Ionization by an electric field: Line disappearance in the Stark effect

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The behavior of the Stark levels of the hydrogen atom in the presence of a strong constant electric field F is investigated. It is shown that as F increases, the level experiences a singularity in the transition to the region which, according to classical mechanics, is where the onset of ionization occurs. A comparison is made with experimental results for three levels of the sodium atom at the magnetic quantum number $m=1$. The concept of "ionization subthresholds" of the atom in the presence of a constant electric field is introduced and analyzed.

INTRODUCTION

The title of our article coincides with that of Section 54 of the monograph by Bethe and Salpeter,[1] and it should be therefore clear that we are talking about the effect long predicted by theorists on the basis of fundamental ideas about the connection between quantum and classical mechanics. However, a detailed theoretical analysis of this subtle effect was not carried out in Ref. 1, and therefore it has remained unclear how it should manifest itself experimentally. This can be explained by the fact that direct experimental detection of this effect remained impossible until the advent of modern laser technology, which has made it possible to examine the ionization (which by no means reduces to just a process of quantum-mechanical tunneling) of highly excited Rydberg states in a constant electric field.

As the electric field increases, the energies of the quasistationary Stark states change and their widths grow. The following conclusion appears almost obvious: the Stark levels preserve their discrete character all the way to the tunneling region, where they suddenly disappear [§3.4.4 in Ref. 2 (review)]. It is assumed that this is precisely how the transition to classical mechanics occurs. An entirely different point of view is expounded in Ref. 1.

The point we are discussing here is by no means purely theoretical, but concerns problems directly tied up with the most recent experimental results.

In theoretical work devoted to the Stark effect, it is frequently overlooked that the very concept of quasistationary states was introduced according to Ref. 3 only for systems with a low probability of decay, i.e., with a narrow linewidth. In no case do the authors of Ref. 3 connect this fact with the complexity of the calculations of the lifetimes of the levels in large fields. Here the concept simply loses meaning. At the same time, experiments on Stark lines[4,5] carried out shortly after the writing of Ref. 2 indicate that the concept of quasistationary states can be usefully broadened. Stark lines continue to distinctly manifest themselves in experiments in fields so strong that their widths cannot be uniquely determined, but only a very rough estimate can be given. This aspect of the behavior of the lines can be understood on the basis of simple physical arguments. As the field increases the lifetimes of the excited states fall and the situation gradually arises in which the process of their creation is indistinguishable from their decay. Hence it is clear that in strong fields we must simply reject the concept of the width of a state, but not as such, since the line is clearly visible in the experiment. The possibility of such behavior of the levels is obvious, but experimental studies pertinent to this question have appeared only recently. Moreover, running ahead, we can assert that such behavior of the Stark lines is a consequence of the transition of quantum mechanics to classical mechanics in the limiting case.

In fact, the effect was predicted in Ref. 1, and was first observed for rubidium for the magnetic quantum number $m=0$ (Ref. 4), and later was studied in the three states of sodium with $m=1$ (Ref. 5). However, in Refs. 4 and 5 the experimenters did not in any way connect the effect with the predictions of Bethe and Salpeter.[1] And in fact this connection is in no way obvious. The effect has acquired a new name: "stabilization of the Stark state at a saddle point," since the experimenters observed it as an almost complete disappearance of the Stark signal while varying the field over a narrow interval. This fact was interpreted as an abrupt decrease (by 3–4 orders of magnitude or more) of the width of the level. With further increase of the field, a weaker signal reappeared. Over a wide interval of the field in the vicinity of the "stabilization" point the width of the Stark line, according to the estimates of Ref. 5, was of the order of 0.2–0.3 cm^{-1}.

We will also consider another indirect manifestation of line disappearance, which was observed in experiments[2,6] on the ionization of Li and Na atoms in a weak field. The experiments showed that the Stark energies of the highly excited states of these atoms for $m=1, 2$ are well described by the hydrogenic theory, but data on their lifetimes, at first glance, appear to lead to just the opposite conclusion. Reinhardt[7] has explained this discrepancy by the influence

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of the core. Also, "stabilization" of the Stark states for Rb and Na (Refs. 4 and 5) is explained by the presence of the core. We will show, however, that the Stark levels behave similarly in the case of hydrogen.

We first consider the numerical solution of the Schrödinger equation. At the conclusion of our treatment we will show that it is possible to do without it, not only for a qualitative understanding of the above-mentioned experiments, but also for a quantitative description of the effect. Nevertheless, a numerical treatment is necessary since it graphically defines the essence of the problem in which such substantial differences of opinion have arisen. Obviously, any analytic (asymptotic) approach to the solution is justified only if it does not qualitatively contradict an exact numerical solution, which for the hydrogenic case is possible.

