

Highly-excited atoms in the electromagnetic field

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A review is given of the properties of highly excited atoms placed in an electromagnetic field. The probabilities of bound-bound and bound-free transitions between quasiclassical atomic states, and also approximate selection rules for such transitions, are examined. The properties of the dynamic polarizability of highly excited states of atoms are investigated. Quantum-mechanical ionization mechanisms (multiphoton and tunneling) are discussed for highly excited states. Much space is devoted to the stochastic dynamics of classical atomic electrons in a varying monochromatic electromagnetic field. The threshold electric field for the stochastic motion of an electron and the ionization of an atom is given as a function of the field frequency, its polarization, and the principal quantum number of the atomic state under consideration. The influence of orbital angular momentum of the state from which ionization takes place on the stochastization process is discussed. Classical diffusion ionization of a highly excited atom in an electromagnetic field is considered within the framework of classical mechanics and the quasiclassical quantum-mechanical approximation. The validity of classical mechanics in relation to the properties of highly excited atoms in an electromagnetic field is examined. The realization of quantum and quasiclassical ionization of highly excited atoms is considered. The final part of the review analyzes experimental data on the behavior of highly excited atoms in a radiofrequency field. Comparison of experimental data with the theory given in this review has demonstrated good agreement between them.

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1. INTRODUCTION

In this review, we shall be concerned with highly excited atoms, the basic properties of which are sufficiently well known.¹ Some of these properties will, nevertheless, be recalled so far as they will be needed in our discussion. By definition, a highly excited state is a state whose principal quantum number is $n \gg 1$. The highly excited states of complex atoms are hydrogen-like, i.e., their wave functions are identical with the wave functions of the hydrogen atom. The energies of the highly excited states have the form

$$E_n = -1/2n^2; \quad (1)$$

where, here and henceforth, we use the atomic system of units in which $e = \hbar = m = 1$. According to the correspondence principle, the classical Kepler frequency Ω of an electron in an atom is given by $\Omega = E_n - E_{n+1}$, and, if we combine this with (1), we obtain

$$\Omega = n^{-3}. \quad (2)$$

It is well known that, in general, the laws of quantum mechanics have to be used in the description of atoms. However, when $n \gg 1$, quantum-mechanical calculations can be performed within the framework of the quasiclassical approximation, and many of the results obtained in this way turn out to be identical with the results obtained in classical mechanics.

In the ensuing review, we shall consider nonlinear phenomena that arise during the interaction between a highly excited atom and a varying electromagnetic field. The interaction between the electromagnetic field and an atom in the ground state, or in one of the low-lying excited quantum states, has been investigated in sufficient detail. In particular, dynamic polarizability, and multiphoton and tunneling ionization of atoms, are now well explored.^{2,3} In this review, we shall discuss nonlinear effects for highly excited atoms.

As a rule, we shall consider electromagnetic fields of frequency of the order of the Kepler frequency (2). For highly excited states, this corresponds to the microwave frequency range. By varying the frequency ω , the electric field \mathcal{E} , and the principal quantum number n of the state under consideration, it is possible to ensure that the adiabatic parameter $\gamma = \omega/n\mathcal{E}$ will assume very different values. It is well known⁴ that the magnitude of this parameter determines whether a given quantum-mechanical ionization process is of the multiphoton or tunneling type. Anticipating a little, we note that the quasiclassical character of highly excited states leads to qualitatively new phenomena that have no analog in ground-state atoms. The most important of these phenomena is the onset of stochasticity in the motion of atomic electrons, which leads to diffusion ionization of atoms. Considerable space will be given to this process in the present review. We note that the motion of a charged particle on a circular orbit in an external resonance field has long attracted the attention of researchers. It is precisely as a result of the solution of this problem that Veksler and MacMillan discovered in the 1940's the well-known phenomenon of phase stability, which is the basis for the operation of all modern cyclic accelerators. Later work, concerned with the motion of particles in magnetic traps, led to the investigation of the phenomenon of dynamic stochasticity of classical systems. In the present review, this phenomenon will be discussed by considering the example of an electron in a highly excited (Rydberg) atom.

2. PROBABILITIES AND APPROXIMATE SELECTION RULES FOR BOUND-BOUND AND BOUND-FREE TRANSITIONS BETWEEN QUASICLASSICAL STATES

It is well known² that the probabilities of multiphoton transitions are determined by composite matrix elements that can be written as products of the matrix elements for single-photon transitions. The latter are, in turn, expressed in terms of the radial dipole matrix elements

$$R_{nl}^{n'l \pm 1} = \int_0^\infty R_{n'l}(r) R_{nl}(r) r^2 dr; \quad (3)$$

where $R_{nl}(r)$ are the radial wave functions and n and l are the principal and orbital quantum numbers. For the hydrogen atom, Gordon has obtained an exact expression for the integral given by (3) in terms of the hypergeometric functions (see, for example, Ref. 5).

However, Gordon's formula is difficult to use for transitions between states with high values of n , both in qualitative estimates and in direct calculations, since all three parameters of the hypergeometric function turn out, in general, to be large.

Various approximate simple expressions for the matrix element (3) can be obtained if $n, n' \gg 1$. A resumé of such expressions is given in Ref. 6. The probabilities of radiative transitions between states with $n, n' \gg 1$ and $\Delta n = n - n' \ll n, n'$, are given in Ref. 6 and in Ref. 1. Heisenberg's correspondence principle then shows that the matrix element (3) reduces to the Fourier

component of the time-dependent classical coordinate of Keplerian motion.

The quasiclassical values of the matrix elements (3) and of the probabilities of radiative transitions are given in Ref. 6 for $n, n' \gg 1$ and $\Delta n \sim n, n'$. For low orbital angular momenta $l \ll n$, the matrix elements (3) are then quasiclassically high, i.e., of the order of $n^{1/3}$. This is a consequence of the strong overlap of the wave functions at short distances r . Moreover, Ref. 6 also gives the matrix elements and the probabilities of radiative transitions for high $l \sim n$. They turn out to be exponentially small. Finally, definite simplifications are achieved in the exact Gordon formulas when one of the quantum numbers is $n \gg 1$ and the other $n' \sim 1$. The hypergeometric functions are then replaced by confluent hypergeometric functions that have simpler properties. Further details can be found in Ref. 6.

Comparison of the quasiclassical values of the different matrix elements leads to the conclusion that, for transitions with $l \sim n \gg 1$, the change in the principal quantum number n is accompanied by a change in the orbital quantum number l , which has an overwhelming probability of varying in the same direction as n . This rule was found empirically by Bethe.⁷ Quasiclassical estimates of the matrix elements show that this rule is violated for low orbital quantum numbers and, especially, for $l \ll n^{2/3}$, for which the results obtained in Ref. 6 show that the quasiclassical dipole matrix element is independent of l , i.e., is identical for transitions with $l' = l \pm 1$. The selection rule just mentioned is generalized in Ref. 8 as follows: a change in l is accompanied by a change in n in preferentially the same direction and by the same amount.

From the matrix elements for bound-bound transitions, we can readily obtain the matrix elements for bound-free transitions by replacing the corresponding principal quantum number n with i/p , where p is the momentum of the electron in the continuous spectrum. In this way, we obtain the photoionization cross sections⁹ for highly excited states.

Analytic continuation in the other principal quantum number n' can be used to obtain the quasiclassical matrix elements describing transitions between quasiclassical states in the continuous spectrum, i.e., states with $p, p' \ll 1$. These matrix elements, and the corresponding bremsstrahlung absorption and emission cross sections for low-energy electrons scattered by a Coulomb center, are given in Ref. 6.

It is important to note that, if we assume that all states with particular magnetic quantum numbers are occupied with equal probability, the average of the resulting probabilities of single-photon radiative transitions over l leads to the well-known Kramers formulas. We emphasize that all these average formulas (for bound-bound, bound-free, and free-free transitions) contain as their main component the contribution due to transitions between states with low orbital quantum numbers $l \ll n$.

Thus, the numerous quasiclassical formulas given in Ref. 6 can be used to describe radiative transitions

when one or both states involved in the transition lie near the boundary between the discrete and continuous spectra.

For complex atoms, we must replace n in all these formulas with $n^* = n - \delta_l$, where δ_l is the quantum defect of the state n, l . This replacement and the corresponding numerical calculations of the radial dipole matrix elements (3) are given in Ref. 9 for $\Delta n \ll n, n'$. The replacement of n with n^* is very important in this case because δ_l is of the order of unity for low l , and Δn undergoes a substantial change when n is replaced with n^* . However, when we are dealing with matrix elements for which $\Delta n \sim n, n'$, the replacement of n with n^* has practically no effect on Δn , and we may conclude that the quantum defect has no effect on matrix elements with $\Delta n \sim n, n'$. Next, when $l \sim n$, the quantum effect is, in general, practically absent, and replacement of n with n^* is unnecessary for both transitions with $\Delta n \ll n, n'$ and those with $\Delta n \sim n, n'$.

The probabilities of quadrupole transitions between highly-excited states of a hydrogen-like atom were calculated in Ref. 10.

To conclude this section, we note that a generalization of the Heisenberg correspondence principle to the case where $\Delta n \sim n, n'$ is given in Ref. 6.

3. PERTURBATION OF HIGHLY EXCITED ATOMIC STATES

The perturbation of ground and low-lying atomic states by the field of a monochromatic wave $\mathcal{E} \cos \omega t$ has been described in detail in the literature.^{2,3} Here, we shall begin by turning to the perturbation of highly excited states of the hydrogen atom, characterized by quantum numbers nlm ($n \gg 1$). To be specific, we shall suppose that the field acting on the atom is linearly polarized along the z axis.

For the moment, we shall postpone the discussion of the linear Stark shift in a varying field, and will turn to the quadratic Stark effect, i.e., to the determination of the dynamic polarizability. This quantity is the proportionality coefficient in the expression for the atomic level shift δE_{nlm} , produced when a monochromatic electromagnetic field is turned on, as a function of the square of the field amplitude:

$$\delta E_{nlm} = -\frac{1}{4} \alpha_{nlm} \mathcal{E}^2.$$

This expression is valid when the frequency ω of the external field is not in resonance with the atomic transition frequencies.

It is well known^{2,3} that, in general, the dynamic polarizability is given by

$$\alpha_{nlm} = 2 \sum_{n'l'm'} \frac{\omega_{nn'}}{\omega^2 - \omega_{nn'}^2} |z_{nlm}^{n'l'm'}|^2, \quad (4)$$

where $\omega_{nn'}$ is the frequency of the atomic transition between states with principal quantum numbers n and n' , i.e.,

$$\omega_{nn'} = 1/(2n'^2) - 1/(2n^2), \quad (5)$$

and $z_{nlm}^{n'l'm'}$ is the dipole matrix element of the operator z between Coulomb wave functions.

For the ground and low-lying atomic states, the coefficient α can be calculated only by numerical methods on a computer, since the matrix elements have a complicated form. In the case of highly excited states, ($n \gg 1$), an analytic expression¹¹ can be obtained for (4) in a relatively simple manner. The dependence on the magnetic quantum number m in (4) can readily be extracted with the aid of Eq. (29.7) of Ref. 7. The summation over l' can be performed explicitly, since it involves only two terms with $l' = l \pm 1$. Thus, to solve the problem, we must evaluate the sum in (4) over the principal quantum numbers n' of the virtual states (including integration over the continuous spectrum). This problem can be divided into two, namely, (1) summation over values of n' that are very different from n , i.e., $\Delta n \sim n$, and (2) summation over n' close to n , i.e., $\Delta n \ll n, n'$.

Let us begin by considering the former case. Substituting the corresponding quasiclassical matrix elements (see Sec. 2), and replacing the quasiclassical summation over n' with integration in accordance with the rule

$$\sum_{n'} \frac{1}{n'^2} (\dots) = \int_{-\infty}^{\infty} d\omega_{nn'} (\dots),$$

we readily verify that the corresponding contribution to the polarizability (4) is equal to zero because the integrand is odd in the variable $\omega_{nn'}$. This is explained by the quasiclassical nature of the spectrum of highly excited states and the resulting symmetry of the summation over $n' > n$ and $n' < n$. We note that, for the ground and low-lying excited states, the above statement is definitely incorrect because the summation over n' is then essentially asymmetric in n .

Thus, the sum in (4) is determined only by values of n' that are close to n , in which case, we cannot replace the sum with an integral because the former then contains a relatively small number of significant terms. Since, in the sum given by (4), states with $n' > n$ compensate to a large extent the states with $n' < n$, we have to use more accurate expressions for the radial dipole matrix elements (3) than those obtained on the basis of the correspondence principle (see Sec. 2), and include terms that follow from the lowest-order approximation in the quasiclassical parameter $1/n$. Moreover, the expression given by (5) must include not only the linear but also the quadratic terms of the expansion in the difference Δn . By taking all these points into consideration, it is possible¹¹ to obtain an analytic expression for α_{nlm} . This expression is too complicated to be reproduced here, and we shall therefore confine our attention to the relatively simple case for which $l = m = 0$:

$$\alpha_{n00} = \frac{2}{3} n^6 \sum_{k=1}^{\infty} \frac{7k^2 - (\omega n)^2}{[k^2 - (\omega n)^2]^2} J_k'^2(k); \quad (6)$$

where $J_k(x)$ is a Bessel function.

