\Delta\omega<0)$, i.e., $\sim\exp[-\Gamma(\Delta\omega/\alpha)^{1/2}/2]$, because the population of the state decreases due to decay. For the same reason, the quantity $(\overline{|b|^2})^{1/2}$, averaged over the oscillations, increases in accordance with the same exponential. We emphasize that the rate of this change is smaller than in the subbarrier region and is independent of Γ. In the case of small Γ, there may also be a second intermediate asymptotic region of values of $\Delta\omega$. In this region, the argument of the exponential is still small, and the main feature is the preexponential factor. The quantity $\overline{|b|^2}$ decreases as $|\Delta\omega|^{-1/2}$.

A formula analogous to (3.5) was introduced by Miller[14] in the theory of Penning ionization with a quantum-mechanical description of the motion of the nuclei. In the time-dependent theory, a similar result was obtained by Gerber and Niehaus.[10] However, both papers ignore the imaginary part in the argument of the Airy function, i.e., the reduction in population due to decay.

§4. BROADENING OF AUTOIONIZATION LINES

Consider the situation where the decay of the autoionization states occurs mainly for large internuclear distances R. The problem of finding the spectrum then reduces to the problem of broadening of the autoionization lines of an isolated atom (this atom is characterized by the position of the level $E_{0\infty}$ and its width $\Gamma_{0\infty}$) due to the long-range part of the potential[2)]

$$E_0(R)=E_{0\infty}+C_n/R^n. \tag{4.1}$$

The behavior of this function for large R is frequently determined by the limit of the continuous spectrum because the interaction between the atomic particles after the emission of the electron is usually stronger than in the initial state.

When the autoionization state is populated in the course of the atom-atom collision, the impact parameter ρ may be regarded as small in comparison with the internuclear distance determining the broadening (§1). We can then substitute $R(t)=v(t-t_0)$, where v is the relative velocity of the atom at infinity. The initial time t_0 then corresponds to a close approach of the particles for which the state (4.1) is populated adiabatically:

$$b(\omega)=-ia(t_0)\int_{-\infty}^{\infty}\left[\frac{\Gamma(t)}{2\pi}\right]^{1/2}\exp\left[-i\int E(t')dt'+i\omega t\right]dt. \tag{4.2}$$

If we evaluate this integral by the method of stationary phase by analogy with §3, using (4.1) and $\Gamma(t)=\Gamma_{0\infty}$, we obtain the following expression for the spectrum:

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2 = \frac{C_n^{1/n}}{nv}\frac{\Gamma}{(\Delta\omega^2+\Gamma^2/4)^{(n+1)/2n}}\exp\left[-\frac{2n}{n-1}\frac{C_n^{1/n}}{v}\left(\Delta\omega^2+\frac{\Gamma^2}{4}\right)^{(n-1)/2n}\right.$$
$$\left.\times\sin\left(\frac{n-1}{n}\mathrm{arctg}\frac{\Gamma}{2\Delta\omega}\right)\right], \quad \Delta\omega=\omega-E_{0\infty}, \tag{4.3}$$

which is valid for

$$\Delta\omega^2+\frac{\Gamma^2}{4}\gg\left(\frac{(n+1)^2}{n}\frac{v}{C_n^{1/n}}\right)^{2n/(n-1)}. \tag{4.4}$$

We are assuming that $n>1$ and $C_n>0$; for $C_n<0$, the amplitude $b(\omega)$ is obtained by reversing the sign of $\Delta\omega$ and taking the complex conjugate.

For the line wings ($|\Delta\omega| \gg \Gamma/2$), Eq. (4.3) yields

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{C_n^{1/n}}{nv}\frac{\Gamma}{(\Delta\omega^2+\Gamma^2/4)^{(n+1)/2n}}\exp\left(-\Gamma\frac{C_n^{1/n}}{v}\Delta\omega^{-1/n}\right), \quad \Delta\omega\gg\frac{\Gamma}{2},$$
$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{C_n^{1/n}}{nv}\frac{\Gamma}{(\Delta\omega^2+\Gamma^2/4)^{(n+1)/2n}}\exp\left[-\frac{C_n^{1/n}}{nv}|\Delta\omega|^{-1/n}\right.$$
$$\left.\times\left(\Gamma\cos\frac{\pi}{n}+\frac{2n}{n-1}|\Delta\omega|\sin\frac{\pi}{n}\right)\right], \quad \Delta\omega\ll-\frac{\Gamma}{2}. \tag{4.5}$$