1. THE PROBLEM OF LINE DISAPPEARANCE

The Schrödinger equation for the hydrogen atom has the form

$$\left(\frac{1}{2}\Delta+\frac{1}{r}-Fz+E\right)\Psi=0. \tag{1}$$

It can be separated in the variables μ, ν, φ:

$$x=\mu\nu\cos\varphi,\quad y=\mu\nu\sin\varphi,\quad z=\tfrac{1}{2}(\mu^2-\nu^2). \tag{2}$$

Introducing the notation

$$\Psi=(\mu\nu)^{-1/2}M(\mu)N(\nu)e^{\pm im\varphi}, \tag{3}$$

and, substituting Eq. (3) into Eq. (1), we obtain the equations

$$\left(\frac{d^2}{d\mu^2}-\frac{1-4m^2}{4\mu^2}+2E\mu^2-F\mu^4+Z_1\right)M(\mu)=0, \tag{4}$$

$$\left(\frac{d^2}{d\nu^2}-\frac{1-4m^2}{4\nu^2}+2E\nu^2+F\nu^4+Z_2\right)N(\nu)=0, \tag{5}$$

$$Z_1+Z_2=4. \tag{6}$$

The behavior of $M(\mu)$ and $N(\nu)$ at zero and at infinity is determined by the formulas

$$M(\mu)\underset{\mu\to 0}{\simeq}\mu^{m+1/2}, \tag{7}$$

$$M(\mu)\underset{\mu\to\infty}{\simeq}\frac{A}{\mu}\exp\left(-\frac{F^{1/2}}{3}\mu^3+\frac{E}{F^{1/2}}\mu\right), \tag{8}$$

$$N(\nu)\underset{\nu\to 0}{\simeq}\nu^{m+1/2}, \tag{9}$$

$$N(\nu)\underset{\nu\to\infty}{\simeq}\frac{B(Z_2)}{\nu}\sin\left[\frac{F^{1/2}}{3}\nu^3+\frac{E}{F^{1/2}}\nu+\varphi(Z_2)\right]. \tag{10}$$

It is correct to assert that since Eq. (1) separates in its partial derivatives, it can be solved exactly numerically. Indeed, numerical integration of Eqs. (4) and (5) does not entail any fundamental difficulties. But when people speak of the possibility of an exact solution of Eq. (1), they usually mean that it is thereby possible, at least in principle, to find arbitrarily accurate values of the Stark energies E_0 and linewidths Γ for any state and any F, no matter how large. Here it is taken as obvious that there is no point in this if only because levels that are too broadened cannot be observed experimentally. In fact, the heading of Section 54 in Ref. 1 confirms that the creators of quantum mechanics did not foresee such a development of the theory. When they spoke of the disappearance of Stark lines, they in no case had in mind that they would simply spread out with increase of the field F.

Bethe and Salpeter[1] defined the threshold for disappearance of a line in terms of classical mechanics, which is the limiting case of quantum mechanics. According to classical mechanics, a state is stable as long as it remains under the barrier. Above the barrier it rapidly disappears. The condition of disappearance of the barrier in Eq. (5), which was derived in Ref. 1, is

$$Z_2=\frac{E_t^2}{F_t} \tag{11}$$

(the value of Z_2 in Ref. 1 is four times smaller than ours).

Let us turn now to a discussion of what can be obtained as a result of numerical integration of Eqs. (4) and (5). Fixing the values of F and E, we can in principle find the exact value of Z_1 for a given quantum number n_1. In the limit $F\to 0$ we go over to the field-free case. Solving Eq. (5) with F and E fixed, we can exactly determine the amplitude $B_E(Z_2)$ for all values of Z_2. In this way we can exactly determine the positions of the minima (and maxima) of the amplitude. As $F\to 0$ the minima gradually go over to the unperturbed eigenvalues of the problem, and the process occurs faster, the smaller the quantum number n_2. Parametrizing the amplitude in the regions of the minima of $B_E(Z_2)$ according to the Breit–Wigner formula

$$B(Z)=B[(Z-Z_0)^2+\gamma^2/4], \tag{12}$$

we can find the values of the parameters Z_0 and γ. Analogously, solving the system of equations (4)–(6) simultaneously, we can determine the Stark energy E_0 and linewidth Γ. Such a procedure is completely justified for small F. In this case the magnitude of Γ is small, and E_0 can differ from the position of the amplitude minimum only by an amount $\sim\Gamma^2$. As F increases, the situation gradually changes—the magnitude of Γ (and also E_0) begins to depend significantly on the points, on the basis of which the parametrization is made. Now we may ask, is it possible to determine E_0 and Γ uniquely?

A procedure has been proposed of summing the perturbation theory (PT) series for the energy in the Borel sense,[7] which converges for all values of Γ. It allows one, in principle, to determine E_0 and Γ, as accurately as one may like, for any values of the quantum numbers n_1, n_2, m. But in no case can it be said that this approach is uniquely rigorous from the mathematical point of view. The PT series diverges asymptotically and terms $\sim\Gamma^2$ which are smaller than the irreducible error of the main series can be sensibly added to it. For small F, summing the new series in the Borel sense, we obtain practically the same results for E_0 and Γ. But for large F, and this is the case that interests us, we get a different answer.