It is clear from (6) that

$$\alpha_{nlm} \sim n^6, \quad (7)$$

provided only we are not in a region of resonance with the discrete atomic states in the neighborhood of the

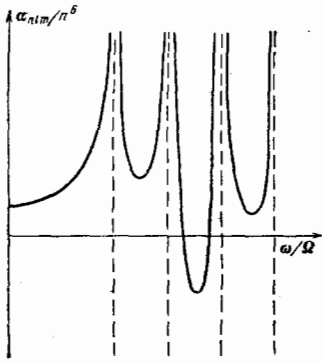


FIG. 1. Dynamic polarizability of a highly excited state (nlm) as a function of the frequency ω of the electromagnetic field. The quantity α_{nlm}/n^6 is plotted against $\omega n^3 = \omega/\Omega$. The vertical asymptotes correspond to resonances with the nearest highly excited states.

n th state. These resonances are given by the obvious conditions

$$\omega = \frac{k}{n^3}, \quad (8)$$

where k is an integer. It is clear from (6) that the quantity α_{nlm} becomes infinite in the neighborhood of each resonance, but does not change sign and remains positive. It is thus clear that the resonance behavior of the dynamic polarizability of highly excited states (Fig. 1) is qualitatively different from the resonance behavior of α_{nlm} for the ground and low-lying excited states for which it changes sign as it passes through resonance (see Figs. 8.1 and 8.2 in Ref. 2). This difference is explained by the fact that, in the case considered here, we have the superposition of resonances with higher- and lower-lying states as compared with n , whereas, for $n \sim 1$, we have a resonance with one particular discrete atomic level corresponding to the given frequency.

This conclusion is, of course, valid provided the anharmonism of the Rydberg states is ignored.

Let us now consider the behavior of the dynamic polarizability in intervals between resonances. It is well known (see, for example, Fig. 8.1 of Ref. 2) that, for the ground states of atoms (in the present case, $n = 1$), the dynamic polarizability in a linearly polarized field will vanish once in each interval between resonances. For low-lying excited states ($n \sim 1$), the relationship is different because, as the frequency increases, there may be resonances both with higher-lying and lower-lying states. In particular, in the intervals between resonances, the dynamic polarizability may not vanish or may vanish twice (but with a change in sign across each resonance). For the highly excited states considered here ($n \gg 1$), the dynamic polarizability is large and positive near the resonance frequencies but, in the intervals between resonances, it can assume negative values because of the large negative term in (6) which corresponds to $k = 1$ for frequencies $\omega > \sqrt{7}/n^3$. Under these conditions, it vanishes twice in the interval between resonances.

It is now important to note that the magnitude of the dynamic polarizability (6) is lower by a factor $\sim n$ than

each of the terms in the sum in (4) that is of the order of n^7 for frequencies $\omega \sim n^{-3}$. This fact is a consequence of the mutual compensation of terms with $n' > n$ and $n' < n$, mentioned above.

In the static case, $\omega n^3 \ll 1$, it follows from (6) that the dynamic polarizability is positive. This is in agreement with the well-known result that the hydrogen energy levels always shift downward as a consequence of the quadratic Stark effect in a constant external field. Actually, the transition from the spherical to the parabolic basis in terms of which the static shifts of the atomic states of hydrogen are expressed can be achieved by multiplying by the squares of the corresponding Clebsch-Gordan coefficients.

A special case arises in the asymptotic limit of high frequencies for which $\omega n^3 \gg 1$. It is then clear from (6) that the dynamic polarizability becomes very low and negative. Using the summation theorem for Bessel functions, we obtain

$$\alpha_{n00} = -\frac{1}{3\omega^2} \ll n^6. \quad (9)$$

The quantity given by (9) determines the vibrational energy of a free electron in an external field of frequency ω . The numerical factor in (9) is connected with the extraction of the spherically symmetric state with $l = m = 0$ from the plane wave characterizing the wave function of the electron in this particular limit. This extraction corresponds to averaging over the solid angle:

$$\frac{\cos^2 \theta}{4\pi} = \frac{1}{3}.$$

All the above conclusions can be transferred without any fundamental change to the case of arbitrary l and m . The universal dependence on m appears in the dynamic polarizability in the limit $l \gg 1$:

$$\alpha_{nlm} \sim \left(1 - \frac{m^2}{l^2}\right). \quad (10)$$

The qualitative form of the dynamic polarizability as a function of ωn^3 is shown in Fig. 1. It illustrates the various properties of the dynamic polarizability of highly excited states that were discussed above.

The condition for the validity of the above expressions is that the next orders of perturbation theory in the electric field must be small in comparison with the quadratic term. This is so when $\mathcal{E} \ll n^{-4}$ (see Sec. 6). Moreover, we have neglected in our discussion the linear Stark shift which, in the case of the varying field, is reflected in the filling of the quasienergy states. The energies of the most highly filled states correspond to the linear Stark shift that occurs in a constant field. According to general theory,^{2,3} the appearance of these quasienergy states, simulating the linear Stark shift, can be neglected when

$$\frac{d\mathcal{E}}{\omega} \sim \frac{n^2 \mathcal{E}}{\omega} \ll 1 \quad (11)$$

where d is the diagonal dipole matrix element of the degenerate state n . This condition sets an upper limit for the electric field \mathcal{E} of the wave and a lower limit for its frequency ω . In deriving the condition given by (11), we used the fact that the characteristic dipole matrix elements (3) are of the order of n^2 when these

elements are taken between highly excited states separated by a small energy interval (see Sec. 2).

Let us now consider the extent to which (11) is a realistic condition. When $\omega \sim n^{-3}$, we find that (11) yields the condition $\mathcal{E} \ll n^{-5}$ whereas, for $\omega \sim n^{-2}$, we have $\mathcal{E} \ll n^{-4}$, which is identical with the above criterion for the validity of perturbation theory.

When we pass from the hydrogen atom to the highly excited states of more complicated atoms, we must bear in mind the difference between n and n' . Firstly, for high orbital angular momenta l (in practice, $l > 2$), it is well known that we can neglect the quantum defect, and the above results remain valid without change. Secondly, for low orbital angular momenta (in practice, $l = 0, 1, 2$), the presence of the quantum defect interferes with the compensation of the $n' > n$ terms by the $n' < n$ terms in (4), owing to the difference between the energies of the corresponding states. The result of all this is that the dynamic polarizability rises sharply and its magnitude becomes of the order of n^7 . Moreover, the behavior of the polarizability becomes similar to that of the polarizability of low-lying excited states (see above), since the $n' > n$ and $n' < n$ resonances occur at different energies.

So far, we have confined our attention to linearly polarized electromagnetic waves. The case of circular polarization does not introduce any fundamental changes because, in the original expression given by (4), only the factors that appear in front of the summation sign over n' and depend only on l, m are modified. The sums over n' themselves remain unaltered. The same remarks apply to the more general case of elliptically polarized fields. So far, there have been no experiments designed to observe the quadratic Stark shift for highly excited states with the condition (11) satisfied (see the note added in proof at the end of this review).

We now turn to the linear Stark shift in a varying field. According to general theory,^{2,3} when the inequality opposite to that given by (11) is satisfied, each level splits into quasienergy states. The probability that the k th quasienergy state will be occupied is proportional to $J_k^2(n^2\mathcal{E}/\omega)$, where J is a Bessel function. This probability is a maximum for quasienergy states whose energy corresponds to the energy of the initial level shifted in the constant field as a result of the linear Stark effect (with $\mathcal{E}_{\text{const}}^2 = \mathcal{E}^{-2}$). The appearance of the quasienergy states is described in detail for the first excited states of the hydrogen atom in Refs. 2, 3, and 12. The effect is qualitatively similar in the case of highly excited states. When the inequality given by (11) is reversed, the quadratic Stark effect is small in comparison with the linear shift. It appears as a small common shift of the entire net of quasienergy states. The inequality opposite to (11) can be realized for low frequencies $\omega < n^{-3}$ and fields $\mathcal{E} > \omega/n^2$.

The experimental confirmation of quasienergy splitting and the quadratic Stark shift of the highly excited states of the hydrogen atom is reported in Ref 13. In this experiment, the hydrogen atoms were excited by laser radiation from the $n = 10$ state. The atoms were

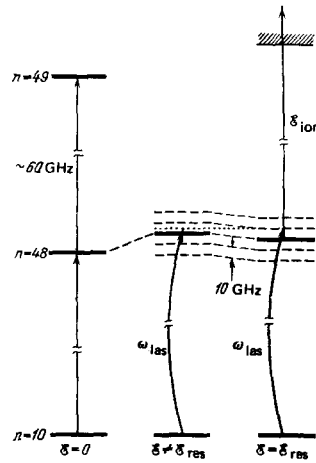


FIG. 2. Schematic diagram illustrating the experiment reported in Ref. 13 on the resonance ionization via the quasienergy harmonics of the $n = 48$ level. Tuning to resonance is achieved by using the Stark shift of the $n = 48$ level in the radio-frequency field $\mathcal{E} = \mathcal{E}_{\text{res}}$.

allowed to traverse a resonator in which a field of frequency $\omega = 10$ GHz was excited. The amplitude of this field could be varied, so that the Stark shift of the $n = 48$ level could be used to tune to resonance between the laser frequency and the frequency corresponding to a transition from the $n = 10$ state to one of the quasienergy harmonics of the $n = 48$ state (Fig. 2). These atoms were then ionized by a third field of frequency of the order of 1 GHz and field strength in excess of the characteristic atomic field for $n = 48$ (of the order of 100 V/cm), so that, when the $n = 48$ state was populated, all such atoms were ionized.

It was found that the yield of ions as a function of the field strength at 10 GHz exhibited a resonance that corresponded to the population of the quasienergy harmonics at energies

$$E_{Kn} = E_{n=48} + K\omega,$$

where $\omega = 10$ GHz and $K = 1, 2, 3,$ and 4 .

This experiment satisfied the condition

$$\frac{n^2\mathcal{E}}{\omega} \gg 1,$$

which is opposite to that given by (11). It is precisely this condition that ensured that the quasiharmonics were populated. We may therefore conclude that the quadratic Stark effect can be observed even when (11) is not satisfied: both the $n = 48$ level itself and its quasienergy harmonics are shifted by the amount corresponding to the quadratic Stark shift, whereas the magnitude of the factor $n^2\mathcal{E}/\omega$ is responsible for the distribution of the population over the quasienergy harmonics.

We note that, in this experiment, the quadratic Stark shift was practically static in character, since it turns out that $\omega n^3 = 1/6$ for the $n = 48$ state. The dipole selection rules for the single-photon $n = 10 \rightarrow n = 48$ transition induced by the laser field ensured that the $n = 48$ states with low orbital quantum numbers were populated.

The order of magnitude of the quadratic Stark shift can be estimated by using the static limit of the expression given by (6) for the dynamic polarizability:

$$\alpha_{n00} \approx 0.6n^6 \text{ for } \omega n^2 \ll 1.$$

The sign of the Stark shift (negative) and the order of magnitude of the shift are in agreement with experimental data.¹³

Subsequent development of these investigations¹⁴ has fully confirmed the main result, namely, the fact that it is possible to observe the population of the quasienergy harmonics of the highly excited atomic states.

From the point of view of the design of the experiment, two differences were introduced in Ref. 14. Firstly, the hydrogen atoms were excited from the $n = 10$ state to states with $n = 44-67$ by the absorption of a quantum of infrared radiation produced by a CO₂ laser and by selecting the kinetic energy of the atoms with the aid of the Doppler effect (see below, Sec. 9^{51, 52}). Secondly, use was made of a radiofrequency field with tunable frequency in the range $\omega \approx 6-8$ GHz.

The number of protons was measured as a function of the kinetic energy of the atoms (i.e., of the quantity n), the frequency ω , and the field \mathcal{E} in the radiofrequency range (i.e., the number k and the degree of population of the different quasiharmonics). It was found that there was a large number of resonances in the proton yield that corresponded to the excitation of different quasienergy states with energies $E_{nk} = E_n + k\omega$.

By determining the maxima corresponding to these resonances, it was possible to determine the probability of excitation of states with given n , k as a function of the field strength \mathcal{E} in the radiofrequency range. It was found that, as \mathcal{E} was increased, this function at first rose sharply and, having reached a maximum, declined gradually. The observed relationship is in agreement with the assumption that the probability of population of the k th quasiharmonic of the state n is proportional to $J_k^2(n^2\mathcal{E}/\omega)$, since this dependence corresponds to the well-known asymptotic properties of the Bessel function. It was also observed that, for a given k , the radiofrequency field \mathcal{E}_{\max} corresponding to the maximum excitation fell sharply with increasing n . This also corresponds to the properties of the Bessel function: the maximum of the function occurs when its argument is equal to its index, i.e., for $\mathcal{E} \sim 1/n^2$.

4. MULTIPHOTON IONIZATION OF HIGHLY EXCITED STATES

All the basic relationships describing the probability of multiphoton ionization from ground and low-lying atomic states are well known.^{2, 3} In principle, they remain valid for the ionization of highly excited atomic states. Thus, the probability of direct multiphoton ionization (i.e., in the absence of intermediate resonances) from a state with principal quantum number n is described by the usual power-type expression

$$w_n = \alpha_n^{(K_0)}(\omega, \rho) \mathcal{E}^{2K_0},$$

where K_0 is the number of field quanta whose absorp-

tion is necessary to ensure that energy conservation is satisfied:

$$K_0 = [1/(2n^2\omega) + 1].$$

The quantity ρ represents the polarization of the field.

The quantity $\alpha_n^{(K_0)}(\omega, \rho)$ is the multiphoton direct ionization cross section. It is obtained from the well-known expression² for the multiphoton matrix elements

$$\alpha_n^{(K_0)} = 2\pi \left| \frac{1}{2K_0} \sum_{k, l, \dots, s} \frac{(re)_{nk}}{(\omega_{kn} - \omega)} \frac{(re)_{kl}}{(\omega_{lj} - 2\omega)} \dots \frac{(re)_{sp}}{(\omega_{pn} - (K_0 - 1)\omega)} \right|^2 N_p, \quad (12)$$

$$e = \frac{\vec{\mathcal{E}}}{\mathcal{E}},$$

where N_p is the density of final states of the electron in the continuous spectrum.

The particular feature of this problem lies in the simplification of the formulas for the multiphoton matrix elements, which results from the simplicity of the analytic expressions for the quasiclassical matrix elements $(re)_{kl}$ (see Sec. 2) and the energy denominators that appear in the multiphoton matrix element.

