The Stark effect for the hydrogen atom in a magnetic field

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The spectrum of the hydrogen atom in weak perpendicular and parallel electric and magnetic fields is computed and analyzed with allowance for the diamagnetic interaction. In either case the energy spectrum of the highly excited states as a function of the electric field intensity for a fixed magnetic field splits up into three qualitatively different regions. A natural explanation of this effect is found in a quasiclassical analysis of trinomial recursion relations to whose solution both problems can be reduced. The cause of this splitting of the spectrum lies in the restructuring of the states, when the relation between the electric- and magnetic-field intensities is changed, as a result of the appearance or disappearance of effective potential barriers. Those aspects of the quasiclassical approximation for the trinomial recursion relations which are necessary for the analysis of both problems and which have hitherto not been discussed in the literature are considered.

1. INTRODUCTION

Recently there has been an upsurge in interest in the problem of the description of the Rydberg states in a weak magnetic field. This is due first and foremost to the discovery of the exponential decrease of the energy-level splitting at the quasicrossing point as the principal quantum number n increases. This behavior of the splitting was discovered first in a numerical calculation[1] and then experimentally.[2] To explain this phenomenon, Zimmerman *et al.*[1] and Delande and Gay[2] surmised the existence of an approximate hidden symmetry. A consistent description of the approximate symmetry and a qualitative explanation of the exponential decrease of the splitting are presented in Ref. 3, where it is shown that for the hydrogen atom in a weak magnetic field **H** the variables of the Schrödinger equation with terms up to the fourth order in H are separable in elliptic cylindrical coordinates on a sphere in four-dimensional momentum space. In Ref. 4 an analytic expression is obtained for the magnitude of the splitting at the quasicrossing point. Other characteristics of the spectrum are also considered in Ref. 4; in particular, it is found there that the lower energy levels in a multiplet with fixed values of n and m (m is the azimuthal quantum number) are approximately twofold degenerate in the case when $n > m\sqrt{5}$. The splitting of these doublets is computed in Ref. 5. The separation of the variables in momentum space is discussed in Refs. 4 and 6. In Refs. 7 and 8 some variants of the quasiclassical approximation are considered which are equivalent to the one used in Ref. 3. In Refs. 4–7 approximate analytic expressions are obtained for the lower and upper energy levels in a given multiplet.

The presence of a magnetic field qualitatively alters the Stark effect for the hydrogen atom. Allowance for the diamagnetic interaction leads to the complete lifting of the degeneracy of the energy levels. On the other hand, the states corresponding to these levels possess a definite parity; therefore, strictly speaking, the linear Stark effect does not occur in a magnetic field. But as Kazantsev *et al.*[9] have noted, for the lower energy levels with $n > \sqrt{5}m$, which are approximately degenerate, the linear Stark effect occurs even in electric fields whose strengths are exponentially small in n.

The spectrum of the hydrogen atom in crossed electric **F** and magnetic **H** fields has been investigated by different authors. This problem was first investigated in first-order quasiclassical perturbation theory in terms of F and H in 1923 by Épsteĭn,[10] who showed that the problem reduces to the quantization of two independent angular momenta. A similar procedure was used by Demkov, Monozon and Ostrovskiĭ[11] for the construction of a first-order quantum perturbation theory. In Ref. 12 it is shown that the second-order corrections in **F** and **H** can also be obtained in elementary form, and their values are given. These results can be relatively easily obtained in the general case, using in the first order the symmetry group $O(4)$ (Ref. 11), and in the second order the dynamical symmetry group $O(4,2)$ (Ref. 12), of hydrogen. Turbiner[13] has computed the higher-order corrections, but only for the ground state.

In the case of perpendicular fields, the problem is complicated by the fact that the degeneracy is not completely lifted in first-order perturbation theory. As shown in Ref. 12, the spectral problem in this case reduces to the eigenvalue problem for the generalized Lamé equation, a problem which is not analytically solvable. The case of parallel fields is also nontrivial; as shown in Ref. 5, the computation of the spectrum amounts to the solution of trinomial recursion relations (TRR).

In the present paper we compute and analyze the spectrum of the hydrogen atom in perpendicular (Sec. 4) and parallel (Sec. 5) fields. In either case the energy spectrum as a function of the electric field intensity splits up into three qualitatively different region. A natural explanation of this effect is found in a quasiclassical analysis of the TRR to the solution of which the two problems can be reduced. The cause of this splitting of the spectrum lies in the reconstruction of the states when the relation between the electric- and magnetic-field intensities is changed, a reconstruction which occurs as a result of the appearance or disappearance of effective potential barriers. Those aspects of the quasiclassical approximation for the TRR which are necessary for the analysis of both problems and which have hitherto not been discussed in the literature are considered in the third section.