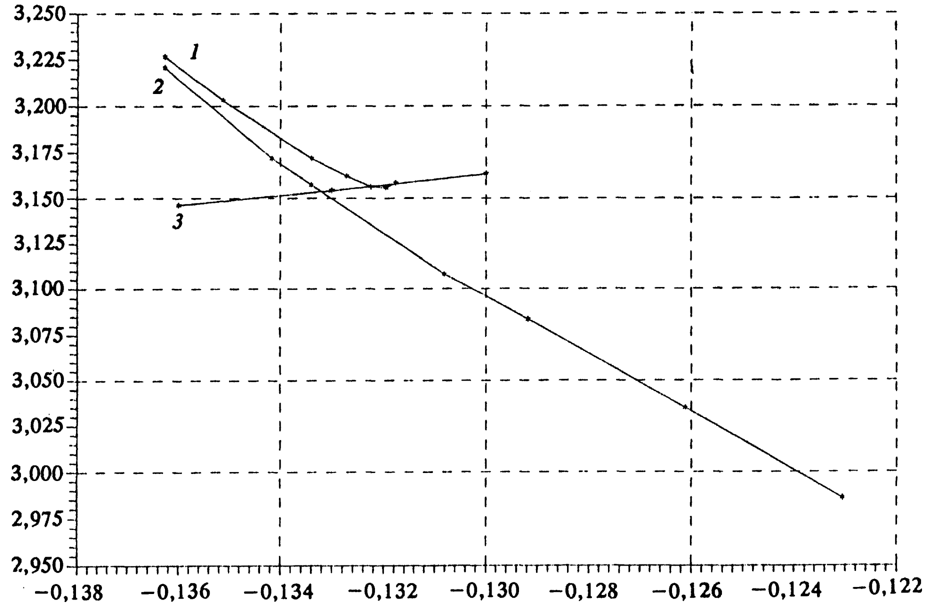

FIG. 1. Dependence of the separation constants $4-Z_1$ and Z_2 on energy E: 1) the values of Z_2 corresponding to the minimum of $B_E(Z_2)$; 2) the values of Z_2 corresponding to the minimum of $B_{Z_2}(E)$; 3) $4-Z_1$, where Z_1 corresponds to the eigenvalue of Eq. (4) for $E=\text{const}$. The intersection point of curves 3 and 1 corresponds to the "stabilization" point of the level $(n_1,n_2,m)=(3,18,1)$. Here $F=0.599\cdot 10^{-6}$ a.u.

It would seem that for large F it should be possible to implement a procedure which makes use of the absence of a diverging wave in the solution. In this case we seek a pole in the complex E plane, whose real part corresponds to the Stark energy, and whose imaginary part corresponds to Γ. As $F\to 0$, the pole converges to the unperturbed solution of the problem, i.e., the approach is well founded. We can require that the absolute value of the coefficient of the diverging wave approach zero, and seek the values of E_0 and Γ in this way. But this approach, although it would seem to be the unique approach, is in no way unique. We can require that the convergence to zero of the real and imaginary parts of the coefficient in question converge to zero in a different way. In such a case we would obtain different values of E_0 and Γ.

Naturally, significant differences between the results of the approaches arise only for large values of F. The fact that the pole in the complex plane cannot be used in a "rigorous" determination of the quasistationary state for any F was implicitly noted in the first edition of the monograph by Landau and Lifshitz.[3] The procedure of introducing a complex energy to describe it has been called the "original" method. Its usefulness is obvious since by this approach the connection between the linewidth and the lifetime of the level is revealed at once. But in the later editions of that book this method came to be called the "formal" method. This served as a reason to assume that the method was rigorously founded and that one could use it to find a unique solution, which one cannot because the problem does not have a unique solution. Thus, at large F we cannot uniquely determine the linewidth either experimentally or theoretically. If the theory were different, then it would contradict experiment.

The minima of $B_E(Z_2)$—if they even exist, which, as we will show, is not always the case—can be found exactly. By solving Eqs. (4) and (5) simultaneously, i.e., satisfying condition (6), where Z_1 corresponds to the exact eigenvalue of Eq. (4), and Z_2 corresponds to the minimum of $B_E(Z_2)$, we can determine the Stark energy E_0. For small F we do not obtain any new results, but for large F this solution method has not yet been used. Let us consider in greater detail the case in which the magnetic quantum number satisfies $m=1$, since here we have the possibility of comparing our results with the experimental data on sodium.[5] We solved Eq. (5) numerically for F held fixed, while varying the magnitude of E and observing the behavior of the minima of $B_E(Z_2)$ (denoted as Z_2) which come out of the unperturbed problem ($F=0$ or $F=\text{const}$, $E\to-\infty$). Since the solution of Eq. (5) does not change when we make the substitutions $F\to A^3F$, $E\to A^2E$, $Z_2\to AZ_2$, where A is an arbitrary positive real parameter, we do not need to solve Eq. (5) numerically for other values of F. These other solutions can be obtained by a scale transformation.