Instead of considering the general case, we begin by turning to the simple example of two-photon ionization. We shall characterize the initial state of the highly excited atom by quantum numbers nlm , where $n \gg 1$. We consider that the frequency of the external linearly polarized field satisfies the condition

$$\omega < \frac{1}{2n^2} < 2\omega,$$

under which single-photon ionization is forbidden by energy conservation. Thus, in order of magnitude the result is $\omega \sim 1/n^2$.

According to the dipole selection rules for two-photon transitions, the orbital angular momentum in the final state is $l' = l \pm 2$. To be specific, let us consider in greater detail only one of these transitions, say, that with $l' = l + 2$. As in the last section, we shall assume that the external field is linearly polarized along the z axis. After standard separation of angular variables in the two-photon matrix element, and averaging the probability (12) over the magnetic quantum number m of the initial state, we are left with the problem of evaluating the sum over the intermediate states n' in the two-photon matrix element. The sum over n' in the quasiclassical approximation consists of terms in the neighborhood of values for which the resonance denominator is $\omega_{n'n} - \omega \approx 0$. When the resonance detuning is small, the sum in (12) is dominated by a single term. When this is so, the term must be retained and the quasiclassical values substituted for the single-photon matrix elements (see Sec. 2).

When the sum is evaluated in the more general case of intervals between resonances, we need only take into account the change in the small energy denominators. The numerators in (12) are taken out at the point $\omega_{n'n} = \omega$. We assume in this process that the orbital quantum number is $l \ll n, p^{-1}$. In the opposite case, one of the dipole matrix elements is exponentially small. The condition that the orbital angular momentum is small is in agreement with the conditions prevailing, in practice, in which the highly excited state is reached through single-photon excitation by a monochromatic

laser field from the ground or a low-lying atomic state. The process is assured by the selection rules for the orbital angular momentum for single-photon transitions.

Assuming that $K_0 = 2$ in (12), and substituting for the matrix elements the quasiclassical estimate taken from Ref. 6 for $\Delta n \sim n$, we finally obtain from (12)

$$\alpha_{nl \rightarrow p l+2}^{(2)} = \frac{(l+1)(l+2)}{(2l+1)(2l+3)} \frac{l^8}{540\pi^6 \omega^4 n^3} \times \text{ctg}^2 \left(\frac{\pi n}{\sqrt{1-2\omega n^2}} \right) \left[K_{2/3} \left(\frac{2}{3} l^3 \omega \right) + K_{1/3} \left(\frac{2}{3} l^3 \omega \right) \right]^4; \quad (13)$$

where $K_p(x)$ is the Macdonald function and p is the momentum of the electron in the final state. In particular, for the ionization of the S-state ($l = 0$), we find from (13),

$$\alpha_{n0 \rightarrow p2}^{(2)} = \frac{3^{5/2} \Gamma^4(2/3)}{4320\pi^6 n^3 \omega^{2/3}} \cot^2 \left(\frac{\pi n}{\sqrt{1-2\omega n^2}} \right). \quad (14)$$

When $p \sim n^{-1}$ and $\omega \sim n^{-2}$, Eqs. (13) and (14) yield the following estimate:

$$\alpha_{nl}^{(2)} = \text{const} \cdot n^{31/3}. \quad (15)$$

Expressions analogous to (13) are obtained for transitions with $l' = l - 2$ and $l' = l$. Our next step is to determine the cross section for two-photon ionization, summed over l' and averaged over the orbital quantum number l of the initial n th state on the assumption that all the substates of the n th level are populated with equal probability. Using (13), it is readily shown that¹⁵

$$\alpha_n^2 = \frac{0.1}{\pi n^6 \omega^{2/3}} \cot^2 \left(\frac{\pi n}{\sqrt{1-2\omega n^2}} \right). \quad (16)$$

When $\omega \sim n^{-2}$, Eq. (16) yields the following estimate:

$$\alpha_n^{(2)} = \text{const} \cdot n^{29/3}. \quad (17)$$

We assumed above that $\omega < 1/(2n^2)$, i.e., that single-photon ionization is forbidden by energy conservation. We now turn to the case where $\omega > 1/(2n^2)$. When this condition is satisfied, we have both two-photon and ordinary single-photon ionization. The cross section for the latter is described by the well-known Kramers formula (see, for example, Ref. 9). In the notation of (12), we have for $K_0 = 1$,

$$\alpha_n^{(1)} = \frac{2}{3 \sqrt{3} \omega^2 n^4}. \quad (18)$$

As far as the two-photon matrix element is concerned, the two situations corresponding to $\omega < 1/(2n^2)$ and $\omega > 1/(2n^2)$ differ in that, in the latter case, there is an additional term in the form of an imaginary part since, for the state n' in the continuous spectrum, we must make the replacement

$$\omega_{n'n} - \omega \rightarrow \omega_{n'n} - \omega + i\delta.$$

Its contribution to the two-photon cross section for the process can be calculated readily by using the quasiclassical matrix elements (see Sec. 2). As a result, it turns out that the imaginary part is much greater than the real part (i.e., it dominates the integral taken in the sense of the principal value), and $\alpha_n^{(2)}$ is given by (16) with $\cot^2(\dots) \rightarrow 1$ (see Ref. 16).

The imaginary part of the two-photon matrix element corresponds to the cascade transition $n \rightarrow p' \rightarrow p$ through a real (and not virtual) state p' . It is clear from the

foregoing that the cascade probability of two-photon ionization is the dominant probability.

Thus, the analysis given above leads us to the following conclusion. In intervals between resonances, two-photon ionization is determined by transitions for which the intermediate states are close to the average between the initial and final states, and the orbital quantum numbers are small in comparison with the corresponding principal quantum numbers. It is only in the case of small detuning of a particular atomic transition from the frequency of the external field that only one resonance term can be retained in the sum over the intermediate states.

We now turn to the question of the validity of perturbation theory in calculations of multiphoton processes occurring from highly-excited states. To answer this question, we must, clearly, consider an open channel of single-photon ionization and compare the probability of two-photon ionization, which is proportional to the quantity given by (16) (with $\cot^2(\dots) \rightarrow 1$), with the probability of single-photon ionization, which is proportional to the quantity given by (18). Equating the probability ratio to unity, we obtain the field \mathcal{E}_0 at which perturbation theory ceases to be valid:

$$\mathcal{E}_0 = 3.5 \omega^{3/3}. \quad (19)$$

In particular, when $\omega = 1/2n^2$, we have from (19)

$$\mathcal{E}_0 = 1.1 \cdot n^{-10/3}. \quad (20)$$

The value $\omega = 1/2n^2$ is the minimum for which the single-photon ionization channel is open.

When $\omega > 1/2n^2$, it is clear from (18) that the field \mathcal{E}_0 for which perturbation theory breaks down is higher. This simply reflects the fact that an increase in the frequency at fixed field strength is accompanied by a reduction in the perturbation produced by the field: this is clear from (16) and (18), where the frequency ω is raised to a high power in the denominator. Thus, the expression given by (20) gives the minimum threshold for the validity of perturbation theory for two-photon ionization.

As we proceed to higher orders of perturbation theory, the algebra becomes much more complicated.¹⁶ This is even more so for n th orders of perturbation theory, which must be included when the probability of ionization by a field of frequency $\omega \sim n^{-3}$ has to be calculated.

However, when the degree of nonlinearity of the ionization process (the number of photons) is high, i.e., $K_0 \gg 1$, the corresponding general expressions¹⁶ can be simplified. Thus, the cross section for direct multiphoton ionization in the field of a linearly polarized wave is given by the following expression¹⁷:

$$\alpha_n^{(K_0)} = \frac{2.4 \omega^{-2/3}}{8\pi^2 c K_0^{3/2} (2K_0 + 1) n^5} \left(\frac{7.05 n^2}{\omega^{2/3}} \right)^{2K_0}.$$

The expression for $\alpha_n^{(K_0)}$ in the case of circularly polarized waves has also been obtained¹⁷ and differs from that given above only by a relatively insignificant numerical factor.

The expression for the multiphoton cross section can be used to determine the characteristic atomic field \mathcal{E}_a for the multiphoton ionization process as the field for which the probability of the process of order $(K_0 + 1)$ becomes comparable with the probability of the process of order K_0 . It is readily shown that

$$\mathcal{E}_a = \frac{\omega^{2/3}}{7.05n^2}$$

for a linearly polarized external field. When $\omega = \Omega = n^{-3}$, this yields

$$\mathcal{E}_a = \frac{1}{7.05n^4} \quad (21)$$

When the radiation is circularly polarized, the numerical factor in the denominator becomes 7.69.

It is important to note the very sharp dependence of the ionization probability on the field strength for high values of K_0 . This dependence has a threshold, so that the ionization process has an essentially multiphoton character for $\mathcal{E} < \mathcal{E}_a$, and is characterized by the degree of nonlinearity K_0 .

5. TUNNELING IONIZATION OF HIGHLY EXCITED STATES

In the last section, we gave a detailed discussion of two-photon ionization of highly-excited states, and briefly mentioned multiphoton ionization from such states. According to general theory,⁴ multiphoton ionization occurs when $\gamma = (\omega/n\mathcal{E}) \gg 1$, i.e., at sufficiently high external-field frequencies (for fixed field strength). In the present section, we turn to the opposite case, namely,

$$\gamma = (\omega/n\mathcal{E}) \ll 1. \quad (22)$$

Since the external field strength is assumed to be less than the atomic field n^{-4} (see below), the above condition signifies that $\omega \ll \Omega$ [see Eq. (2)]. The electron will then tunnel through the slowly time-varying potential barrier, and the problem for the theory is to determine the probability of this type of tunneling per unit time.

The solution of this problem for the ground state of the hydrogen atom ($n = 1$) is well known²:

$$w_1 = 4 \sqrt{\frac{3}{\pi\mathcal{E}}} \exp\left(-\frac{2}{3\mathcal{E}}\right). \quad (23)$$

This result is obtained by averaging the probability of tunneling from the ground state in a constant electric field over the period of the external field, $T = 2\pi/\omega$, if we substitute $\mathcal{E} \rightarrow \mathcal{E} \cos \omega t$ and use the saddle-point method to determine the probability.

When we pass from the ground to the highly excited states, we must start with the well-known expressions for the probability of tunneling in a constant field.¹⁸ Proceeding by analogy with the derivation of (23), we obtain the following expression for the probability of tunneling in a varying field:

$$w_n = \sqrt{3\mathcal{E}/\pi n^3} w_{n, \mathcal{E}=\text{const}} = \sqrt{\frac{3\mathcal{E}}{\pi n^3}} \left(\frac{4}{n^2\mathcal{E}}\right)^{n-n_1+n_2} \frac{\exp[-2/(3\mathcal{E}n^3) + 3(n_1-n_2)]}{2n_2!(n-n_1-1)!}, \quad (24)$$

where $n_1 < n_2$ are the parabolic quantum numbers characterizing the initial state of the atom, which remain in

the limit as $\omega \rightarrow 0$. It may be verified that the probability given by (24) is small when $\mathcal{E} \ll n^{-4}$.

When we are concerned with highly excited states of complex atoms, characterized by a definite orbital quantum number l and magnetic quantum number m , the probability of tunneling ionization in a varying field (per unit time) is given by

$$w_n = \sqrt{3\mathcal{E}/\pi n^3} w_{n, \mathcal{E}=\text{const}} = \sqrt{3\mathcal{E}/\pi n^3} \cdot 2^{2n-|m|-1} (2l+1) (l+|m|)! \times [(n+l)!(n-l-1)! (|m|)! (l-|m|)!]^{-1} \times (2/\mathcal{E}n^3)^{2n-|m|-1} \exp(-2/3\mathcal{E}n^3), \quad (25)$$

where it is implied that $n \sim n^*$. This formula is valid when the perturbation $n^2\mathcal{E}$ is small in comparison with the energy separation between the levels of the atomic multiplet under consideration, so that the orbital angular momentum l remains a good quantum number when the field is turned on.

We now draw attention to the very large preexponential factor in (24) and (25), which is absent in the case of ionization from a well that is present for only a short period of time. At the same time, the arguments of the exponential in the case of the Coulomb potential and the potential representing the short-lived well are the same for the same level energy. We note that it is precisely because account has been taken of the preexponential factor that the atomic field \mathcal{E}_a for which tunneling ionization occurs in the characteristic atomic time is of the order of E_n^2 in the Coulomb field, where E_n is the energy of the state from which ionization takes place. At the same time, in the case of the short-lived potential, the atomic field is determined only by the argument of the exponential in the ionization probability and, obviously, is of the order of $E_n^{3/2}$.

When $n \gg 1$, the dependence of the probabilities (24) and (25) on \mathcal{E} is very sharp, and these two expressions become virtually step functions. It is readily seen from (24) and (25) that the atomic fields determining the position of a step of this kind are the same as in the case of ionization by a constant field. According to Ref. 1, we have

$$\mathcal{E}_a = \frac{4}{Cn^4}, \quad (26)$$

in which $C(n_1, n_2)$ varies with n_1, n_2 from 4.5 to 9.2, where $0 \leq n_1, n_2 \leq n-1$.

It is interesting to compare the magnitude of the atomic field for tunneling and multiphoton ionization from highly excited states [Eqs. (26) and (21), respectively]. It is clear from (21) and (26) that these quantities are of the same order of magnitude. There is no doubt that, in the intermediate case where $\gamma \sim 1$, the atomic field is of the same order of magnitude.

It is shown in Ref. 19 that, actually, the result given by (24) is valid provided a condition that is more stringent than (22) is satisfied, namely,

$$\frac{\omega^2}{n\mathcal{E}^2} \ll 1.$$

When only (22) is satisfied, the initial energy level exhibits significant splitting into quasienergy levels (this

is the analog of the linear Stark effect in the constant field), and tunneling from these levels is different. The corresponding formulas are very complicated and are given in Ref. 19. The result given by (25) remains unaltered, since the corresponding quasienergy states in the varying field are generated by a time-dependent perturbation that is a quadratic function of the field strength.