In the calculation we neglect the relativistic correc-

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tions, and assume that perturbation theory is applicable. In the atomic system of units this leads to the following limitations on the field intensity values:

$$10^{-4}\ll Fn^5\ll 1, \quad 10^{-4}\ll Hn^3\ll 1.$$

2. FORMULATION OF THE PROBLEM

For an arbitrary mutual orientation of the fields **F** and **H**, the correction to the energy in first-order perturbation theory has the form[10,11] ($\hbar = m = e = 1$)

$$E_1=\omega_1 n'+\omega_2 n'', \quad n', n''=-j, -j+1, \ldots, j, \quad j=(n-1)/2, \tag{1}$$

where ω_1 and ω_2 are the moduli of the vectors

$$\boldsymbol{\omega}_1=\frac{1}{2c}\mathbf{H}-\frac{3}{2}n\mathbf{F}, \quad \boldsymbol{\omega}_2=\frac{1}{2c}\mathbf{H}+\frac{3}{2}n\mathbf{F},$$

c being the velocity of light. The correct functions $\psi_{nn'n''}$ of the zeroth approximation are eigenfunctions of the operators $I_{1\alpha}$ ($I_{1\alpha}$ is the component of $\mathbf{I}_1$ along $\boldsymbol{\omega}_1$) and $I_{2\alpha}$ ($I_{2\alpha}$ is the component of $\mathbf{I}_2$ along $\boldsymbol{\omega}_2$)[11]:

$$I_{1\alpha}\psi_{nn'n''}=n'\psi_{nn'n''}, \quad I_{2\alpha}\psi_{nn'n''}=n''\psi_{nn'n''}.$$

The operators $\mathbf{I}_1$ and $\mathbf{I}_2$ are given in terms of the angular-momentum operator **L** and the Runge-Lenz vector **A** by the relations

$$\mathbf{I}_1=(\mathbf{L}+\mathbf{A})/2, \quad \mathbf{I}_2=(\mathbf{L}-\mathbf{A})/2.$$

The spectrum described by the expression (1) has an extremely simple form, and is a superposition of two equidistant spectra with frequencies ω_1 and ω_2, and second-order perturbation theory only gives corrections to it, with the exception of the case of commensurable frequencies.

In the case of perpendicular fields ($\omega_1=\omega_2=\omega$) the first-order correction (1) depends only on the sum $q=n'+n''$ of the quantum number n' and n'', and the degeneracy is not completely lifted. The problem of the lifting of the residual degeneracy in second-order perturbation theory is investigated in Ref. 12, where it is shown that the problem of finding the energy spectrum, like the problem of the quadratic Zeeman effect,[3] is solved through the separation of the variables in elliptic cylindrical coordinates on a sphere in four-dimensional momentum space. Introducing the notation $\gamma=3ncF/H$ ($0\leqslant\gamma<\infty$) for the parameter characterizing the relative strengths of the electric and magnetic fields, we can write the expression obtained in Ref. 12 for the energy in second-order perturbation theory in the form

$$E=E_0+E_1+\frac{n^4F^2}{16}\left[3q^2-17n^2-19-\frac{6}{1+\gamma^2}(n^2-3q^2-1)\right] +\frac{n^2H^2}{16c^2}(3n^2+1-q^2+\varepsilon). \tag{2}$$

Here ε is the eigenvalue of the operator

$$\hat{h}=b(I_{1\alpha}-I_{2\alpha})^2-16I_{1\beta}I_{2\beta}, \tag{3}$$

in which

$$b=\gamma^2-1-2/(1+\gamma^2), \quad -3\leqslant b<\infty, \tag{4}$$

and $I_{i\beta}$ ($i=1,2$) is the component of the operator $\mathbf{I}_i$ in the direction perpendicular to the vector $\boldsymbol{\omega}_i$, and lying in the (ω_1,ω_2) plane. The eigenvalues of the operator $\hat{h}$ can be computed by either separating the variables in elliptic cylindrical coordinates,[12] or constructing for this operator a secular equation in the basis of hydrogen functions with fixed values of n and q. In the basis of the functions $\psi_{nn'nn''}$ with a fixed index sum $n'+n''=q$ and varying difference $n'-n''=k$, the matrix of the operator $\hat{h}$ is tridiagonal. Below, for uniformity with the case of parallel fields, we use the second method. In this case the problem of finding the eigenvalues and the vectors of the operator $\hat{h}$ reduces to the solution of the TRR