The solution shows that as E increases, the minimum of the amplitude becomes continually broader and shallower, and, as a result, the Breit–Wigner parametrization becomes correspondingly less reliable. But we can determine the positions of the minima themselves (and also the accompanying maxima) precisely. The result of one of these calculations of Z_2 is shown in Fig. 1.

As E grows, Z_2 decreases, as it should if we are to believe perturbation theory. But at some $E=E_t$ it turns around and begins to grow, and afterwards the minimum in $B_E(Z_2)$ rapidly disappears, merging with the higher maximum. For $E>E_t$ it is no longer possible to talk of the width of the level, or even of a level as such; it has simply disappeared.

Table I gives some data on these points and related information for different values of the quantum number n_2, and also a comparison with formula (11).

It is clear from Table I that Eq. (1) is asymptotically correct as $n_2\to\infty$, as it should be according to Ref. 1. By solving the Schrödinger equation, we have obtained the transition to classical mechanics, in the process dispensing with the unrigorous (in the strong-field region) concept of

TABLE I. $m=1$. $F=0.638544\cdot 10^{-6}$. E_t is the value of E at which Z_2 begins to grow.

n_2	$Z_2(E_t,n_2)$	$\cdot 10^{-4}E_t$	$\frac{E^2}{F}=Z_2'$	$\frac{Z_2}{Z_2'}$	$\cdot 10^{-4}R$	$6f$	$\frac{Z_2(E_t,n_2)}{4\sqrt{-2E_t}(n_2+1)}$
15	2.54610	-12.165	2.318	1.099	13.302	0.12770	0.80653
16	2.76716	-12.710	2.523	1.094	12.456	0.12705	0.80712
17	2.99299	-13.246	2.748	1.089	11.707	0.12644	0.80763
18	3.22340	-13.770	2.970	1.086	11.045	0.12591	0.80820
19	3.45818	-14.288	3.197	1.082	10.450	0.12540	0.80864
21	3.94042	-15.296	3.664	1.075	9.435	0.12455	0.80957
23	4.43854	-16.275	4.148	1.070	8.596	0.12379	0.81041
29	6.02057	-19.068	5.694	1.057	6.778	0.12201	0.81313

$E^2/F = Z_2'$ is the asymptotic formula (11) from Ref. 1.

quasistationary states, which entails width as well as position. Such an approach is natural, if only for the reason that in classical mechanics there is no concept of width: the level either exists and is stable or is simply absent. Thus, the transition from quantum mechanics to classical mechanics does not have to take the form of a simple washing out of the quasistationary state. In fact, this point was discussed in Section 54 of Ref. 1.

On the basis of the results presented in Table I, we can introduce a quantum-mechanical correction in formula (11) which follows from classical mechanics:

$$Z_2=\frac{E^2}{F}\left(1+\frac{A}{n_2}\right), \tag{11'}$$

where $A\approx 1.6$.

The disappearance of the minima of $B_E(Z_2)$ appear paradoxical if we proceed in an unrigorous way from perturbation theory. It is just in this way that physicists usually proceed, and in the majority of cases such an approach is justified. Indeed, we can find Z_2 from the formula

$$Z_2=4\sqrt{-2E}\left[n_2+\frac{m+1}{2}-(6n_2^2+6n_2m+6n_2+m^2+3m+2)R-\dots\right], \tag{13}$$

where

$$R=\frac{F}{4}(-2E)^{-3/2}, \tag{14}$$

including in it a large enough number of decaying (in magnitude) terms and discarding the growing ones. For the case shown in Fig. 1, for all E, including $E=E_t$, around ten terms in formula (13) decay. It would seem that the series (13) is entirely suitable for the calculation of Z_2 since the problem in question does not generally require great accuracy. But in this case, how are we to understand the disappearance of the level, taking into account that all the terms in Eq. (13) except the first are negative? The answer to this question is contained in the strict formalism of higher-order perturbation theory, which has been developed only in recent years.[8] We will not delve deeply here in the far-from-trivial mathematical subtleties of this question. We will only point out that the series (13) is sign-constant (the situation with sign-changing series is different) and asymptotically divergent, i.e., for any arbitrarily small R its terms, starting at some smallest term, grow. Therefore, the complete asymptotic expansion of Z_2, analogous to the expansion of the center of a doublet for symmetric two-well problems,[9] together with the power-law terms in R, contains some exponentially small terms (different from the imaginary terms which characterize the width of the level). These terms do not manifest themselves at small values of the field, especially for small n_2. For this reason their influence cannot be noticed if we compare the results of very accurate numerical calculations of Z_2 with the results obtained using formula (13) for small F. However, starting at some value of F, these terms begin to grow very rapidly, causing the disappearance of minima.