6. STOCHASTIC DYNAMICS OF A CLASSICAL ELECTRON IN AN ALTERNATING FIELD

A. Introduction

The basic feature of the multiphoton and tunneling ionization discussed above is the purely quantum-mechanical nature of the process. However, when $n \gg 1$, the highly-excited atom is a quasiclassical system, and the effect of an external field on an electron in the system can be described in terms of the laws of classical mechanics. It is well known that, within the framework of classical mechanics, the process of above-barrier transition may result in the ionization of the atom. By an analogy with the case of the constant external electric field, this process corresponds physically to the above-barrier transition of an electron from the potential well to the continuous spectrum under the influence of a field of frequency $\omega \ll n^{-3}$. Ionization then takes place in approximately one period of revolution in the unperturbed orbit, $\sim n^3$. This type of above-barrier ionization is possible only for a sufficiently high alternating field strength that is comparable with the atomic field strength in a constant field (26).¹

However, it is clear that the greatest interest attaches to frequencies ω of the order of the Kepler orbital frequency of an electron, $\Omega = n^{-3}$, since the effect of the varying field on the electron is then resonant in character.

It turns out that, in a strictly monochromatic wave with $\omega \sim \Omega$, for which the field strength is strong enough but still such that $\mathcal{E} \ll \mathcal{E}_a$, the nonlinear oscillations of the electron (the frequency of the unperturbed oscillations Ω depends on the principal quantum number n) becomes stochastic,²⁰ which leads to diffusion ionization of the atom. Here, it is important to emphasize that diffusion in the system arises not because of the random character of the external electromagnetic field, which is strictly monochromatic, but because of the nonlinearity of the classical equations of motion. The mechanism responsible for diffusion ionization was first discussed in Ref. 21. The phenomenon of diffusion ionization due to stochasticity was discovered as a result of numerical experiments.²² An estimate for the stochasticity threshold was first obtained analytically in Ref. 23.

At this point, we should like to emphasize once again the qualitative difference between diffusion and multiphoton ionization (Fig. 3). In fact, diffusion excitation corresponds to a *gradual* increase in the energy of the classical electron from the initial value to the value corresponding to ionization. The characteristic time

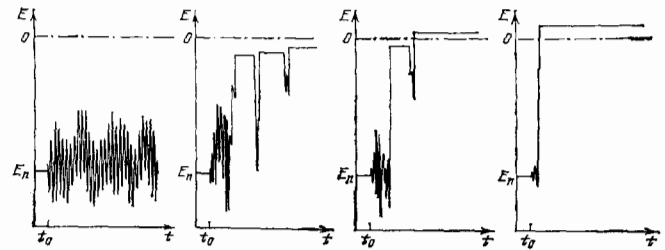


FIG. 3. Results of a computer simulation of the onset of stochastic instability of an electron in a highly excited atom and diffusion ionization of the atom.²² The external field \mathcal{E} increases from left to right. E is the binding energy of the electron in the atom and t is the time of interaction with the field.

τ_D for this excitation is substantially greater than the unperturbed orbital period: $\tau_D \gg n^3$ (see Sec. 7). It follows that the probability of classical diffusion ionization will continue to be equal to zero (the electron will not succeed in acquiring sufficient energy) for a time τ containing a number of orbital periods ($\tau \ll \tau_D$). In the quantum-mechanical analysis, the ionization probability $W = w_n \tau$ will be different from zero after a time $\tau \sim n^3$, where w_n is the probability of multiphoton ionization per unit time.

The condition for the appearance of stochasticity resulting in diffusion excitation of the atom is that the nonlinear resonances must overlap.^{20, 24, 25} This leads to the existence of a sharply defined limit for the electric field, which has been estimated in Ref. 23. The diffusion excitation of the atom (right up to ionization) occurs in fields exceeding this critical value $\mathcal{E} > \mathcal{E}_c$, whereas, for $\mathcal{E} < \mathcal{E}_c$, the energy of the classical electron oscillates between finite limits, and the amplitude of these oscillations decreases with decreasing \mathcal{E} (see Fig. 3).

B. Nonlinear resonance for circular orbits

Let us now consider how the circular electron orbit becomes deformed under the influence of a weak linearly polarized monochromatic field. Since the circular motion is purely harmonic, the Hamiltonian for the system in a varying electric field $\mathcal{E} \cos \omega t$ has the simple form

$$H = -\frac{1}{2n^2} + \mathcal{E} n^2 \cos \omega t \cdot \cos \lambda, \quad (27)$$

where it is assumed that the electric field lies in the plane of the orbit and n, λ are canonically conjugate variables, namely, classical action and angle. The Hamiltonian given by (27) is the sum of the unperturbed energy and the dipole interaction between the field and the atomic electron, and λ is the phase of the orbitals motion of the electron, which, in the case of a circular orbit, is equal to the angle between the radius vector of the electron and the direction of the field. It is assumed in (27) that the orbital angular momentum l of the electron remains constant. This approximation turns out to be valid by virtue of the fact that the rate of change $\dot{l} \sim \mathcal{E}$ in a weak field is much less than $\dot{n} \sim \mathcal{E}^{1/2}$ (see below).

The perturbation in the Hamiltonian given by (27) produces the greatest change $\Delta n = n - n_0$ (n_0 characterizes the initial state of the electron) in the case of resonance between the field frequency ω and the frequency of the Kepler motion of the electron $\Omega = n^{-3}$. Let us expand the unperturbed part of the Hamiltonian (27) around the resonance $n_r = \omega^{-1/3}$, and retain in the perturbation only the slowly-varying terms. To eliminate the explicit dependence of the Hamiltonian on time, we introduce the new phase $\theta = \lambda - \omega t$ and its new conjugate action $I = n - n_r$. In terms of these new variables, and apart from a constant term, the Hamiltonian (27) assumes the form

$$H_r(I, \theta) = -\frac{3I^2}{2n_r^2} + \frac{1}{2} \mathcal{E} n_r^2 \cos \theta. \quad (28)$$

The new Hamiltonian does not explicitly depend on time and is therefore conserved. The fact that the system described by (28) is one-dimensional implies that it is integrable. The equations of motion obtained from (28) are identical with the equations of motion of a physical pendulum with "mass" given by

$$M = \left| \frac{d\Omega}{dn} \right|^{-1} = \frac{1}{3} n_r^4.$$

The region of the nonlinear resonance corresponds to the oscillations of the "pendulum" (bounded variation of the phase θ) and lies in the interior of the separatrix that separates oscillatory motion from rotation. The frequency of small (in comparison with the size of the separatrix) oscillations of the "pendulum" is given by

$$\Omega_\phi = \left(\frac{1}{2M} \mathcal{E} n_r^2 \right)^{1/2} = \frac{1}{n_r} \left(\frac{3}{2} \mathcal{E} \right)^{1/2}. \quad (29)$$

This quantity defines the frequency of fluctuations ($\Omega_\phi \ll \Omega$) in the orbit of the electron in the field when the initial values $I_0 = n_0 - n_r$ and $\theta_0 = \lambda_0$ lie near the position of equilibrium of the pendulum: $I_s = 0$, $\theta_s = 0$. The energy of the electron is then also found to fluctuate in time with frequency Ω_ϕ . The phenomenon we have just described lies at the basis of the principle of phase stability as it applies to particles in cyclic accelerators.

Similar energy oscillations are observed in numerical experiments performed with the classical atom in a circularly polarized field.²⁶

The number of levels within the nonlinear resonance $(\Delta n)_r$, is determined by the width of the separatrix in units of action. According to the condition $H_r = -\frac{1}{2} \mathcal{E} n_r^2$, we have

$$I = \pm \left(\frac{2}{3} \mathcal{E} \right)^{1/2} n_r^2 \cos \left(\frac{1}{2} \theta \right),$$

which we can now use to determine the width of the nonlinear resonance in units of action I :

$$(\Delta n)_r = 2 \left(\frac{2}{3} \mathcal{E} \right)^{1/2} n_r^2 = 4\Omega_\phi M. \quad (30)$$

This expression also enables us to deduce the half-width of the nonlinear resonance in units of frequency:

$$\Delta v = \frac{(\Delta n)_r}{2M} = 2\Omega_\phi, \quad (31)$$

which we shall find useful in the ensuing discussion.

The nonlinear resonance approximation discussed above is valid when $(\Delta n)_r \ll n_r$ and $\Omega_\phi \ll \Omega$, which imposes a restriction on the external field, namely, $\mathcal{E} \ll n_r^{-4}$. From (29) and (30), we find that the condition $(\Delta n)_r \gg 1$, which is necessary for the validity of the

classical approach, is satisfied for $\mathcal{E} \gg n_r^{-6}$. We may therefore conclude that, in fields such that

$$n_r^{-6} \ll \mathcal{E} \ll n_r^{-4}$$

the fluctuations in the classical orbit of the electron are restricted to a region confined within the limits of the separatrix of the nonlinear resonance.

On the other hand, when the electron starts outside the nonlinear resonance region, i.e., $|\omega - \Omega| \gg \Omega_\phi$, its oscillation amplitude turns out to be much smaller:

$$\Delta n \sim \frac{\mathcal{E} n_0^2}{|\omega - \Omega|} \sim \mathcal{E} n_0^2$$

for $|\omega - \Omega| \sim \Omega = n_0^{-3}$.

C. Overlap of resonances for elongated orbits

Let us now consider the opposite case of very elongated orbits with eccentricity given by

$$e = \left(1 - \frac{l^2}{n^2} \right)^{1/2} = 1.$$

We shall assume that the electric field vector is parallel to the electron orbit. The Hamiltonian for the system then takes the form

$$H = -\frac{1}{2n^2} + \mathcal{E} n^2 \cos \omega t \left(-\frac{3}{2} + 2 \sum_{k=1}^{\infty} x_k \cos k\lambda \right), \quad (32)$$

where

$$n^2 x_k = \frac{n^3}{k} J'_k(k\epsilon) \quad (33)$$

are the Fourier components of the dipole moment of the electron²⁸ and $e = 1$.

The resonance condition $\omega = k\Omega_k = kn_k^{-3}$ determines the resonance values of n_k . By analogy with the case of the circular orbit, considered above, we retain only the resonance term in the Hamiltonian (32). By analogy with (30), the frequency half-width of the resonance separatrix is given by²⁵

$$\Delta v_k = \frac{2}{n_k} \left(3\mathcal{E} x_k \right)^{1/2}, \quad (34)$$

and this determines the characteristic frequencies of electron fluctuations in the external field against the background of the unperturbed orbital frequency Ω_k .

We must now determine the critical field \mathcal{E}_c in which the k th and the $(k+1)$ th nonlinear resonances overlap, leading to the stochastic behavior of the electron. It will be useful to introduce the parameter s given by

$$s = \frac{\Delta v_k + \Delta v_{k+1}}{\Omega_k - \Omega_{k+1}}, \quad (35)$$

to characterize the degree of overlap of neighboring resonances. When $s \ll 1$, the influence of neighboring resonances can be neglected and the bounded oscillations of the electron can be described in the approximation of a single isolated nonlinear resonance, as was done in subsection b.

The value $s = 1$ corresponds to the situation where the separatrices corresponding to unperturbed resonances touch one another. According to the results reported in Ref. 25, the trajectory begins to undergo a random transition from one resonance to another when the following condition is satisfied:

$$K \approx 2.5s^2 = \frac{\mathcal{E}}{\mathcal{E}_c} > 1. \quad (36)$$

The semiempirical numerical factor in this expression represents resonances of higher harmonics, the distortion of unperturbed separatrices under the influence of neighboring resonances, and the finite width of the stochastic layer that appears near the unperturbed separatrix. This factor is not very sensitive to the form of the system under consideration, and numerical experiments²⁵ have shown that it lies in the range 2.2–2.5, depending on which model is used. We shall adopt the value 2.5, which corresponds to the so-called standard model 25 (see also Ref. 29).

Using the resonance condition $\omega = k\Omega_k$ together with Eqs. (34)–(36), we obtain the following expression for the critical field when $l = 0$:

$$\mathcal{E}_c = \frac{1}{\gamma_k n^4}, \quad (37)$$

where

$$\gamma_k = 30(k+1)^2 \left[|x_k|^{1/2} + |x_{k+1}|^{1/2} \left(1 + \frac{1}{k}\right)^{-1/3} \right]^2. \quad (38)$$

For the fundamental resonance $k = 1$, Eqs. (37) and (38) yield

$$\mathcal{E}_c = \frac{1}{84n^4}. \quad (39)$$

According to (39), the value of \mathcal{E}_c is lower by a factor of three than the estimate obtained in Ref. 23, and appears to provide the minimum value of the field for which the stochastic behavior of the electron sets in.

If we use the asymptotic expression for (33) when $k \gg 1$, i.e., $x_k \approx 0.4k^{5/3}$, we find from (37) and (38) that

$$\mathcal{E}_c \approx \frac{1}{49(\omega n^3)^{1/3} n^4}. \quad (40)$$

Actually, the asymptotic behavior begins as early as $k = 5$.

Thus, the increase in the frequency $\omega = k\Omega_k$ at constant initial n is accompanied by a reduction in the threshold for stochasticity. The reason for this is connected with the reduction in the separation between the nonlinear resonances with increasing k , and the sufficiently slow reduction in the higher harmonics of the dipole moment.

Adjacent resonances overlap for $\mathcal{E} > \mathcal{E}_c$. Resonances with the higher n correspond to greater k and, according to (40), undergo greater overlap. This results in the onset of the diffusion excitation of the electron (see Sec. 7). Each individual orbit is then a very complicated and tortuous figure, and neighboring trajectories diverge in time at an exponential rate. The characteristic time for stochasticization is of the order of the width of the nonlinear resonance $\tau_c \sim \Delta\omega_k^{-1}$. When $k \sim 1$, we find that $\tau_c \sim \Omega^{-1}$.