$$\{[(n-q)^2-(k-1)^2][(n+q)^2-(k-1)^2]\}^{1/2}C_{k-2}+(bk^2-\varepsilon)C_k +\{[(n-q)^2-(k+1)^2][(n+q)^2-(k+1)^2]\}^{1/2}C_{k+2}=0, \tag{5}$$

where the C_k are the coefficients in the expansion of the correct zeroth-order functions in terms of the basis functions. Depending on the parity of the number $n-q-1$, the index k assumes either even or odd values.

In the case of parallel fields the angular-momentum component $L_z=m$ is an exact integral of the motion (the fields are oriented along the z axis); therefore, the role of the linear-Zeeman-effect-related interaction HL_z amounts to a trivial correction to the energy, and the character of the spectrum is determined by the relation between the diamagnetic interaction and the interaction with the electric field. We shall use the notation

$$\beta\equiv 12c^2F/5n^2H^2, \quad 0\leqslant\beta<\infty \tag{6}$$

for the parameter determining the relative strengths of these interactions. In the basis of the hydrogen wave functions $\psi_{nn_1n_2}$ in the parabolic system of coordinates, the energy correction calculation in which the sum $n_1+n_2=n-m-1$ is fixed and the difference $n_1-n_2=k$ is varied also reduces, as shown in Ref. 5, to the solution of the TRR

$$\{[(n-m)^2-(k-1)^2][(n+m)^2-(k-1)^2]\}^{1/2}C_{k-2} +(3n^2+1-m^2-3k^2+10n\beta k-\varepsilon)C_k +\{[(n-m)^2-(k+1)^2][(n+m)^2-(k+1)^2]\}^{1/2}C_{k+2}=0. \tag{7}$$

The index k here also assumes either only even, or only odd, values. The energy can be expressed in terms of the eigenvalues ε of the TRR (7) as follows:

$$E=E_0+\frac{1}{2c}Hm+\frac{H^2n^2}{16c^2}\varepsilon. \tag{8}$$

We investigate below the solutions to the TRR (5) and (7) for the case in which the principal quantum number n is large.

3. POTENTIAL CURVES OF THE TRINOMIAL RECURSION RELATIONS

For large n in Eqs. (5) and (7) the coefficients of the unknown C_k are slowly varying functions of the index k. This enables us to use in the analysis of the solutions to the TRR the discrete analog, worked out in Refs. 5, 14–19, of the WKB method. Within the framework of this method, one of the present authors (P.A.)[17] introduced the concept, which plays a major role in the discussion below, of potential curves of the TRR. In the present section we give the necessary

information about the properties of the potential curves of TRR, and investigate the typical features of these curves.

Let us consider the Hermitian TRR

$$p_k C_{k-2}+(w_k-E)C_k+p_{k+2}C_{k+2}=0, \tag{9}$$

where p_k and w_k are slowly varying functions of k that are defined for nonintegral values of k as well, and $p_k>0$. Its potential curves are the plots of[17]

$$U_k^{\pm}=w_k\pm 2p_{k+1}, \tag{10}$$

as functions of k. These functions determine the fundamental properties of the spectrum of the TRR (9). Their role is most easily elucidated by investigating the classical mechanics problem corresponding to this TRR, and obtained in the limit $\hbar\to 0$. It is not difficult to show that this passage to the limit leads to a classical system with one degree of freedom, whose Hamiltonian has the form[5,19,20]

$$H(\xi,\vartheta)=W(\xi)+2P(\xi)\cos 2\vartheta. \tag{11}$$

Here ξ is the classical coordinate connected with the discrete quantum variable k by the relation $\xi=\hbar k$; ϑ is the classical momentum; W and P are connected with the coefficients of the TRR (9) by the relations

$$w_k=W(\hbar k),\quad p_{k+1}=P(\hbar k).$$

The variable ξ has different physical meanings in different problems. For example, in the TRR (7) the index k is the eigenvalue of the operator z, the component of the Runge-Lenz vector **A**; accordingly, ξ coincides with the classical quantity A_z. A Hamiltonian of the form (11) plays an important role in classical mechanics (it appears in the construction of the equations of motion in perturbation theory in the action-angle variables[21]). The canonical equations corresponding to the function (11) are easily integrated; their first integral can be written in the form[5,19]

$$d\xi/dt=2\{[U^+(\xi)-E][E-U^-(\xi)]\}^{1/2}, \tag{12}$$

where $U^{\pm}(\xi)=U_k^{\pm}$. In atomic units $\xi=k$ and $U^{\pm}(k)=U_k^{\pm}$.