Thus, when $C_n>0$, the line is shifted toward higher energies, since the corresponding wing is formed through classically allowed population. The wing $\omega<E_0$ decreases exponentially. For the line center, we can neglect

$$\int^{t}\frac{C_n}{R^n(t)}dt,$$

in (2.7) in the case of sufficiently fast collisions, and this yields the Lorentz profile corresponding to the autoionization of an isolated atom:

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{1}{2\pi}\frac{\Gamma}{\Delta\omega^2+\Gamma^2/4}. \tag{4.6}$$

A closed expression for the line profile in terms of the Macdonald function can be obtained for $n=2$, which is important in practice and corresponds to the charge-dipole interaction between the particles after ionization:

$$b(\omega)=-iV^*a(t_0)\left[\frac{4C_2}{v^2(\Delta\Omega+i\Gamma/2}\right]^{1/2}$$
$$\times K_1\left(\left[-\frac{4C_2(\Delta\Omega+i\Gamma/2}{v^2}\right]^{1/2}\right)e^{i\omega t_0}.$$

It is a simple matter to take this expression to the limiting cases of (4.3)–(4.6).

The case of ion states, which is important in practice when the two atomic particles carry charges Z_1 and Z_2 (this is the so-called Stark shift), requires separate analysis. In this case, $n=1$, $C_1=-Z_1Z_2$ and (2.6) yields

$$b(\omega)=Va(t_0)\left(-\Delta\omega-\frac{i}{2}\Gamma\right)^{-iC_1/v-1}\Gamma\left(1-\frac{C_1}{v}\right)\exp\left(\frac{-\pi}{2}\frac{C_1}{v}+i\omega t_0\right), \tag{4.7}$$

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{\Gamma}{\Delta\omega^2+\Gamma^2/4}\frac{C_1}{2v\,\mathrm{sh}\,\pi C_1/v}\exp\left(\pi\frac{C_1}{v}-2\frac{C_1}{v}\operatorname{arctg}\frac{\Gamma}{2\Delta\omega}\right). \tag{4.8}$$

In the case of fast collisions, we obtain the Lorentz profile (4.6) but, for slow collisions, the line becomes strongly broadened and, in its wings,

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{C_1}{v}\frac{\Gamma}{\Delta\omega^2+\Gamma^2/4}\exp\left(-\frac{2C_1\pi}{v}-\frac{C_1\Gamma}{v\Delta\omega}\right), \quad \Delta\omega\gg\Gamma/2. \tag{4.9}$$

$$\left|\frac{b(\omega)}{a(t_0)}\right|^2=\frac{C_1}{v}\frac{\Gamma}{\Delta\omega^2+\Gamma^2/4}\exp\left(-\frac{C_1\Gamma}{v\Delta\omega}\right), \quad \Delta\omega\ll-\Gamma/2, \quad \pi C_1/v\gg1. \tag{4.10}$$

The last expression (without the term $\Gamma^2/4$ in the denominator) is, in fact, the Berry formula[7] which is commonly used in the analysis of experimental data.[8-11] It can be obtained on the basis of simple phenomenological considerations.[9] It is important to emphasize, however, the limited range of validity of (4.10), which is connected with the fact that this expression is obtained by summing the decay probabilities (and not the amplitudes), and the contribution of interference to the spectrum is not taken into account. The Berry formula cannot, therefore, be taken to the limit of the horizontal term ($C_1/v\to0$), and does not describe the line center, or the classically forbidden wing for sufficiently small C_1/v, although it does provide the correct position of the line maximum $\Delta\omega_{max}=-C_1\Gamma/2v$. The figure shows that, when $C_1/v\leq5$, calculations based on the exact expression (4.8) are not very different from those obtained from the approximate expression (4.10). In particular, the width of the spectrum calculated from (4.8) for $C_1/v=5$ is smaller by a factor of two than the width calculated from the Berry formula.