To calculate the Stark energies, we must solve Eqs. (4) and (5) while simultaneously satisfying condition (6). We will not describe this quite simple procedure. One example of the numerical determination of the critical values of the field F_d and the energy E_d at which "stabilization" of the level $n_1=3$, $n_2=18$, $m=1$ occurs is shown in Fig. 1. At fields $F<0.599\cdot 10^{-6}$ a.u. the above-mentioned Stark state exists, while for larger fields the condition $Z_1+Z_2=4$, where Z_2 corresponds to the minimum of $B_E(Z_2)$ for $n_2=18$, cannot be satisfied, and therefore the level disappears.

On the basis of the results presented in Table I, we propose an approximate analytic procedure which makes it possible to determine the "stabilization" points of the levels at various values of n_2 and small n_1. We see that for all n_2

$$\frac{Z_2(E_t,n_2)}{4(n_2+1)\sqrt{-2E_t}}\approx 0.8086\dots . \tag{15}$$

This result can be understood on the basis of formula (13), which for $m=1$ can be represented in the form

$$\frac{Z_2(E,n_2)}{4(n_2+1)\sqrt{-2E}}=1-6(n_2+1)R-[68(n_2+1)^2+10]R^2-\dots . \tag{16}$$

Of course, we will not use formula (16) to calculate Z_2, but only to clarify at which R the level disappears for large n_2. It is clear that the left side of expression (16) depends significantly only on the quantity

$$f=(n_2+1)R. \tag{17}$$

For the turning points of E_t, as can be seen from Table I,

$$f_t \approx 0.021\dots. \tag{18}$$

Basing ourselves on these observations and using the PT formula for Z_1, which is unquestionably valid for the fields under consideration and $n_1 \ll n_2$, and also condition (6), we obtain

$$E_d=-\frac{1}{2(Z_1'+Z_2')^2}, \tag{19}$$

$$F_d=\frac{0.084}{(n_2+1)}(-2E_d)^{3/2}, \tag{20}$$

where

$$Z_2'=0.8086(n_2+1), \tag{21}$$

$$Z_1'=(n_1+1)\left[1+\left(\frac{n_1+1}{n_2+1}\right)\cdot 0.126-\frac{17}{9}\left(\frac{n_1+1}{n_2+1}\right)^2 \times 0.126^2+\dots\right]. \tag{22}$$

Formulas (19)–(22) not only agree well with the exact numerical calculations which we carried out for a few cases, but also make it possible to reliably decipher the results of McNicholl *et al.*,[5] who obtained three experimental points on the "stabilization" of the Stark levels of sodium. Of course, it is not experimentally possible to determine the quantum numbers n_1 and n_2. The magnetic quantum number $m=1$ was determined from the conditions of the experiment.

The experimental technique of McNicholl *et al.*,[5] in principle developed already in earlier investigations of the dependence of the behavior of the Stark levels of alkali atoms on the magnitude of the field F, is described in Ref. 2. The atomic beam technique was used. The Rydberg states of the Na atom were populated by two-step photoexcitation with the help of dye lasers. The Na^+ ions that form by the decay of Na atoms give evidence of the presence of the Stark level. If the field F is varied slowly by scanning the laser frequency, i.e., varying the energy E, the evolution of the Stark line can be traced out. In their studies of the Stark levels, McNicholl *et al.*,[5] were able to achieve significantly larger values of F than those achieved in previous studies.[2,6] They observed that at certain values of F_d and E_d characteristic of the three levels the Na^+ signal abruptly decreased.

Table II presents a comparison of the experimental and theoretical values. Formulas (19)–(22) show at once that there are no other values of F_d and E_d simultaneously in "reasonably" close intervals about F and E. In discussing these results we should first of all note that our calculation is for the hydrogen atom, and the experiment—for sodium. For this reason alone we are at pains to expect better agreement. Still more important is the fact that the accuracy of the experimental measurement of the field F (Ref. 5) is less than the typical accuracy for experiments of this type, which is 2–3%. The very accurate experimental field values adduced in Table II are in fact not such (as was clearly noted by the authors of Ref. 5), but were "refined" by comparison with theoretical data of a model which takes the core into account. According to this model and in contradiction with Section 54 of Ref. 1, there should be no "stabilization" effect for the hydrogen atom.[4,5]

TABLE II. Comparison of the experimental data with the theoretical calculations of the fields and energies at which the Stark lines disappear.

		E_d	F_d	n_2	n_1	n
A	a	$-12.79\cdot10^{-4}$	$0.6457\cdot10^{-6}$			
	b	$-12.51\cdot10^{-4}$	$0.6185\cdot10^{-6}$	16	5	23
B	a	$-12.77\cdot10^{-4}$	$0.6378\cdot10^{-6}$			
	b	$-12.86\cdot10^{-4}$	$0.6087\cdot10^{-6}$	17	4	23
C	a	$-13.00\cdot10^{-4}$	$0.5873\cdot10^{-6}$			
	b	$-13.20\cdot10^{-4}$	$0.5995\cdot10^{-6}$	18	3	23

a—experimental results,[5] given in atomic units.
b—calculations based on formulas (19)–(22).