In contrast to the usual equation

$$dx/dt=\{2m^{-1}[E-U(x)]\}^{1/2},$$

Eq. (12) contains two functions having the meaning of potential energy. This deviation from the standard form is due to the nonquadratic dependence of the energy on the momentum ϑ. Nevertheless, Eq. (12) allows us to analyze qualitatively the character of the motion of the system. In particular, from the requirement that the radicand be positive it follows that the classically admissible values of ξ are those values for which the following inequalities are simultaneously satisfied:

$$U^+(\xi)>E,\quad U^-(\xi)<E. \tag{13}$$

The boundaries of the classically admissible region (the turning points) are determined by the points of intersection of the curves $U^+(\xi)$ and $U^-(\xi)$ with the lines of constant energy E. An important consequence of the inequalities (13) is the fact that the energy of a system with a Hamiltonian of the form (11) is bounded not only from below, but also from above:

$$E\geqslant \min U^-(\xi),\quad E\leqslant \max U^+(\xi). \tag{14}$$

In the quantum formulation of the problem, the inequalities (14) determine the precise limits of the spectrum.[17,18] In the quasiclassical approximation the solution $\{C_k\}$ differs significantly from zero at values of the index k lying within the classically admissible region, and attenuate exponentially outside this region. The eigenvalues of the TRR can be found from the quantization rules, the analogue of the Bohr-Sommerfeld formula[17] [see the formula (A3) in the Appendix].

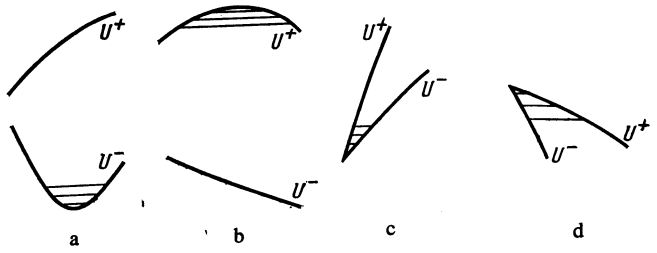

FIG. 1. Potential-curve configurations leading to the appearance of oscillator level series in the spectrum.

The dynamics of the systems described by Eq. (12) is quite unique. We shall describe the properties of its solutions corresponding to some typical configurations of the potential curves. Below, δ denotes a small positive number.

1. Let the function $U^-(\xi)$ have a minimum at some $\xi=\xi_0$ (Fig. 1a). Then for $E=U^-(\xi_0)+\delta$ the solution to Eq. (12) will be a harmonic oscillation about ξ_0 with frequency

$$\Omega=[2(U^-)''(U^+-U^-)]^{1/2}|_{\xi=\xi_0}. \tag{15}$$

2. Let $U^+(\xi)$ have a maximum at $\xi=\xi_0$ (Fig. 1b). Then for $E=U^+(\xi_0)-\delta$ the solution to (12) will also be a harmonic oscillation about ξ_0 with frequency

$$\Omega=[2(-U^+)''(U^+-U^-)]^{1/2}|_{\xi=\xi_0}. \tag{16}$$

3. Let the potential curves intersect at the point ξ_0: $U^+(\xi_0)=U^-(\xi_0)\equiv U_0$, with $(U^+)'(U^-)'>0$ at the point of intersection. Then for $E=U_0+\delta$ [if $(U^+)'>(U^-)'>0$; see Fig. 1c] or $E=U_0-\delta$ [if $(U^-)'<(U^+)'<0$; see Fig. 1d] the solution to Eq. (12) will be a harmonic oscillation with frequency

$$\Omega=2[(U^+)'(U^-)']^{1/2}, \tag{17}$$

between the turning points.

In the quantum problem there corresponds to all the enumerated cases a roughly equidistant spectrum with a level spacing equal to $\hbar\Omega$. Let us point out that in the cases 2 and 3 [for $(U^-)'<(U^+)'<0$] the equidistant series abuts on the upper limit of the energy spectrum, i.e., the oscillator spectrum is "inverted" in comparison with the normal situation.