A closed expression for the line shape in terms of the incomplete gamma function γ can also be obtained for the exponentially varying energy term, which physically corresponds to the overlap of the atomic shells at small and intermediate interatomic distances. In this case,

$$E(R)=E_{0\infty}+Ce^{-\alpha R}\approx E_{0\infty}+C\exp[-\alpha v(t-t_0)],$$

$$b(\omega)=-ia(t_0)V^*\left(\frac{i\alpha v}{C}\right)^{-i\Delta\Omega/\alpha v}\gamma\left(-\frac{i\Delta\Omega}{\alpha v},-\frac{iC}{\alpha v}\right)\exp\left(i\omega t_0-\frac{iC}{\alpha v}\right), \tag{4.11}$$

where $\Delta\Omega=\Delta\omega+i\Gamma/2$.

where $\gamma(\alpha,x)$ is the incomplete gamma function.

5. CONCLUSIONS

We have confined our attention mainly to the various features present in the electron spectrum emitted during autoionization. Direct comparison of the formulas given in §§3 and 4 with experiment would, in general,

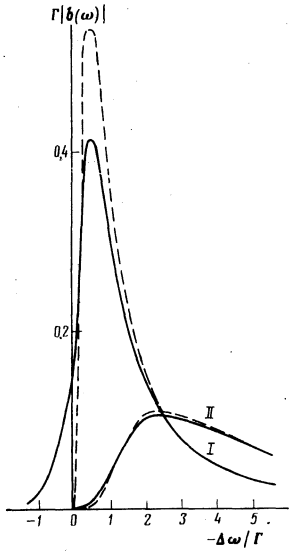

FIG. 1. Stark broadening of autoionization lines $[\Gamma|b(\omega)|^2]$. Solid curve—calculation based on (4.8), dashed curve—calculation based on (4.10); I—$C_1/v=10$, II—$C_1/v=5$.

require the use of the coincidence method in which the spectra would be measured for a fixed angle of scattering of the heavy particles. However, in most experiments, the scattering angle is not held constant, so that the corresponding formulas for the spectrum must be averaged over the impact parameter ρ.

In general, this averaging tends to smooth out the oscillations, but the spectrum, nevertheless, retains a certain structure. The position of this structure is determined by the difference between the autoionization molecular state and the limit of the continuous spectrum, at the point of its extremum. The characteristic scale of the structure along the energy axis should, as a rule, occupy an intermediate position between the relatively narrow autoionization lines (§4) and the broad maxima appearing due to the vanishing of $|b(0)|^2$ for non-Coulomb potentials.[2,3]

The persistence of the oscillations may be connected with the population of states during close collisions (small ρ). When the state populated in this way has a extremum, the oscillations remain in the spectrum even after averaging over ρ. On the other hand, if the state interacts with another, the oscillations may persist in the total cross sections[15] (for example, in the case of excitation of a given autoionization line).

Interesting spectrum features may appear during an interaction between several autoionization states. The simplest case (interaction between two states) can be described by the Landau-Zener model. Interference-type oscillations connected with the population of states in the continuous spectrum at two different instants of time are found to appear in a certain range of electron energy. At other energies, only single population takes place, and the corresponding amplitude contains the Landau-Zener transition amplitude as a factor. A more detailed analysis of this problem will be given elsewhere.

In addition to the oscillations discussed above, which appear during the initial population of one autoionization state, there may be other oscillations connected with

interference between electrons of the same energy but emitted at different instants of time from different states when several autoionization states are excited during the collision.[17] These oscillations can also be investigated by the method outlined above.

There are also other properties of the spectra such as inflections, which appear when a new autoionization channel is opened,[16] but these are difficult to observe.

In the analysis given above, the motion of the nuclei was described classically. A quantum-mechanical description is required for small relative velocities of the colliding particles and for the description of the scattering of light particles (an example of this is given by Ostrovskiĭ[18]).

The authors are indebted to Professor Yu. N. Demkov and Professor N. P. Penkin for their interest in this work.

[1)]The quadratic approximation to the state energy was used previously by Ostrovskiĭ[4] to investigate spectrum features due to the turning point in the radial motion of the nuclei.

[2)]As already noted, $E_0(R)$ is the difference between the energy of the discrete term and the limit of the continuous spectrum.