When $k \gg 1$ and $\mathcal{E} \sim \mathcal{E}_c$, the resonance part of the perturbation in the Hamiltonian (32) turns out to be smaller by a factor of k^2 than the unperturbed part. This fact ensures the validity of the approximation we have used and of the expression given by (40) for the critical field. We also note that, when $k \gg 1$, the network of resonances becomes uniform ($\Omega_k - \Omega_{k+1} \approx \Omega_{k+1} - \Omega_{k+2}$) and can be described locally by the standard model.²⁵ It is this that dictates the choice of the numerical factor in (36).

Less favorable for the theory is the case $k \sim 1$, for which, formally, the perturbation is not small. Nevertheless, the fact that the perturbation is numerically small in comparison with the unperturbed Hamiltonian (it is of the order of $1/42$ for $k = 1$) assures the validity of the expressions given by (37)–(39) for the critical field.

D. The general case

We now consider the case of an arbitrary orbit. The Hamiltonian for an electron in the field of a Coulomb center and a monochromatic external electromagnetic field, written in terms of the action and angle variables for the unperturbed problem, has the form

$$H = -\frac{1}{2n^2} + \mathcal{E}n^2 \cos \omega t \left(1 - \frac{m^2}{l^2}\right)^{1/2} \times \left[-\frac{3}{2} e \sin \varphi + 2 \sum_{k=1}^{\infty} (x_k \sin \psi \cos k\lambda + y_k \cos \psi \sin k\lambda) \right], \quad (41)$$

where l and m are the angular momentum of the electron and its component along the external field \mathcal{E} , respectively, ψ and ϕ are the conjugate Euler angles,³⁰ respectively, and the quantities x_k [see (33)] and

$$n^2 y_k = \frac{n^2 \sqrt{1-e^2}}{ke} J_k(ke) \quad (42)$$

are the Fourier components of the dipole moment of the electron.²⁸ The quantity e is the eccentricity of the orbit. The component m of the angular momentum is a constant of the motion.

Since the frequency of the variation in l and ψ is proportional to \mathcal{E} , it turns out to be smaller than the frequency of the variation in n and $\theta = \lambda - \omega t$, which is proportional to $\mathcal{E}^{1/2}$ when the resonance condition $\omega = k\Omega_k$ is satisfied (see above). We can therefore separate the fast (n, θ) and slow (l, ψ) subsystems which, in turn, enables us to introduce the resonance approximation into the Hamiltonian (41) by analogy with the case of the elongated orbits considered above.

Proceeding by analogy with the determination of the critical field for elongated orbits, we can show that, in the present case, the critical field is given by (37), where

$$\gamma_k = 30(k+1)^2 \left[\sqrt{r_k} + \frac{\sqrt{r_{k+1}}}{\left(1 + \frac{1}{k}\right)^{1/3}} \right]^2 \left(1 - \frac{m^2}{l^2}\right)^{1/2}; \quad (43)$$

in which $2r_k^2 = x_k^2 + y_k^2$ and, for simplicity, we have substituted the average value

$$\langle \sin^2 \psi \rangle = \langle \cos^2 \psi \rangle = \frac{1}{2}.$$

Generally speaking, this results in an overestimate for \mathcal{E}_c by a factor of $\sqrt{2}$ when $x_k \ll y_k$ or $x_k \gg y_k$.

It follows²⁸ from the asymptotic behavior of the Fourier components x_k and y_k for $k \gg 1$ that the resonances will overlap only for highly elongated orbits with eccentricity $e \sim 1$. For orbits with smaller eccentricity, the quantities x_k, y_k decrease exponentially with increasing k . This exponential reduction is absent and, consequently, the orbits exhibit stochastic behavior, only for small angular momenta

$$l \leq l_c = \left(\frac{3}{\omega}\right)^{1/3}. \quad (44)$$

The dependence of the critical field \mathcal{E}_c on l when $k \gg 1$ can be obtained from (37) and (43) has the form

$$\mathcal{E}_c = \frac{1}{\kappa_l (n^2 \omega)^{1/3} (1 - m^2/l^2)^{1/2} n^4}, \quad l \leq l_c. \quad (45)$$

We shall not reproduce the rather complicated expression for κ_l that is obtained from the asymptotic formulas for the Fourier components x_k, y_k .²⁸ We merely note that κ_l is a very slowly varying function of l when $l \leq l_c$. Thus, for example, $\kappa_0 \approx 35$ and $\kappa_{l_c} \approx 22$.

In the case of fundamental resonance $k = 1$, the dependence of \mathcal{E}_c on l is also slight, according to (43). Thus, when $l = n/2$ and $l = 3n/4$, Eq. (43) shows that $\mathcal{E}_c n^4 = 1/77$ and $1/80$, respectively (when $m = 0$). These values are not very different from the value $1/84$ given by (39) for $l = 0$. Thus, in fields exceeding the critical value given by

$$\mathcal{E}_c = \frac{1}{77n^4}, \quad (46)$$

the resonances will overlap for most of the possible values of l .

Moreover, for orbits with eccentricity $e \ll 1$, the amplitude of the harmonics x_k, y_k with $k \geq 2$ is found to be very small ($\sim e^{-k+1}$). Hence, for $\mathcal{E} \sim \mathcal{E}_c$, resonances with $k = 2$ and $k = 3$ do not overlap, and ionization from such states is highly suppressed. It can occur only because small regions of stochasticity appear as a result of the overlap of the $k = 1$ and $k = 2$ resonances, and these regions enable the electron to leave the region with $e \sim 1$, so that ionization can then take place.

Numerical experiments²⁵ have shown that, when $K = (\mathcal{E}/\mathcal{E}_c) \approx 1$, the structure of the phase space is a very complicated interlacing of stable and stochastic components whose measures are roughly equal. However, as early as $\mathcal{E} = 4\mathcal{E}_c$, the measure of the stable component is found to be 10%, and developed stochasticity is present.

So far, we have confined our attention to the case $k \gg 1$. When $k < 1$, there are no resonances in n . Nevertheless, because of the finite width of the higher resonance with $k = 1$, the trajectory may enter the region of stochasticity of this resonance. Thus, for example, for highly elongated orbits and $\mathcal{E} = \mathcal{E}_c$, we find from (34) and (39) that $\Delta\omega_1 = 0.22\omega$. Hence, it follows that effective excitation occurs for frequencies beginning with $\omega \geq 0.78\Omega$. As the field is increased to $\mathcal{E} = 5\mathcal{E}_c$, this value reaches 0.52Ω . These results are in agreement with numerical experiments,³¹ which suggest that stochastic excitation occurs for fields $\mathcal{E} = (5-6)\mathcal{E}_c$ and $\omega = 0.4\Omega$.

E. Stochasticity in a low-frequency field

It is interesting that, despite the absence of resonances in n for $k \ll 1$ and $\mathcal{E} \ll n^{-4}$, the presence of Kepler degeneracy (i.e., degeneracy in l) also gives rise to the stochasticization of the motion of the atomic electron.³² In this section, we turn to the examination of this type of stochasticity. A detailed discussion will be found in Ref. 32, and we shall reproduce only the leading results.

Since the electric field varies slowly, it is convenient to write the classical Hamiltonian in terms of the action and angle variables defined for the motion of the particle in parabolic coordinates for the instantaneous value of the field. In addition to the unperturbed energy, the Hamiltonian contains the linear Stark shift which contains time as a parameter, and the analogous quadratic Stark shift. Both shifts are expressed in terms of the action variables corresponding to the parabolic quantum numbers of the hydrogen atom in a constant electric field. Finally, the Hamiltonian also includes a low-frequency term that appears because the perturbation is an explicit function of time.

In the approximation that we shall employ, we shall have both an exact constant of motion, namely, the component of the angular momentum along the electric field, and conservation of the principal quantum number n .

The condition for the overlap of the nonlinear resonances (36) is satisfied when the critical field³²

$$\mathcal{E}_c \approx \frac{(\omega n^3)^{1/3}}{2n^4} \ll \frac{1}{n^4} \quad (47)$$

is exceeded for parameter values for which

$$\omega n^3 \ll 1.$$

When $\omega/n \ll \mathcal{E} < \mathcal{E}_c$, the parabolic quantum numbers oscillate within a small bounded interval near their initial values. On the other hand, when $\mathcal{E} > \mathcal{E}_c$, they vary randomly within the interval $[0, n - |m|]$, and the plane of the orbit precesses in a random fashion around the direction of the field.

Let us consider observable effects that result from this stochasticity. Suppose that, initially, the electron occupies the n th level and has parabolic quantum numbers n_1, n_2 . When a weak field $\mathcal{E} < \mathcal{E}_c$ is turned on, the quantum numbers n_1, n_2 become approximate constants of motion³³ (they are exact constants of motion in a constant field). Spontaneous radiative transitions will therefore take place only from this state (n, n_1, n_2) to some other lower-lying atomic states. The situation is quite different for $\mathcal{E} > \mathcal{E}_c$. In the latter case, the resonances overlap, and the values of n_1 and n_2 are no longer constants of motion. After a certain interval of time following the introduction of the electric field, the electron can have with equal probability any parabolic quantum numbers satisfying the condition $n_1 + n_2 = n - |m|$. There is a corresponding change in the probability of spontaneous radiative transitions, and this change can be recorded. Similarly, a transition from fields $\mathcal{E} < \mathcal{E}_c$ to fields $\mathcal{E} > \mathcal{E}_c$ results in a change in the probability of ionization by these fields because these probabilities are very dependent on the quantum numbers n_1, n_2 .

We note in conclusion that, according to (47), the critical field for stochasticization decreases with decreasing ω , i.e., as we approach the static limit. However, the stochasticity itself develops over an increasing time, namely, over a time given by $\tau_c \sim \omega^{-1}$.

F. Circular polarization

Let us now consider the case of circularly polarized radiation, which was examined in Refs. 26 and 27. The

motion of the electron remains qualitatively the same as in the linearly polarized field. Actually, since l , m and the associated angles are slowly varying functions, the dynamics of highly elongated orbits is, as before, described by the Hamiltonian (32). It is assumed that the orbit lies in the plane of polarization of the radiation. From this, it follows immediately that \mathcal{E}_c is given by (37)–(40), as for the linearly polarized field. When $k = 1$, the critical field [see (39)] turns out to be lower by a factor of about 2.5 than that found in Ref. 27. As in the case of linear polarization, this difference is explained by the more accurate allowance for the width of the nonlinear resonances and the frequency difference between them. The result given by (39) is found to be close to that deduced from numerical experiments²⁶ in which ionization of the atom is found to occur for $\mathcal{E}n^4 > 1/100$.

We now turn to the general case of arbitrarily elongated orbits. We shall confine our attention to two-dimensional trajectories lying in the plane of polarization of the external field. Proceeding by analogy with our treatment of the critical field for linearly polarized radiation, we find that, for $k = 1$ and $l = 0$, $n/2$, $3n/4$, we have

$$\mathcal{E}_c n^4 \approx \frac{1}{84}, \frac{1}{149}, \frac{1}{184} \quad (48)$$

respectively.

Thus, in a circularly polarized field and when $k = 1$, the orbits with intermediate values of eccentricity are the most readily stochasticized. The critical field is then given by

$$\mathcal{E}_c = \frac{1}{\kappa_l (n^3 \omega)^{1/3} n^4} \quad (49)$$

The quantity κ_l in this expression is a slowly varying function of l . Thus, in particular, $\kappa_0 \approx 49$ and $\kappa_{l_c} \approx 43$.

For three-dimensional orbits, the critical field is given by the same expression (49), but with a somewhat different numerical constant κ_l .

The question whether stochasticity occurs in a circularly polarized field for $\omega n^3 \ll 1$ requires further investigation.

We now introduce our concluding remarks about the dependence of the critical field on the parameters defining it. Firstly, as the frequency rises from $\omega = \Omega = 1/n^3$, the critical field \mathcal{E}_c is found to decrease [see (40), (45), and (49)]. As the frequency is reduced from a value $\omega \ll 1/n^3$, the critical field is also found to decrease [see (47)]. We now turn to the dependence of \mathcal{E}_c on the orbital angular momentum l . Let us consider, to begin with, the case where the frequency is given by $\omega = 1/n^3$. It is clear from the discussion preceding (46) that there is now practically no dependence of \mathcal{E}_c on l if we exclude values of l close to n (orbits with small eccentricity) for which the critical field increases sharply. This conclusion refers to linearly polarized radiation. On the other hand, in a circularly polarized field, the critical field decreases with increasing l [see (48)]. When $\omega \gg 1/n^3$ ($k \gg 1$), the critical field varies slowly with $l \leq l_c$ for both linearly and circularly polarized fields, but rises sharply for $l > l_c$.

As far as the dependence of \mathcal{E}_c on the polarization of the external field is concerned, comparison of (45) with (49) enables us to draw the perfectly definite conclusion that, for high frequencies ($k \gg 1$), the critical field \mathcal{E}_c is somewhat lower in the circularly polarized field than in the linearly polarized field. When $k \sim 1$, the critical field for $l = 0$ is independent of the polarization, and for $l > 0$, the critical field \mathcal{E}_c is lower in the circular than in the linear field. In the phrases just given, the words "less than" signify a difference by a factor of 1.5–2.