4. If the function U^- has a maximum at $\xi=\xi_0$, then the period of the motion tends to infinity as $E\to U^-(\xi_0)$: the particle "gets stuck" in the region $\xi\approx\xi_0$ (Fig. 2a). The same sticking occurs when U^+ has a minimum at $\xi=\xi_0$ (Fig. 2b) and $E\to U^+(\xi_0)$. Thus, the maximum of U^- and the minimum of U^+ are potential-barrier analogues.

5. The motion has a special character if the potential curves intersect at $\xi=\xi_0$, but the derivatives at the point of intersection have different signs (Fig. 3). Then as $E\to U^+(\xi_0)=U^-(\xi_0)$ the period tends to infinity as a result of the sticking of the point in the vicinity of ξ_0. This situation

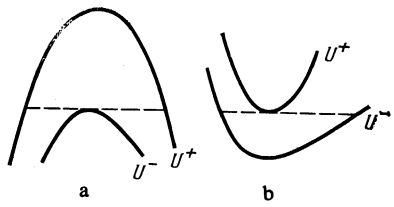

FIG. 2. Types of effective potential barriers in a TRR: a) barrier; b) "inverted" barrier.

is reminiscent of the behavior of a particle in the vicinity of the top of a potential barrier, with the difference that we do not have here two separated, classically admissible regions. We shall call such a singularity of the potential curves a quasibarrier; the point of intersection of the potential curves is called the top of the quasibarrier.

The boundedness of the spectrum from above, and the appearance of inverted oscillator level series are a consequence of the nonquadratic dependence of the Hamiltonian on the momentum ϑ. A similar situation occurs in solid-state theory, where the nonquadratic dependence of the Hamiltonian on the quasimomentum (an analog of which is ϑ) leads to the appearance of hole levels.

4. THE HYDROGEN ATOM IN MUTUALLY PERPENDICULAR ELECTRIC AND MAGNETIC FIELDS

We shall consider the main properties of the spectrum of the problem for the particular case in which $q = 0$; the characteristics that arise as a result of the deviation of q from zero are discussed at the end of the section.

For $q = 0$ the potential functions of the TRR (5) have the form

$$U_k^+ = 2n^2 + (b-2)k^2, \quad U_k^- = -2n^2 + (b+2)k^2. \tag{18}$$

As the parameter γ characterizing the relative strengths of the electric and magnetic fields increases, the coefficient b increases monotonically from -3 ($F = 0$) to $+\infty$ ($H = 0$). The values $\gamma_1 = (\sqrt{2}-1)^{1/2} \approx 0.64$ and $\gamma_2 = (\sqrt{6}+1)^{1/2} \approx 1.85$ then turn out to be the preferred values. It is not difficult to verify that $b(\gamma_1) = -2$ and $b(\gamma_2) = 2$, so that the functions U_k^- and U_k^+ are constants at the points γ_1 and γ_2 respectively. We divide the whole range of γ values into three regions: $0 \leqslant \gamma \leqslant \gamma_1$, $\gamma_1 \leqslant \gamma \leqslant \gamma_2$, $\gamma_2 \leqslant \gamma \leqslant \infty$. As will be shown below, a reconstruction of the spectrum of the problem occurs at the points γ_1 and γ_2. The values γ_1 and γ_2 are again distinguished by the fact that in these cases the problem admits of an exact analytical solution.

We shall not write out the explicit form of the quantization rules, which is obtained through a trivial substitution of the functions (18) into the formula (A3) in the Appendix (the integral in the quantization rule then becomes a complete elliptic integral). Instead, we shall limit ourselves to a qualitative investigation of the spectrum; we shall also give explicit approximate formulas for the lower and upper levels in a multiplet of states with fixed n and q. To illustrate the relationships discussed below, we present in Fig. 4 the results of a numerical computation of the eigenvalues of the TRR (5) for $n = 10$ and $q = 0$.

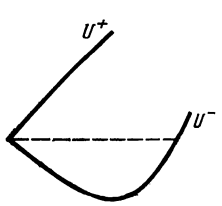

FIG. 3. Quasibarrier.