From their discussion in Section 54 of Ref. 1 it is obvious that Bethe and Salpeter checked formula (11) against the quasiclassical calculations of Lanczos and the experimental data of Traubenberg on the optical observation of the disappearance of the Stark lines of the Balmer series in a field. This comparison did not show good agreement between the formula and experiment. The reason for the discrepancy as indicated by Bethe and Salpeter is that Traubenberg's experiment did not directly observe ionization of the atoms in a field, and the spectral lines were suppressed as a result of quantum tunneling even at considerably smaller fields. McNicholl *et al.*,[5] observed the ionization of the Stark levels directly. And here even the fact that they observed ionization in sodium, and not in hydrogen, did not lead to any significant difference between calculation and the experimental data.

We have obtained values of E_d and F_d from an exact solution of the Schrödinger equation. But in practice the same results can be obtained in a simpler way. To determine E_d and F_d for given values of n_1 and n_2 and $m=1$, we can use formula (11) in combination with the PT formula for the energy, retaining 4–5 terms in the latter. Such a calculation makes sense for small n_1 and large n_2. In the calculation of Z_2 in formula (11) the relation $Z_2=4-Z_1$ should be used, where Z_1 can be calculated using perturbation theory. The results of such a calculation give values of E_d and F_d which differ from the "exact" values by not more than 2–3%, which is completely insignificant for practical applications. Thus we arrive at a completely paradoxical conclusion: perturbation theory is valid in practice not only qualitatively, but also quantitatively all the way to the actual disappearance of the level.

Previously we considered the case $m=1$. It is specifically about this case that the discussion centers in Ref. 1.

But analogous results obtain also for the case $m=2$. However, the case $m=0$ is special. Here the minimum of $B_E(Z_2)$ does not disappear upon crossing the barrier, it just becomes less pronounced. Mathematically, this result differs from the others in that here the centrifugal potential $(1-m^2)/4\nu^2$ in Eq. (5) has a different sign. In such a potential in classical mechanics the particle "falls" into the center.

In our opinion—despite the convincing agreement between the theoretical and experimental values of F_d and E_d, we have nonetheless not yet completely explained the experimental results of McNicholl *et al.*,[5] even qualitatively. Indeed, their experimental studies clearly show that with further increase of the field, starting at F_d, the level is regenerated anew, but in a more broadened form. Thus, the arguments of Section 54 of Ref. 1, despite their unquestioned validity, do not give the complete picture of the behavior of the Stark lines in a field. Therefore, in their interpretations of their own data, the authors of Refs. 4 and 5 were not able to correlate them with the predictions of Section 54, Ref. 1.

In order to clarify this situation, let us again turn our attention to the procedure of exact solution of Eqs. (4)–(6). What then did we miss in the foregoing consideration? The traditional approach to solving these equations, starting from perturbation theory, was first applied by Schrödinger and proceeds as follows: the value of E is fixed in Eqs. (4) and (5) and one then solves the problem of finding the eigenvalues Z_1 and Z_2 for given values of the quantum numbers n_1, n_2, and m. These problems are actually eigenvalue problems since the use of perturbation theory assumes that the wave functions decay exponentially at infinity, i.e., the decay of the atom is not taken into account. After determining Z_1 and Z_2 for arbitrary E, its true value is found from condition (6). But there is another way to solve this problem. One can fix the values of Z_1 and Z_2 in Eqs. (4) and (5) and then, having determined the eigenvalue E, satisfy condition (6). Of course, within the framework of perturbation theory, as in the case $F=0$, we do not obtain any new solutions. But, solving out the problem exactly according to the traditional scheme, we departed from the framework of perturbation theory. And only such an approach allowed us to find the "stabilization" points of the levels.

Likewise, considering the second possible approach to solving Eqs. (4)–(6), we again had no choice but to depart from the framework of perturbation theory. As for Eq. (4), which even for $F\neq 0$ remains an eigenvalue problem, we do not obtain anything new via the second approach. Solving Eq. (5), we now fix the value of Z_2 and find the minima of the function $B_{Z_2}(E)$ for fixed values of n_2. Again, as before, we are able to determine their positions exactly. For small F both minima have almost the same values of Z_2 and E. They merge into one true eigenvalue only for $F=0$. At larger values of F the positions of the minima corresponding to the same value of n_2 diverge abruptly. An example of the calculation of the minima is shown in Fig. 1. One should bear in mind the small scale of this figure, which dramatizes the differences in the positions of the minima. From the practical point of view, the difference in the positions of the minima is substantial only in the immediate vicinity of the disappearance of the minima of $B_E(Z_2)$. Calculation shows that the minima of $B_{Z_2}(E)$ do not disappear as E grows. They only become more and more washed out. The presence of a series of minima in $B_{Z_2}(E)$ reflects the other face of quantum mechanics, namely its wave character. Using the value of Z_2 found from $B_{Z_2}(E)$, we can determine what we will choose to call the second component of the Stark line for the given values of n_1 and n_2.