[1]U. Fano, Phys. Rev. 124, 1866 (1961).
[2]Yu. N. Demkov, in: Voprosy teorii atomnykh stolknovenniĭ (Problems of the Theory of Atomic Collisions), izd. LGU, 1975; Yu. N. Demkov and V. N. Ostrovskiĭ, Metod potentsialov nulevogo radiusa v atomnoĭ fizike (Method of Zero-Range Potentials in Atomic Physics), izd. LGU, 1975.
[3]E. A. Solov'ev, Zh. Eksp. Teor. Fiz. 70, 872 (1976) [Sov. Phys. JETP 43, 453 (1976)].
[4]V. N. Ostrovskiĭ, Vestn. Leningr. Univ. Fiz. Khim. No. 16, 31 (1972).
[5]V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 66, 1981 (1974) [Sov. Phys. JETP 39, 975 (1974)].
[6]A. Z. Devdariani, V. N. Ostrovskiĭ, and Yu. N. Sebyakin, Zh. Eksp. Teor. Fiz. 71, 909 (1976) [Sov. Phys. JETP 44, 477 (1976)], Tezisy dokladov VI Vsesoyuznoi konferentsii po fizike élektronnykh i atomnykh stolknovenii, Tbilisi (Abstracts of Papers read to the Sixth All Union Conference on the Physics of Electronic and Atomic Collisions, Tbilisi), 1975, p. 46.
[7]R. B. Barker and H. W. Berry, Phys. Rev. 151, 14 (1966).
[8]Yu. S. Gordeev and G. N. Ogurtsov, Zh. Eksp. Teor. Fiz. 60, 2051 (1971) [Sov. Phys. JETP 33, 1105 (1971)].
[9]G. N. Ogurtsov, Rev. Mod. Phys. 44, 1 (1972).
[10]G. Gerber and A. Niehaus, J. Phys. B 9, 123 (1976).
[11]A. Gleizes, P. Benoit-Cattin, A. Bordenave-Montesquie, and H. Merchez, J. Phys. B 9, 473 (1976).
[12]I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Chap. 10, Fizmatgiz, 1963 (English Transl., Pergamon Press, Oxford, 1972).
[13]J. Macek and J. S. Briggs, J. Phys. B 7, 1312 (1974); W. Lichten, Phys. Rev. A 9, 1458 (1974).
[14]W. H. Miller, J. Chem. Phys. 52, 3563 (1970).
[15]H. M. Rosenthal and H. M. Foley, Phys. Rev. Lett. 23, 1480 (1969).
[16]F. I. Dalidchik, Zh. Eksp. Teor. Fiz. 66, 849 (1974) [Sov. Phys. JETP 39, 410 (1974)]; F. I. Dalidchik and G. K. Ivanov, Opt. Spektrosk. 38, 633 (1975) [Opt. Spectrosc. (USSR) 38, 359 (1975)].
[17]R. Morgenstern, A. Niehaus, and U. Thielman, Phys. Rev. Lett. 37, 199 (1976).
[18]V. N. Ostrovskiĭ, Zh. Eksp. Teor. Fiz. 72, 2079 (1977) [Sov. Phys. JETP 45, 1092 (1977)].

Translated by S. Chomet

Theory of excitation of a quantum nonlinear oscillator by a harmonic force

M. V. Kuz'min and V. N. Sazonov

P. N. Lebedev Physical Institute, U.S.S.R. Academy of Sciences
(Submitted December 8, 1976)
Zh. Eksp. Teor. Fiz. 73, 422–429 (August 1977)

The first quantum corrections to the classical equations of motion of a nonlinear oscillator are derived. Experiments on the excitation and dissociation of molecules by laser radiation are discussed. It is shown that a molecule can be excited to considerably larger quantum numbers than is indicated by elementary theory: for typical values of the parameters this difference amounts to one and one-half orders of magnitude.

PACS numbers: 03.65.Ge, 33.10.Cs

Experiments on the excitation of molecular vibrations by laser radiation pose problems in the theory of vibrations whose solution requires that quantum effects must not be neglected. Even in the simplest case, however, that of a one-dimensional nonlinear oscillator, inclusion of quantum effects is an extremely complicated problem. There have been many papers[1–24] on attempts to solve this problem using various simplifying assumptions. Although a number of interesting results have been obtained in these papers, there still exists no consistent theory of such excitation, so that in many experimental researches on excitation of molecules the results are

 0038-5646/77/4602-0220$02.40