7. DIFFUSION IONIZATION

A. Introduction

In the last section, we obtained estimates for the critical electric field \mathcal{E}_c for which nonlinear resonances are found to overlap. For fields $\mathcal{E} > \mathcal{E}_c$, the electron begins a stochastic transition from one resonance to another, and its trajectory becomes exceedingly complicated, random, and unpredictable.²⁵ However, owing to the stochasticity of each individual trajectory, it is possible to use a statistical description of the excitation of the atomic electron.^{24,25,34} One can then identify two characteristic scales of time in the course of the temporal evolution, namely, the time τ_c for the stochasticization of the motion, and the time τ_D during which the electron executes a random walk over the resonances. As we shall see later, the latter time is much greater than τ_c . On time intervals exceeding τ_c , the phase distribution becomes homogeneous, and the evolution of the distribution function $f(n, t)$, i.e., the number of particles with given n at time t , over action is described by the Fokker-Planck-Kolmogorov equation. When the degree of overlap between the resonances is high enough, the measure of the stable component turns out to be negligible. Detailed balancing then prevails in the system, and the nondiffusion current is absent from the Fokker-Planck-Kolmogorov equation.³⁵ The result is that this equation reduces to the usual diffusion equation

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial n} \left(D_n \frac{\partial f}{\partial n} \right) \quad (50)$$

The problem for the theory is to determine the diffusion coefficient D_n and, since this coefficient depends on n , the diffusion equation describes a nonlinear diffusion process.

B. Determination of the diffusion coefficient

We shall now follow Ref. 34 and determine the diffusion coefficient for the case of highly elongated orbits ($l = 0$). Using the Hamiltonian (32), we obtain the equation for n :

$$\frac{dn}{dt} = -\frac{\partial H}{\partial k} = \sum_{k=1}^{\infty} F_k \cos(\omega_k t + \theta_k(t)), \quad (51)$$

where

$$\left. \begin{aligned} F_k &= \chi n^2 k x_k, \\ \omega_k &= k\Omega - \omega, \\ \theta_k(t) &= k(\lambda - \Omega t) - \frac{\pi}{2}. \end{aligned} \right\} \quad (52)$$

The phases $\theta_k(t)$ in (52) vary slowly with time on a time scale of the order of τ_c .

Integration of (51) with respect to time yields

$$\Delta n \equiv n - n_0 \approx \sum_{k=1}^{\infty} \left(\frac{F_k}{\omega_k} \right) [\sin(\omega_k t + \theta_k) - \sin \theta_k]. \quad (53)$$

We now square (53) and recall the fact that, owing to stochasticity, the phases $\theta_k(t)$ are random variables on the interval $[0, 2\pi]$. Consequently, the squares of sines and cosines can be replaced with $1/2$, and the first powers of trigonometric functions can be set equal to zero. Replacing the sum by an integral, we obtain

$$\overline{(\Delta n)^2} = \pi \left(\frac{F_k}{\Omega} \right)^2 t, \quad (54)$$

where the resonance value is given by $k = \omega/\Omega = \omega n^3$. According to general relationships that are known to be valid for one-dimensional diffusion, we have

$$\overline{(\Delta n)^2} = 2D_n t. \quad (55)$$

Comparison of (54) with (55) finally gives us the required diffusion coefficient:

$$D_n = \frac{\pi}{2} \mathcal{E}^2 \omega^2 n^3 x_k^2. \quad (56)$$

In particular, when $k \gg 1$, and if we use the asymptotic expression for x_k , Eq. (56) yields

$$D_n \approx 0.65 \mathcal{E}^2 n^3 \omega^{-4/3}, \quad (57)$$

whereas, for $k = 1$, we have

$$D_n \approx 0.17 \mathcal{E}^2 n^7. \quad (58)$$

An analogous analysis of the diffusion coefficient can be given for the general case of arbitrary eccentricity. The coefficient D_n is obtained from (56) by introducing the replacement

$$x_k^2 \rightarrow \frac{1}{2} (x_k^2 + y_k^2) \left(1 - \frac{m^2}{l^2} \right).$$

For two-dimensional orbits in circularly polarized radiation, we must introduce the replacement $x_k^2 \rightarrow x_k^2 + y_k^2$ in (56). Equation (56) is also approximately valid for three-dimensional orbits. For all these cases, we obtain an expression of the form of (57) with slightly different numerical factors in the asymptotic limit $k \gg 1$.

An estimate for the time τ_D , during which diffusion results in the ionization of the atom, can be obtained from condition $\overline{(\Delta n)^2} \sim n^2$ [see (55)], where n represents the principal quantum number of the initial state of the electron. Consequently, we have from (55)

$$\tau_D \approx \frac{n^2}{2D_n}. \quad (59)$$

The inverse quantity $w_D = \tau_D^{-1}$ can be referred to as the probability of diffusion ionization. However, it must then be remembered that, when $t \ll \tau_D$, the fraction of ionized particles is equal to zero and not to $w_D t$. Equation (57) yields the following estimate:

$$w_D \sim \mathcal{E}^2 n \omega^{-4/3}, \quad \omega n^3 \gg 1. \quad (60)$$

For $\omega n^3 \approx 1$ and linearly polarized radiation, the ionization probability is given by

$$w_D \approx \frac{2D_n}{n^2} = \frac{1}{3} \mathcal{E}^2 n^5. \quad (61)$$

In particular, when $k = 1$ and $\mathcal{E} n^4 = 1/77$ or $1/12$, we have $\tau_D = 2 \times 10^4 n^3$ and $\tau_D = 460 n^3$, respectively. We thus see that the time τ_D is substantially greater than

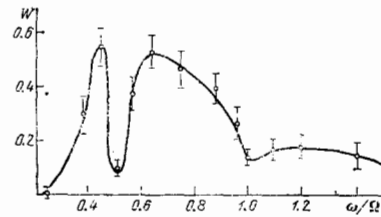


FIG. 4. The result of a numerical calculation³¹ of the fraction W of ionized particles as a function of the external-field frequency. W is plotted against the ratio ω/Ω . The interval of time during which the field interacts with the atom is assumed to be $300 \pi n^3$ and the field strength is $\mathcal{E} = n^4/12$.

the electron orbital time n^3 on a Kepler orbit, in accordance with the general considerations given at the beginning of this section.

Numerical experiments³¹ involving linearly polarized radiation with $\mathcal{E} n^4 \approx 1/12$ have shown that, for $k \approx 1$ ($\omega \approx \Omega$) and field interaction time $T = 300 \pi n^3$, the fraction of ionized particles is approximately 40% (Fig. 4). The above estimates are in good agreement with numerical experiments.

The dependence of τ_D on the field \mathcal{E} and frequency ω is also in qualitative agreement with numerical experiments³¹ (Fig. 5). However, more accurate numerical experiments will be necessary for a more detailed verification of the power-type dependence of τ_D on ω .

It is interesting to note that the ionization probability w_D decreases with increasing ω , despite the reduction in the threshold for stochasticity.

C. Some features of diffusion excitation

As we have seen in Sec. 6, the theory becomes much simpler for high external-field frequencies $\omega \gg \Omega$, and we can then analyze in greater detail the nature of the diffusion excitation and ionization as compared with the general case of arbitrary frequency.

According to (44), diffusion occurs only for states with low orbital angular momenta $l \leq l_c$. The Hamiltonian (41) can then be used to obtain the equation for the change in l by analogy with the procedure used above to obtain the equation for the change in n . This shows that the coefficient of diffusion in l is smaller by a factor of $(\omega/\Omega)^2$ than the coefficient of diffusion in n . This leads to the fact that, at high frequencies $\omega \gg \Omega$, the diffusion

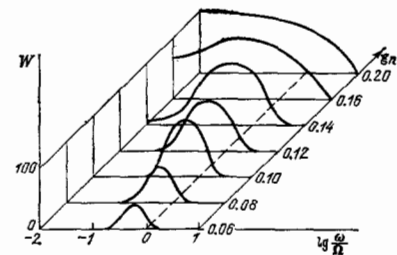


FIG. 5. The results of a numerical calculation³¹ of the fraction W of ionized particles as a function of the external field \mathcal{E} (in units of n^4) and the field frequency ω (in units of Ω).

process is quasi-one-dimensional, i.e., the diffusion takes place only in n . When this is so, the spreading over all the orbital angular momenta $0 \leq l \leq l_c$ cannot occur during the diffusion ionization time τ_D . We note that the random walk of the electron over the spectrum is asymmetric since, for $n \leq n_c = (49\mathcal{E}\omega^{1/3})^{-1/5}$, the resonances do not overlap [see (40)], so that there is no diffusion below n_c .

It has been noted in the course of numerical experiments^{22, 26, 31, 36} that the diffusion process consists of a sequence of rapid changes in n that occur when the perihelion of the orbit is traversed, and nonaccumulating small oscillations in n during the motion over the remainder of the orbit. For highly excited electrons, the time interval between the times of passage through the perihelion is very large (of the order of n^3). This apparently leads to the appearance of persistent, nonionizing, highly excited trajectories that have been seen in numerical experiments.^{22, 26}

When $\omega n^3 \ll 1$ and $\mathcal{E} \geq \mathcal{E}_c$ [see (47)], the quantities n_1, n_2 undergo a stochastic deviation that leads to diffusion in n with an exponentially small diffusion coefficient

$$D_n \sim \exp\left(-\frac{\Omega}{\Delta\omega}\right),$$

where $\Delta\omega \approx 3\mathcal{E}^2 n^{5/8}$ (see Refs. 32 and 42). Thus, the ionization time turns out to be exponentially large in this case.

D. Quasiclassical calculation of the diffusion time

All the preceding discussion of diffusion was based on the laws of classical mechanics. The quasiclassical approximation to quantum mechanics was used in Ref. 21 to derive a diffusion equation similar to (50) for the random walk of an electron along the energy axis. It was then used in the balance equations for the electron in a highly excited state in which a large number of single-photon transitions between neighboring levels occurred in the presence of an external field. We shall now reproduce the diffusion equation obtained within the framework of this approach. To be specific, we shall confine our attention to the region of the first resonance $\omega = \Omega$. From each state n , we then have transitions to neighboring states $n \pm 1$. Detailed examination of these transitions²¹ leads to the following expression for the diffusion time:

$$\tau_D \sim \frac{E_n^2}{w\omega^2}, \quad (62)$$

where w is the probability of the single-photon transition per unit time between states with principal quantum numbers n and $n+1$, which is given by Fermi's Golden Rule No. 2:

$$w = \frac{\pi}{2} |z_{n+1, n}^{n+1, m}|^2 \mathcal{E}^2 n^3. \quad (63)$$

The last factor, n^3 , in (63) represents the density of final states of the electron (cf. the transition from the quasiclassical summation to integration in Sec. 3). The quasiclassical matrix element in (63), which is written down for the case of linearly polarized fields, is evaluated on the basis of the results given in Sec. 2. If we average (63) over the magnetic quantum number m ,

sum over the two values $l' = l \pm 1$, in accordance with the dipole selection rules, and follow this by the substitution of (63) in (62) and set $\omega = \Omega$, we obtain

$$\tau_D \sim \mathcal{E}^{-2} n^{-5}. \quad (64)$$

This expression is in good agreement with (61).

8. CONDITIONS FOR THE REALIZATION OF DIFFUSION AND QUANTUM-MECHANICAL IONIZATION

Let us begin by considering the condition for the validity of classical mechanics in the description of diffusion ionization. From the standpoint of quantum mechanics, this condition is equivalent to demanding that the corrections to the quasiclassical wave function of the electron in the field of the residual ion and the external electromagnetic field must be small. It is important to note that these corrections increase with time,³⁸ i.e., the precision of the quasiclassical approximation deteriorates. Let δ denote the mean relative correction to the classical wave function corresponding to the next after the lowest order of the quasiclassical approximation. The quasiclassical approximation is valid if δ remains small during the electron diffusion time, i.e., $\delta \ll 1$. The following estimate is reported for δ in Refs. 39 and 40:

$$\delta \sim \frac{\gamma_0}{\tau_c} \left(\frac{\tau}{\tau_c}\right)^{1/2},$$

where $\gamma_0 = 3n^{-4}/2$ is the nonlinearity of the classical system. When $\omega \approx \Omega \sim \tau_c^{-1}$, the diffusion time is given by (64), from which we obtain

$$\delta \sim \frac{3}{2} n^{-5} \mathcal{E}^{-1} \ll 1. \quad (65)$$

In particular, under the conditions obtaining in the experiment reported in Ref. 41, Eq. (65) yields $\delta \sim 18n^{-1}$ for $\mathcal{E}n^4 = 1/12$ and $\delta \sim 1/4$ for $n = 65$, which indicates that the classical analysis is valid. However, near the stochastic limit given by (39), Eq. (65) gives $\delta \sim 120n^{-1}$, from which it follows that the classical analysis is valid only up to $n \geq 120$.

When $k = \omega/\Omega \gg 1$ and $\mathcal{E} \sim \mathcal{E}_c$, we have $\tau_c \sim k/\Omega$ and, hence, following Ref. 39, we obtain an estimate that differs from (69), namely,

$$\delta \sim 75 k^{3/2} n^{-1}.$$

We note that this condition is more stringent (if we suppose that $\delta \ll 1$) than the condition $\omega \ll E_n$ that lies at the very basis of the question whether diffusion ionization of a highly excited atom is possible.

When $\delta \geq 1$, the theoretical description of the ionization process encounters considerable difficulties that have not as yet been overcome (see, for example, Refs. 37, 42, and 43). However, preliminary numerical experiments⁴⁴ with simple quantum-mechanical models (that are unrelated to the atomic ionization process) show that diffusion excitation occurs in multidimensional systems even for $\delta \gg 1$. This means that diffusion ionization of the atom will probably occur even in the essentially quantum-mechanical region $\delta \geq 1$.

We now turn to quantum-mechanical ionization, i.e., to tunneling and multiphoton ionization.