We omit the Stark energies for any concrete levels as functions of the magnitude of the field F, calculated using our technique. The quantitative difference between them and the results which can be obtained using the standard perturbation theory for the energy, taken out to 4–5 terms, proves to be insubstantial even for the region where "stabilization" is observed. The two components of the Stark line, from the practical point of view, coincide. The presence of the "second component" is manifested in experiment as the regeneration of the Stark line in a still more washed-out form after it "disappears" at the "stabilization" point.

The two solutions of Eq. (1) found above are exact and explicitly manifested in experiment. We emphasize that we are talking here about not just qualitative, but also quantitative agreement of theory with experiment. By quantitative here we mean that an accuracy of 2–3% in the determination of F_d and E_d is sufficient for error-free identification of the "stabilization" points.

To conclude this section, we note one important circumstance tied up with the concept of quasistationary states. Usually, in the solution of physical problems we have the Schrödinger equation with prescribed boundary values and a unique solution. Even if we are not able to solve it exactly, we are firmly convinced of the existence of a solution. In the consideration of quasistationary states, and not only in the Stark effect, we are faced with a different situation. The Stark energy and linewidth are not quantities which can be determined, that is to say, calculated with arbitrary accuracy.[3]

It is useful to compare the Stark problem with the problem of auto-ionization states of atomic He or H^-. Further, we may consider the elastic scattering of an electron from He^+ or H. Solving this rigorously posed, nonrelativistic quantum-mechanical problem numerically, we can, in principle, calculate the phase of the elastic scattering exactly and thereby find the partial scattering cross section. If the phase varies rapidly by the amount π when the energy varies over some interval, we can introduce the concept of auto-ionization states of He or H^-. However, this concept is only approximate. The usefulness of such a concept is obvious and not only for the reason that the calculation of energies and linewidths of auto-ionization states of He or H^- on the basis of an approximate consideration of the Schrödinger equation is significantly simpler than calculating them from the exact scattering problem. But in no way does it follow that one should ascribe the concept of an exact value to an approximate value in attempting to determine the energies and widths with superfluous accuracy, as is sometimes done. In those cases in which the widths turn out to be too large, the concept of auto-ionization states simply loses meaning, but the scattering problem from which it arose continues to be exact. As regards the Stark states, rejecting only the concept of their widths, we can go a little further than in the problem of auto-ionization states of an atom, namely to their complete disappearance.

2. BEHAVIOR OF THE "IONIZATION" THRESHOLD OF THE HYDROGEN ATOM IN A CONSTANT ELECTRIC FIELD ($m>1$)

In this section we will explain the experimental results of Littman, Zimmerman, and Kleppner on the behavior of the Stark lines of Li and Na for $m=1$, 2 for total quantum number $n=12$–19 mentioned in the Introduction.[2,6] Toward this end, we will briefly describe the technique of the experiment.

Atoms, located in a field, were excited by a tunable laser. In small fields, the atoms, in the process of being excited to the Stark states, did not decay since their lifetimes vis-à-vis decay in such fields are very large. After some delay, during which they do not undergo any considerable radiative decay, the atoms became ionized by the strong momentum of the field, and the Stark energies were determined from the ion signal. For Na as well as for Li, for $m=1$, 2, they turned out to be practically indistinguishable from the corresponding hydrogen energies. However, for certain critical but still very small values of the field, the signals indicating the presence of the Stark states disappeared. On this basis the authors concluded that in such fields the corresponding states suddenly disappear. (We think that another conclusion is possible—namely, that in such fields the number of atoms entering into these states abruptly decreases.)

According to the estimates for the hydrogen atom, in the fields under consideration the indicated states have huge lifetimes vis-à-vis decay in the field. In addition, according to the hydrogenic theory the longest-lived states for a given total quantum number are those deepest in energy. But the experiment on Li and Na[2,6] would seem to give just the opposite picture. In their original report, Littman *et al.*,[6] note one more important experimental fact which in their subsequent review article[2] they did not discuss, namely the nonmonotonic decrease of the lifetime as a function of the field for the above-mentioned states, which also at first glance sharply contradicts the hydrogenic theory.