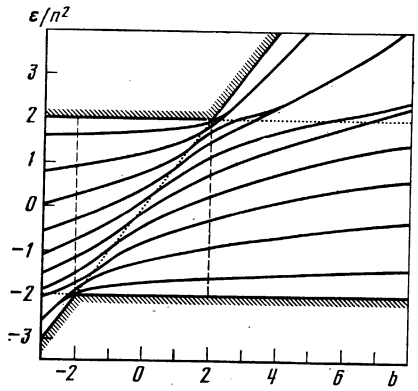

FIG. 4. The eigenvalues ε for the case of perpendicular fields ($n = 10$, $q = 0$). The hatching indicates the spectral boundaries that follow from the inequalities (14). The dots indicate the position of the barrier in the interval $-3 < b < -2$, the inverted barrier in the region $b > 2$, and the quasibarrier in the interval $-2 < b < 2$.

a) $0 \leqslant \gamma \leqslant \gamma_1$. In this range of γ values the spectrum is qualitatively similar to the case of the purely diamagnetic splitting ($\gamma = 0$). Since here $-3 \leqslant b \leqslant -2$, the potential curves are parabolas that are open underneath (Fig. 5a). The limits of the energy spectrum are given by the inequalities

$$\min U_k^- = bn^2 \leqslant \varepsilon \leqslant \max U_k^+ = 2n^2.$$

The nature of the spectrum in this region is determined by the potential barrier (the maximum of the function U_k^-) present. The presence of the barrier leads to the splitting of the energy spectrum into two regions: the region below and the region above the top of the barrier $\max U_k^- = -2n^2$. There exist two symmetric classically admissible regions of motion for $bn^2 < \varepsilon < -2n^2$ and one such region for $-2n^2 < \varepsilon < 2n^2$.

In the region $bn^2 < \varepsilon < -2n^2$ the spectrum in the WKB approximation is twofold degenerate, with the lower levels given by the approximate expression ($N = 0,1,2,\ldots$)

$$\varepsilon_N \approx bn^2 + (N+{}^1/_2)4n(b^2-4)^{1/2} + (N+{}^1/_2)^2 4b. \tag{19}$$

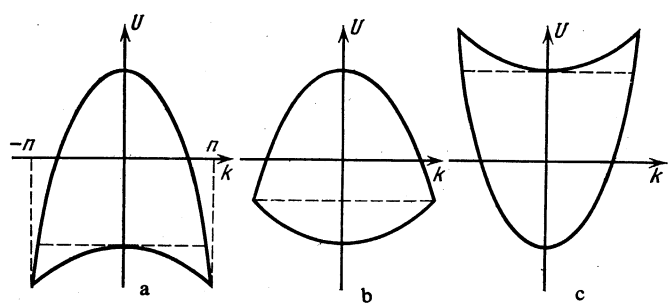

FIG. 5. The potential curves of the TRR (5): a) for $-3 < b < -2$, b) for $-2 < b < 2$, and c) for $b > 2$.

The coefficient attached to $N+1/2$ coincides with the frequency of the classical harmonic oscillations [see the formula (17) in the case 3 in the preceding section]; the term quadratic in $N+1/2$, which takes account of the anharmonicity, can be obtained from the formulas of Ref. 19. The degenerate levels split up when allowance is made for the tunneling. For large n the magnitude of the splitting is exponentially small, and can be computed in the same way as is done in zero electric field.[5]

The energy levels in the region $[-2n^2, 2n^2]$ lie above the top of the barrier, and are nondegenerate. The upper levels form an approximately equidistant series described by the formula ($N' = 0,1,2,...$)

$$\varepsilon_{N'} \approx 2n^2 - (N'+{}^1/_2)4n(2-b)^{1/2} - (N'+{}^1/_2)^2({}^1/_2 b - 3). \quad (20)$$

Let us emphasize that the quantum number N' numbers the energy levels, starting from the top level.

The ratio of the number of lower (doublet) levels to the number of upper (singlet) levels depends on γ. As γ increases, the number of singlet states increases [according to the quantization rule (A3), it is equal to $(2n/\pi)\arcsin(2/(2-b)^{1/2})$]. The increase of the number of singlet levels occurs as a result of the fact that the lower twofold degenerate levels intersect in turn the top of the barrier, splitting up and producing in the process two roughly equidistant levels of the upper group. This situation is illustrated in Fig. 4, in which the dotted line indicates the position of the top of the potential barrier. At $\gamma = \gamma_1$ the barrier disappears, which leads to the disappearance of the twofold degenerate levels.