From the standpoint of the theory given in the entire preceding text, we must divide the experimental situation into two cases, namely, $\mathcal{E} < \mathcal{E}_c$ and $\mathcal{E} > \mathcal{E}_c$, where \mathcal{E}_c is the critical field for classical stochastic ionization (see Sec. 6). Diffusion ionization does not occur when $\mathcal{E} < \mathcal{E}_c$. This case corresponds to fields that are small in comparison with the characteristic atomic fields for the highly excited levels under consideration. For such fields, we have the well-known theory⁴ in which the nature of the ionization process is determined by the adiabatic parameter γ . Tunneling occurs for $\gamma \ll 1$ and the multiphoton ionization process takes place for $\gamma \gg 1$; $\gamma \sim 1$ corresponds to intermediate cases. These statements are valid in the absence of resonances between the external-field frequency and the frequencies of the atomic transitions. When a resonance occurs, the electron undergoes a transition to a lower-lying resonance level and is then removed from this level by some quantum-mechanical mechanism determined by γ , or by a diffusion process if $\mathcal{E} \geq \mathcal{E}_c$ is valid for this particular level.

In the opposite case, where the field is $\mathcal{E} > \mathcal{E}_c$, we find, in accordance with the foregoing discussion, that diffusion ionization of highly-excited atoms with $n \gg 1$ occurs for $E_n \gg \omega \geq \Omega$. Under these conditions, diffusion ionization may proceed in parallel with multiphoton ionization. There is, however, an obvious qualitative difference between these two processes, namely, multiphoton ionization occurs as a result of the simultaneous absorption of a number of photons by the atomic electron, whereas diffusion ionization occurs as a result of a series of successive single-photon absorption-emission events. To establish the relative importance of these two competing ionization processes, we must compare the corresponding total ionization probabilities in the presence of an external field or, and this is much simpler, we must determine the critical field strengths.

We now turn to the resonance case for which $\omega \approx \Omega$. The critical linearly polarized field for the stochastic instability of an atomic electron is given by (39) whereas, for multiphoton ionization, it is given by (21). We recall that (21) gives the atomic field for which the ionization probability in $(K_0 + 1)$ th order perturbation theory is equal to the probability corresponding to order K_0 . Since $K_0 \gg 1$, the dependence of multiphoton ionization on the field strength is very sharp and is practically of the threshold type. Accordingly, for all fields less than \mathcal{E}_a , including the field $\mathcal{E}_c < \mathcal{E}_a$, the quantum-mechanical ionization process is essentially multiphoton in character and, because K_0 is large, the probability of this process is vanishingly small in comparison with the probability of diffusion ionization which, in quantum-mechanical language, constitutes a set of a large number of photon absorption and emission events. Accordingly, the diffusion ionization process takes place for external fields in the range

$$\mathcal{E}_c \ll \mathcal{E} \ll \mathcal{E}_a.$$

When, on the other hand, the condition $\omega \ll \Omega$ is satisfied for fields $\mathcal{E} \geq \mathcal{E}_c$, there is practically no diffusion ionization. Tunneling ionization then takes place

for fields $\mathcal{E} < \mathcal{E}_a$ (\mathcal{E}_a is defined in Sec. 5), and the probability of this process is exponentially small and is equal to the probability of tunneling ionization in a constant field, apart from the factor $(3\mathcal{E}n^2/\pi)^{1/2}$ (see Sec. 5). The condition for the validity of this mechanism is $(\omega/n\mathcal{E})^2 n \ll 1$ (it is discussed in Sec. 5), which is obviously equivalent to the condition $\omega \ll \mathcal{E}n^{1/2}$. When the less stringent condition $\omega < \mathcal{E}n$ is satisfied, we again have tunneling ionization but, in this case, the process occurs in a different way for different quasienergy states associated with the n th level.¹⁹ When $\mathcal{E} > \mathcal{E}_a$, tunneling ionization goes over into an above-barrier electron transition which occurs in the characteristic atomic time of the order of n^3 .

The above situations exhaust all the ranges of frequency ω and field \mathcal{E} for which there are different mechanisms of ionization of highly excited atomic states.

In conclusion, we turn to a numerical estimate of the quantum number $n \gg 1$ above which quasiclassical diffusion ionization can take place. It is clear that the necessary condition for quasiclassical ionization is that there should be no appreciable effects associated with the discrete structure of the atomic spectrum, and that the stochastic random walk of the electron should take place over many levels. This is equivalent to demanding that the width of the nonlinear resonance in n , which is indicated by (30) as being of the order of $n\mathcal{E}^{1/3}$, must be greater than unity. From this inequality, we can obtain an estimate for the necessary field strength. If we then compare this estimate with the condition for stochasticity, given by (46), we obtain the required value of the principal quantum number, namely, $n > 5$. It is clear that this value is not very high, so that quasiclassical ionization is not necessarily confined to atoms excited to very high-lying states.

9. OBSERVATION OF NONLINEAR IONIZATION OF HIGHLY EXCITED ATOMS

Experimental data on nonlinear ionization of highly excited atoms are exceedingly scarce. However, they not only clearly show the existence of the phenomena itself, but also enable us to draw a number of important conclusions in relation to its basic properties. Before we turn to these results, let us consider the basic problems that arise in the design of the experiment, which is basically different from the standard formulation of experiments on nonlinear ionization of ground-state atoms by optical radiation.⁴⁵

Experiments on nonlinear ionization of highly excited atoms involve the resolution of two specific difficulties, namely, the development of targets consisting of atoms excited to a particular state with a given large principal quantum number n , and the production of the ionizing radiofrequency field.

We first turn to the ionizing field and recall that we are dealing with nonlinear effects that occur at external field frequencies $\omega \ll E_n$ for $n \gg 1$. It is clear from the foregoing that frequencies close to the Kepler frequency (2) are of particular interest. Starting from (1) and (2),

and assuming different high values of n , we can readily show that a radiofrequency field is necessary for ionization. For example, the binding energy corresponding to the $n = 50$ state is $E_{50} \approx 5 \cdot 10^{-3}$ eV and the Kepler frequency is $\Omega_{50} \approx 50$ GHz, which corresponds to a photon energy $\hbar\omega \approx 2 \cdot 10^{-4}$ eV. It is thus clear that, to achieve a resonance interaction with the classical (Kepler) frequency, we need a microwave field with a frequency ω of the order of 10 GHz, i.e., with a wavelength of the order of 1 cm. If we use (39) to estimate the threshold for diffusion ionization of the atom excited to the $n = 50$ state, we find that the ionizing field strength is $\mathcal{E}_c = 2 \cdot 10^{-9}$ a.u. = 10 V/cm, i.e., the intensity of the microwave radiation must be $F_c = 0.1$ W/cm².

The technology for producing radiofrequency fields with given metric, field strength, and polarization is well established.⁴⁶ Depending on the particular practical conditions, it is possible to produce radiofrequency fields both in the interior of a resonator and in the space between antennas (horns) or the plates of a plane-parallel capacitor.

When a radiofrequency field is employed, particular attention must be paid to the field frequency, wavelength, path length traversed by the atom in the field, the velocity of the atom, and the spontaneous lifetime of the atom in the excited state. These parameter values must be such as to ensure that the time spent by the atom in the field is long enough, so that the field is essentially variable and not constant. The most critical case is that where the kinetic energy of the atoms is high and the field frequency is low.

We now turn to the problem of producing highly excited atoms. Here again, the experimental techniques available for producing such atoms are sufficiently well developed.

The first method, which has been developed in the greatest detail, consists of the cascade ionization of atoms from the ground state to a given highly excited state with the aid of a number of lasers (usually, tunable dye lasers). The possibilities of this method and the necessary technology are well known, since they form the basis for the selective photoionization of atoms, which is of major practical importance.^{47, 48} One way is to cross a laser beam with an atomic beam at right angles, so that the linear Doppler effect can be avoided. Moreover, the limiting spectrum width of 10^{-3} cm⁻¹ can be achieved by using single-frequency laser generation. The maximum value of the principal quantum number of the excited state that can be achieved is determined by the laser frequency instability. The highest value that has been reached so far is $n = 65$.⁴⁹ The efficiency of excitation of atoms in the atomic beam can be close to unity.⁵⁰ At the same time, the density of the atomic beam can be up to 10^{13} cm⁻³. We note that this method restricts the orbital angular momentum of the highly excited atom to low values because of the restricted number of excitation stages.

In principle, this method can be used to produce highly excited states of any atoms that are in the atomic rather than the molecular state in the gaseous or vapor

phase. Atomic beams are particularly easy to produce from materials with low melting and boiling points, for example, the alkali metals.

The second method is a development of the classical charge-transfer technique that is widely used in the physics of atomic collisions. Its main advantage is that it can be used to produce highly excited hydrogen atoms. A beam of protons from an accelerator capable of producing 10-keV particles is scattered by a gas. As a result of charge exchange excited neutral hydrogen atoms are produced in states with different principal quantum number n . The probability of excitation to these states is proportional to n^{-3} . An infrared beam from a CO₂ laser is directed along the axis of the beam of excited atoms, the energy of the infrared photons being of the order of 0.1 eV. The latter energy is approximately in resonance with the atomic hydrogen transition from the $n = 10$ to the $n = 50$ state. Precise tuning to resonance with the transition to a state with given n can be produced in two different ways. In one of these methods, the energy of the excited hydrogen atoms is varied by varying the energy of the accelerated protons in such a way that the Doppler effect can be exploited to establish resonance between the energy of the $n = 10 \rightarrow n = 50$ transition and the energy of a laser photon.^{51, 52} The results reported in Ref. 53 show that, individual states with $n \approx 50$ can be produced in this way. The selectivity of this method is determined by the precision with which the energy of the accelerated protons can be maintained at a given value. We note that this method can be used to excite only states with low orbital angular momenta.

The method has been used⁵¹ to produce a beam of atoms with $n \approx 50$ and intensity of 2.5×10^5 atoms/sec. It is expected that, by optimizing the experimental conditions, the intensity will be raised⁵¹ to 10^{10} atoms/sec.

Another method available for precise tuning to resonance is to use the Stark shift of the levels of the excited atom in a strong (of the order of 1000 V/cm) constant electric field.⁵⁴ We note that this method can produce resonances between states characterized by parabolic quantum numbers (n, n_1, n_2) , i.e., states with different orbital quantum number l . The selectivity of this method is determined by the precision with which one can maintain the high-frequency voltage across the capacitor producing the constant field. In both cases, the maximum achievable values of the quantum number of the excited states is again determined by the stability of the frequency and by the spectrum width of the CO₂ laser beam.

Experimental data on the process of nonlinear ionization of highly excited atoms can be found in the literature.^{14, 41, 53-55} We now turn to Ref. 41, which reports results that are of the greatest interest for the problem of nonlinear ionization of highly excited atoms.

Figure 6 shows a block diagram of the apparatus used in Ref. 41. It relies on the second of the above two methods of producing highly-excited atoms, i.e., charge exchange between a gas and a proton beam. The 11-keV proton beam undergoes charge exchange on a xenon-gas

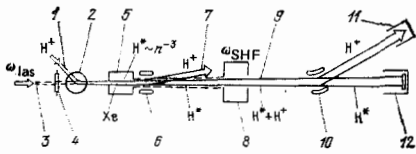


FIG. 6. Schematic diagram of the apparatus used in Ref. 41: 1—beam of accelerated H^+ ions; 2, 6, 10—deflecting magnets; 3—laser beam; 4—window of vacuum chamber; 5—charge-exchange chamber for H^+ on Xe; 7—extracted H^+ ion beam; 8—microwave ionization chamber; 9— $H^+ + H^+$ beam; 11— H^+ detector; 12—detector of excited hydrogen atoms (H^*). See text for further details.

target. The beam is allowed to pass through an electrostatic filter that removes charged particles and leaves behind only neutral atoms in different excited states. This experiment did not use a laser beam for the resonance excitation of particular highly excited states. Instead, a difference technique was employed in which states with $n > n_c$ were cut off by a constant electric field as a result of above-barrier ionization. The relation used for the critical constant field was $\mathcal{E}_a = Cn_c^{-4}$, where C was determined from the calculations given in Refs. 56 and 57 and the experiments reported in Refs. 56 and 58. On the basis of all their data, the authors concluded that they were able to determine values of n to within ± 5 units. The difference experiment defined the range of n amounting to about 5 units and lying between $n = 69$ and $n = 63$. Atoms with $n \approx 65$ selected in this way were ionized in a field of a particular frequency and configuration. The following fields were used in turn: a transverse field with a frequency of 0.9–1.8 GHz between parallel plates, an axial TM_{01} field at 9.9 GHz, and an electrostatic Einzel lens which could be used to produce a field with a principal Fourier frequency component of about 30 MHz. Comparison of the velocity of the excited atoms with the linear dimensions of the field at 30 MHz (wavelength of the order of 10 m) shows that the effect of the field in this case is equivalent to that of a constant field. Protons produced as a result of ionization of the highly excited atoms were detected by a Faraday cup.

Figure 7 shows the proton signal amplitude recorded by the Faraday cup⁴¹ as a function of the radiofrequency field. Data obtained for different frequencies of the ionized field are normalized to the saturated ion signal. Each curve represents the probability of ionization of hydrogen atoms excited to the $n \approx 65$ state as a function of the field strength.

For the data obtained at a fixed radiation frequency, we can introduce the critical field \mathcal{E}_a corresponding to the signal amplitude equal to one-half of the maximum amplitude. The values of \mathcal{E}_a obtained in this way can be expressed in the following form:

$$\mathcal{E}_a \approx \frac{1}{Cn^4},$$

where the frequency-dependent quantity C is deduced from experimental data. For field frequencies $\omega = 9.9$ GHz, 1.5 GHz, and 30 MHz, it is found that C is, respectively, equal to 25, 17, and 8. It is thus clear that,

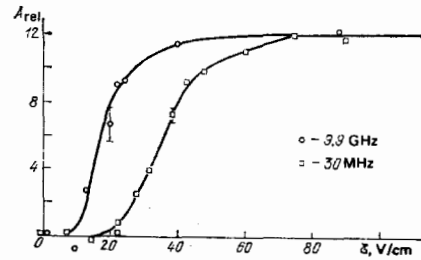


FIG. 7. Amplitude of the proton signal in relative units as a function of the field strength \mathcal{E} (the results of the experiment reported in Ref. 41).

in the above frequency range, the critical field decreases with increasing frequency of the ionizing field.