One more feature in their observations should be noted. The signals from the indicated states do not vanish completely at the critical field values. In the second approach to the measurements, when additional momentum to knock the electron out of the excited atom is not used, it is clear directly from the decay of the atom that the Stark states continue to exist and behave in a way similar to the hydrogen states even in fields which are above critical. But in fields which are somewhat below critical, in such an approach it is impossible to directly register the signals from the Stark states. Kleppner *et al.*[2] arrived at an almost correct explanation of their results, based on the simple saddle-point model. According to this model, an atom can ionize when its energy reaches a critical value:

$$E=-2F^{1/2}. \tag{23}$$

They also gave a second interpretation of their results—a valid one and one which does not contradict their model. When critical fields are reached, the states with large n_1 and small n_2 having vanishingly small width with respect to decay in the field begin to intersect with very wide levels which have large total quantum numbers n and large n_2. This then explains the observed "disappearance" of the long-lived states. Starting from valid premises, Kleppner *et al.*[2] then arrive at the strange conclusion that such decay behavior is possible only for atoms which have a core. In their opinion, true hydrogenic states should not "mix," thanks to the fact that this case is purely Coulomb. Experimental studies on hydrogen, analogous to those for Li and Na, are still lacking. In all probability, the experimental results of Traubenberg[1] on the optical observation of the behavior of the spectral lines of the hydrogen atom with varying field had an influence on their conclusions. These data, at first glance, seem to contradict (strongly!) the observations for Li and Na. But in fact the large difference in the results of these two experiments is due only to the fact that the examined states had different total quantum numbers.

Let us then refine the conclusions reached in Ref. 2. According to Section 54 of Ref. 1 and our treatment

$$E=-(Z_2F)^{1/2}, \tag{24}$$

where $Z_2=4-Z_1$.

It will be useful to give a physical interpretation of Eq. (24), which is asymptotically exact for $F\to 0$.

For $F=0$ the ionization spectrum of the atom begins at $E=0$. In the presence of a field the ionization threshold is lowered and is described by Eq. (24). In a way analogous to the splitting of stationary energy levels in a field, the ionization threshold also split with respect to the conserved quantum number n_1. The observation of the disappearance of the Stark levels upon reaching the first ionization "subthreshold" defined by formula (24), with $n_1=0$, is linked with their penetration into the energy region where ionization of the atom becomes possible and suppresses excitation of atoms to the quasistationary states. But, in contrast to the case $F=0$, some of the atoms fail to decay completely even above the ionization subthreshold, as is clear from the experiment.[2,6] As the subsequent ionization subthresholds at $n_1=1$, 2,... are reached, the situation repeats itself. This explains the nonmonotonic behavior of the atomic decay probability with increasing F reported in Ref. 6.

We will not adduce the results of calculations based on Eq. (24) since there are no experimental data as yet on hydrogen. As for quantitative results, they hardly differ from those obtained from Eq. (23) (with additional, semiempirical small corrections) by Kleppner *et al.*,[2] which they compared with the results of their experiment on Li.

We will explain how this large difference arises between the experimental results of Traubenberg and those reported in Refs. 2 and 6. Comparing the formula for the linewidth[10]

$$\Gamma=\frac{R^{-2n_2-m-1}}{n^3 n_2!(n_2+m)!}\exp\left[-\frac{1}{6R}-\frac{n^3F}{4}\left(34n_2^2+34n_2m\right.\right.$$
$$\left.\left.+46n_2+7m^2+23m+\frac{53}{3}\right)\right] \tag{25}$$

with the formula for the ionization subthresholds (24), one can easily convince oneself that with growth of the total quantum number n the Stark states reach the ionization region, in the process becoming narrower and narrower. Thus, in the limiting case $n_1\rightarrow\infty$ for small n_2 the linewidth behaves on the ionization curve like

$$\Gamma\sim\exp(-\tfrac{23}{3}n_1). \tag{26}$$

For small n the Stark levels decay significantly in the process of tunneling without reaching the ionization curve. For large n such decay does not take place. The experiments of Kleppner *et al.*[2,6] were carried out for $n=12$–19, and the optical observations of Traubenberg, for $n=4$–7. This difference in the total quantum numbers is completely sufficient to explain the huge qualitative difference in the obtained results. Of course, quantum tunneling still operates in the same way, i.e., for the same quantum number n it is greater for deeper states. But in the experiment[2,6] it simply could not manifest itself. Thus we see why when speaking of ionization of an atom in a field, Bethe and Salpeter[1] did not have in mind its decay by quantum-mechanical tunneling. Certain hindrances to an understanding of this circumstance could have been caused by the fact that Bethe and Salpeter referred to the tunneling phenomenon as ionization by wave mechanics. But together with this phenomenon, the quasistationary state, for certain fields and energies, simply ceases to exist, in a way analogous to that in which there are no stationary states for $E>0$ in atoms for $F=0$. The quasistationary spectrum for $F\neq0$ can be characterized by the quantum numbers n_1, n_2, m. But, in contrast to the discrete spectrum, which does not penetrate into the energy region where ionization is possible, the quasidiscrete spectrum penetrates partially into this region. On the other hand, in arbitrarily small fields, for some negative energies quasistationary states with finite values of the quantum number n_2 disappear, which is impossible for the discrete spectrum. Thus, the "continuous" and "discrete" spectra for the hydrogen atom for $F\neq0$ interpenetrate.

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