b) $\gamma_1 \leqslant \gamma \leqslant \gamma_2$. In this region $-2 \leqslant b \leqslant 2$. The potential curves circumscribe in the (U, k) plane a convex figure (Fig. 5b), and the spectrum of the TRR lies in the interval

$$\min U_k^- = -2n^2 \leqslant \varepsilon \leqslant \max U_k^+ = 2n^2.$$

In contrast to the case a), here there is no potential barrier and no doublet levels occur. On the other hand, there is in this region of γ a singularity, called a quasibarrier in Sec. 3 (case 5). In Fig. 4 the position of the top of the quasibarrier (actually, of two quasibarriers—left and right) is indicated by the dots. As can be seen from the figure, it is the locus of the points of inflection for the eigenvalues. This is explained by the fact that at energies close to the top of the quasibarrier, the system gets stuck in the quasibarriers at $k \approx \pm n$ (see Sec. 3), and the mean value of the quantity k^2 attains its maximum. Using the Gell-Mann-Feynman theorem for the eigenvalues of the operator $\hat{h}$ ($\partial\varepsilon/\partial b = \overline{k^2}$), we find that at the moment of intersection of the quasibarrier $\partial^2\varepsilon/\partial^2 b = 0$, which corresponds to a point of inflection. Here, as in the case a), we can obtain an approximate expression for the lower levels ($N = 0,1,2,...$)

$$\varepsilon_N \approx -2n^2 + (N+{}^1/_2)4n(b+2)^{1/2} - (N+{}^1/_2)^2({}^1/_2 b + 3). \quad (21)$$

For the upper levels the approximation (20) remains valid.

c) $\gamma > \gamma_2$. This region corresponds to weak magnetic and relatively strong electric fields. The potential curves are parabolas that are open at the top (Fig. 5c), and the eigenvalue spectrum lies in the interval

$$\min U_k^- = -2n^2 \leqslant \varepsilon \leqslant \max U_k^+ = bn^2.$$

As in the case a), this interval splits up into two. For

$$-2n^2 \leqslant \varepsilon \leqslant \min U_k^+ = 2n^2$$

we have a single classically admissible region; accordingly, the spectrum of the problem is nondegenerate in this region, and the lower levels are given by the approximate formula (21). For $2n^2 \leqslant \varepsilon \leqslant bn^2$ there exist two symmetric classically allowed regions separated by an inverted potential barrier (see Sec. 3 and Fig. 2b). As a result, the energy levels in the WKB approximation turn out to be twofold degenerate. For the upper levels we can derive the approximate expression ($N' = 0,1,2,...$)

$$\varepsilon_{N'} \approx bn^2 - (N'+{}^1/_2)4n(b^2-4)^{1/2} + (N'+{}^1/_2)^2 4b. \quad (22)$$

The upper energy levels split up when the tunneling is taken into account. An unusual situation arises here: because of the fact that the barrier in this case is inverted, the splitting of the doublet levels increases as the energy decreases. The possibility of such behavior of the level splitting has, as far as we know, not been discussed in the literature.

It follows from the quantization rule (A3) that the number of lower singlet levels is equal to $(2n/\pi)\arcsin[2/(2+b)^{1/2}]$, and decreases as γ increases. Thus, we have in this case a pattern that is the inverse of the one found in the case a): as γ increases, the levels of the lower group go up to the vertex of the inverted barrier in pairs, and, merging, form a doublet level belonging to the upper group. The vertex of the barrier is the boundary at which the twofold degenerate levels are formed. This can be clearly seen in Fig. 4, in which the position of the barrier vertex is indicated by dots.

In the limit as $\gamma \to \infty$, we go over to the purely Stark splitting; the lower group of nondegenerate levels disappears, and we have strictly twofold degeneracy. The formula (22) with allowance for the relation (2) leads in the limit to the exact result for the quadratic Stark effect.

For $q \neq 0$ the potential functions of the TRR (5) have the more complicated form

$$U_k^{\pm} = bk^2 \pm 2\{[(n+q)^2-k^2]\,[n-q)^2-k^2]\}^{1/2}. \quad (23)$$

As in the $q = 0$ case, we can distinguish three regions of values of the parameter b in which the spectrum has different characters. Let us introduce the notation

$$\mu = 2(n^2+q^2)/(n^2-q^2).$$

Then for $-3 < b < -\mu$ the lower levels will be roughly twofold degenerate; for $-\mu < b < \mu$ all the levels will be nondegenerate; and for $b > \mu$ the upper levels turn out to be roughly twofold degenerate. As q increases, the intervals where some of the levels have the doublet structure shorten. When $q > n/\sqrt{5}$ the interval in which the lower levels are degenerate disappears.