To make any kind of deduction about the nature of the ionization process, we must compare the experimental data (frequencies and critical fields) with theoretical data on critical fields and their dependence on the radiation frequency. This comparison is made in the next section.

We now turn to experimental data⁵³ on ionization from highly-excited states of the hydrogen atom. The proton beam with an energy of about 11 keV was made to undergo charge exchange on a xenon-gas target. The laser beam was then used to induce single-photon transitions from lower-lying excited states of the hydrogen atom to states with $n = 45$ –57. The microwave field of frequency between 9.4 and 11.6 GHz was applied to these atoms with the result that they become ionized. It was found that the ion yield as a function of the microwave field frequency went through a resonance. The authors of Ref. 53 ascribe such resonances to the fact that the condition $k\omega = \Omega$ was satisfied at certain particular frequencies ω (the Kepler frequency Ω is equal to the separation between neighboring highly excited states); in this expression, $k = 2, 3, 4$. Since the Kepler frequency Ω varies with n , the position of the resonances is different for different n at constant k . We are thus dealing with a multiphoton resonance between neighboring highly excited states of the hydrogen atom. The experimental confirmation of the existence of these resonances is not a trivial matter from the theoretical point of view since, on the face of it, one would not expect any resonances to appear because the characteristic linear Stark splitting $n^2 \mathcal{E}$ under the conditions of this experiment is greater by a factor of three than Ω , and by a factor of 10–15 than the frequency ω . The authors of Ref. 53 emphasize that the resonances should not have occurred for a further reason, namely, the condition $\gamma \sim 1$ has to be satisfied by characteristic experimental quantities. According to general theory,⁴ this should prevent multiphoton absorption of radiofrequency photons. Thus, the problem for the theory is to explain the origin of the resonances in the ion yield.

10. COMPARISON OF THEORY AND EXPERIMENT

The experiment reported in Ref. 53 demonstrated the ionization of highly excited atoms for external-field

frequencies that were lower than the Kepler frequency by a substantial factor (a factor of approximately 5), so that there are good grounds for concluding that classical ionization did not occur in this experiment. For $\omega = 10$ GHz and $n = 45$, the adiabatic parameter is $\gamma = 3$. It follows that the process occurring in this experiment was multiphoton ionization. However, absorption of photons will not, of course, occur right up to the continuous-spectrum limit because the probability of multiphoton ionization near this limit is negligible (see Sec. 4). Something like 5–10 photons are likely to be absorbed, after which the external field reaches the atomic value or $\sim \mathcal{E}_c$ for the corresponding n . Accordingly, if we suppose that $n = 60$ and $\mathcal{E} = 75$ V/cm, we find that these values satisfy the relation $\mathcal{E} = 1/5n^4$. This estimate of the critical field for multiphoton ionization is in reasonable agreement with (21).

In accordance with the excitation conditions, these states have low orbital angular momenta, i.e., they are approximately spherically symmetric. In terms of parabolic variables, this means that $n_1 \approx n_2$ (for $n_1 > n_2$, the probability of finding the particle with $z > 0$ is greater than the corresponding probability for $z < 0$, whereas the reverse situation prevails for $n_1 < n_2$). Consequently, the linear Stark shift, which is proportional to $n_1 - n_2$, is practically absent in the above low-frequency field. Since the field is variable, it would be more correct to speak not of the linear Stark effect but of the population of the quasienergy states for the corresponding quasienergy harmonics, but this has no effect on the conclusion made above. As far as the quadratic Stark effect is concerned, the results of Sec. 3 indicate that it is approximately $0.15n^6\mathcal{E}^2$ for low orbital angular momenta. For the fields and values of n indicated above, the shift turns out to be of the order of $\Omega/40$. Moreover, the shift is almost the same for neighboring levels, so that the difference between level energies remains practically undisturbed. It is this that is responsible for the resonances that are observed experimentally when the Kepler frequency is a multiple of the microwave field frequency.

We now turn to an analysis of the experiment reported in Ref. 41. In this experiment, the values of n were much greater, namely, $n \approx 65$. For these states, a radiofrequency field with $\omega \approx 10$ GHz, i.e., $\omega \approx 0.43\Omega$, turns out to correspond to a field strength above the threshold (39) for stochastic ionization. The ionization was observed for fields $\mathcal{E} > 10$ V/cm, which is in agreement with (39); $\mathcal{E}_c \approx 5$ V/cm. Figure 8 shows the experimental data taken from Ref. 41 and the results of the numerical experiment,²² giving the fraction of ionized particles as a function of \mathcal{E} . It is clear that there is good agreement. Under these quasiresonance conditions, the only competitor to diffusion ionization is multiphoton ionization. However, the field strength for which the ionization was observed was much less than the critical field strength (21) for multiphoton ionization which, in this case, was of the order of 50 V/cm, so that multiphoton ionization is described by a power-type law, and its probability estimated from the relationships given in Sec. 4 turns out to be low in this case.

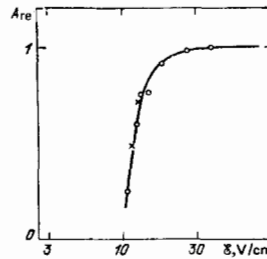


FIG. 8. Amplitude of the proton signal (relative units) recorded in the experiment described in Ref. 41 as a function of the field strength \mathcal{E} for $n = 65$. Points—experimental; crosses—numerical calculation.²² The field frequency was $\omega = 9.9$ GHz (the experimental values correspond to the curve drawn through the open circles in Fig. 7).

On the whole, the results of this comparison are not inconsistent with the assumption that this experiment is, so far, the only example of stochastic ionization of a highly excited atom, and of the observation of diffusion ionization of a highly excited atom.

Let us now analyze the experimental data⁴¹ for $\omega = 30$ MHz (see Fig. 7) from the point of view of the theory. We note that this frequency is lower by a factor of one thousand than the Kepler frequency Ω , so that there is, of course, no question of stochastic ionization. In this case, ionization is produced in a practically constant field and is the result of above-barrier passage of the electron across the potential barrier. In accordance with general theory (see Ref. 1 in Sec. 5), the above-barrier motion of the electron occurs for atomic fields given by (26). Experiment shows that the ionization process occurred for fields $\mathcal{E} \approx 1/8n^4 = 30$ V/cm, which is in reasonable agreement with the estimate given by (26).

The case $\omega = 1.5$ GHz, for which $\gamma \sim 1$, is intermediate between multiphoton and tunneling cases of quantum-mechanical ionization. The experimental field strength for which ionization takes place at this frequency is also intermediate, as we have seen in Section 8. Since, under these conditions, $\omega = 0.065\Omega$ and $\mathcal{E} > \mathcal{E}_c$, the situation is closer to the above-barrier transition of the electron, which is impeded by the fact that the field is still not constant.

To summarize, we may conclude that the results of experiments with highly-excited hydrogen atoms, the results of numerical computer experiments, and the conclusions ensuing from the analytic description of the ionization of highly excited atoms indicate that there is good qualitative and quantitative agreement between them. We thus have confirmation of the existence of a new, quasiclassical process of diffusion ionization of highly excited atoms. It is important to note, however, that, so far, there is no published experiment that unambiguously confirms the diffusion nature of the ionization process. Such an experiment is not simple but possible, in principle. As an example, we suggest measurement of the ion yield as a function of the duration of the interaction with the external field. In the case of multiphoton ionization, for which the ion yield is characterized by the probability of ionization per unit

time, the yield is directly proportional to the duration of the interaction with the external field. In the case of diffusion ionization, this relationship is obviously not valid.

Another possible way of confirming experimentally the existence of diffusion ionization is to frequency-modulate the external field: $\mathcal{E}(t) = \mathcal{E} \cos(\omega t + \lambda \sin \omega_m t)$. When $\omega \sim \Omega$ and $\lambda \omega_m \geq \omega/3$, the modulation depth is of the same order as the separation between the resonances $\Delta\Omega = \omega/2$. This means that the condition for the appearance of diffusion ionization is that there should be overlap between the much more closely spaced modulation resonances with $\Delta\Omega = \omega_m \ll \omega$, since we are assuming that $\lambda \gg 1$. Thus, modulation of the external field results in a reduction by a factor of $\lambda^{3/2}$ in the critical field (46) for diffusion excitation. Thus, for example, when $n = 65$, $\omega/2\pi = 20$ GHz, $\omega_m/2\pi = 1.1$ GHz, and $\lambda = 6$, we have $\mathcal{E}_c \approx (84n^4\lambda^{3/2})^{-1} \approx 0.2$ V/cm. The diffusion coefficient is then still given by (56). Modulation of the external field has little effect on the number of photons involved in the multiphoton ionization process because the maximum frequency of the perturbing field is increased by only 30%. Correspondingly, there is also very little change in the critical field for the multiphoton ionization process.

11. CONCLUSIONS

It is well known that, in the general case, the interaction between the external electromagnetic field and the atom is essentially quantum-mechanical in nature. The above discussion of the interaction with a highly excited atom has shown that, in this special case, the interaction is quasiclassical. The use of classical mechanics has enabled us to describe a new mechanism for the ionization of a highly excited atom, which has no analog in the case of multiphoton or tunneling ionization. Analysis of the classical equations of motion shows that, under certain definite conditions, the dynamics of an atomic electron in the external field is stochastic in character (although there is not external perturbation). This results in the diffusion of the electron along the energy scale, leading to the ionization of the atom. We note once again the qualitative difference between the diffusion ionization process and the quantum-mechanical ionization processes, such as photoionization and nonlinear multiphoton and tunneling ionization. Whatever the specific mechanism involved, the process of quantum-mechanical ionization always consists of a single transition of an electron from an initial bound state to a final free state. Diffusion ionization, on the other hand, consists of a large number of transitions of the electron in which its energy changes in a random fashion both in sign and magnitude. This is why, in the description of quantum-mechanical ionization, we have introduced the concept of probability per unit time, whereas diffusion ionization can be described only in terms of the total probability.

Numerical experiments in which diffusion ionization of a highly excited atom was simulated on a computer have led to results that are in good agreement with the analytic description of this process. As far as actual

experiments are concerned, the number of these is exceedingly small. The results of the only experiment reported so far,⁴¹ in which the experimental conditions corresponded to the conditions for diffusion ionization, are in good agreement with the predictions of the theory. However, the conclusive experiment that would unambiguously confirm that it is the diffusion ionization and not quantum-mechanical ionization that is being observed has not as yet been performed. This type of experiment would be of interest, above all, for the resolution of the problem of ionization of highly excited atoms. However, the interest in this experiment actually extends beyond the confines of the above problem because the highly excited atom constitutes one of the realistic models capable of reflecting the characteristics of the dynamics of quantum-mechanical systems that are stochastic in the classical limit.

Although the main interest attaches at present to experiments with highly excited atoms, there are a number of important questions that, so far, have not been answered by the theory.

One of these questions is the description of above-barrier ionization in a variable field. In above-barrier ionization (and in the case of tunneling ionization), the difference between a variable and a constant field is that the barrier varies with time. By analogy with the tunnel effect, we have to assume that the conditions that must be satisfied for above-barrier ionization to take place must involve not only the field strength (barrier height) but also field frequency.

If we now turn to diffusion ionization, we find that the most fundamental problem is, perhaps, that of the role of quantum-mechanical corrections to the classical theory of the stochastic excitation of an atomic electron and its diffusion along the energy scale. It is important to draw attention to the fact that, in the course of time, the quantum-mechanical corrections may lead to radical changes in the dynamics of the system (see, for example, Ref. 37).

As regards traditional approaches to the description of diffusion ionization, it is desirable to continue and develop numerical experiments with a view to obtaining data on the probability of diffusion ionization in a broader range of frequencies and for lower field strengths, and also data on the limit for the appearance of stochastic excitation of an atomic electron.

The natural question that arises from all this is: to what extent do the above phenomena occur not only in atoms but also in highly excited molecules? As far as molecules in highly-excited electronic states are concerned, there is no doubt that all that we have said above in connection with highly excited atoms applies to them as well. However, there are no direct experimental data relating to this case. Analogous phenomena may also occur for molecules in highly excited vibrational states. The greatest practical interest is in the excitation of complex molecules to vibrational states by infrared laser radiation, resulting in the dissociation of the molecules.^{59,60} The possibility of the dissociation of a molecule as a result of its stochastic insta-

bility and diffusion excitation has been noted in the literature.^{61,62} The critical field is given in Ref. 62 for a number of complex vibrationally excited molecules. Theoretical estimates of the critical field are in satisfactory agreement with experimental results.^{59,60} It cannot be said, however, that stochastic instability and diffusion excitation of molecules are the generally accepted explanation of the dissociation of molecules by infrared laser radiation.^{59,60} For example, we note Ref. 63, in which the excitation of high vibrational states of a polyatomic molecule in an infrared field is described within the framework of quantum mechanics for a particular model of the molecular spectrum. The overall situation in the case of molecules is the same as in the case of atoms: the classical process of stochastic instability and diffusion excitation explains the experimental data but there are alternative explanations.

Finally, since the phenomena described above in a qualitative way do not depend on the particular shape of the potential, it would be interesting to investigate the external multiphoton photoelectric effect as well. From the standpoint of the theory, this case is particularly interesting because the potential is one-dimensional in character, which substantially simplifies both analytic calculations and numerical simulation.⁶⁴

Summarizing the situation as a whole, we may conclude that research into the process of perturbation of the ionization of excited atoms in low-frequency fields remains a highly promising field of activity for both experimenters and theoreticians.

Note added in proof. The results of an experiment in which the shift (which is quadratic in the field) of the $22P$ state of the rubidium atom was observed are reported in Ref. 65.

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