It is not difficult to verify that Eq. (5) is invariant under the substitution $b \to -b$, $C_k \to (-1)^{k/2} C_k$, and $\varepsilon \to -\varepsilon$. There follows from this the symmetry property (t is the eigenvalue number and $p = n - q$ is the number of energy levels with given n and q)

$$\varepsilon_t(b) = -\varepsilon_{p-t}(-b), \quad (24)$$

i.e., the level pattern is symmetric about the point $\varepsilon = 0$, $b = 0$ (see Fig. 4).

In the border cases $\gamma = \gamma_1$ and $\gamma = \gamma_2$ ($b = \pm 2$) we can

derive exact expressions for the energy levels and the wave functions. To do this we must take account of the following circumstance, which is pointed out in Ref. 12. In the operator (3) the components of the operators $\mathbf{I}_2$ and $\mathbf{I}_1$ are taken in different coordinate systems, but since they commute with each other, the eigenvalues of the operators $Q = I_{1\alpha} + I_{2\alpha}$ and $\hat{h}$ are as they would be if the components were computed in one and the same coordinate system. The operator Q is, in this sense, equivalent to the operator L_z, while the nontrivial part of the operator $\hat{h}$ for $\gamma = \gamma_1$ is equivalent to L^2. The exact eigenvalues ε in this case are equal to $(L = 0,1,\ldots, n-q-1)$

$$\varepsilon = 2[2L(L+1) - q^2 - n^2 + 1]. \tag{25}$$

For $\gamma = \gamma_2$ $(b = 2)$ the eigenvalues ε are obtained from (25) with the aid of the symmetry property (24). The case $b = 2$ differs from the $b = -2$ case by the fact that the quantum number L numbers the levels not from the bottom up, but from the top down.

5. PARALLEL ELECTRIC AND MAGNETIC FIELDS

Let us begin the analysis with the case when the magnetic quantum number m is equal to zero. Then the potential functions of the TRR (7) have the form

$$U_k^{\pm} = 3n^2 - 3k^2 \pm 2(n^2 - k^2) + 10n\beta k. \tag{26}$$

The parameter $\beta = 12c^2F/5n^2H^2$ characterizes the relative electric- and magnetic-field strengths. The value $\beta = 0$ corresponds to the case of purely diamagnetic splitting. In this case, because of the presence in the k representation of two symmetric potential wells, the lower levels are roughly twofold degenerate, and the eigenfunctions possess definite parity.[5] The application of an electric field breaks the symmetry of the potential curves. As a result, even in very weak electric fields (whose contributions to the energy are comparable to the exponentially small—in n—tunneling splitting of the doublets), the doublet states possessing definite parity are replaced by a pair of states, one localized in the left and the other in the right potential well. Therefore, for the lower levels the linear Stark effect occurs even in fields of exponentially small—in n—intensities.

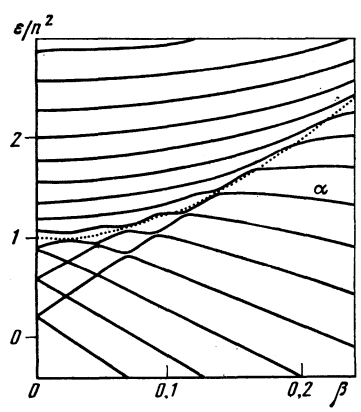

FIG. 6. The eigenvalues ε in the case of parallel fields for the lowest fifteen energy levels with $n = 20$ and $m = 0$. The dots indicate the position of the top of the barrier that becomes a quasibarrier when $\beta > 0.2$.

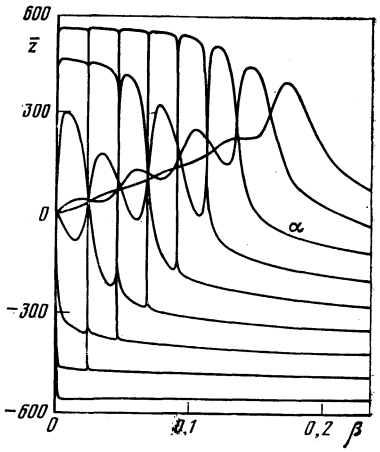

FIG. 7. The mean value of the z coordinate of the electron in the case of parallel fields for the lowest nine energy levels with $n = 20$ and $m = 0$.

For the upper levels that are nondegenerate when $\beta = 0$ the quadratic Stark effect occurs at small β values; as β increases, the electric-field dependence of the energy of these levels also becomes linear.

The results of this section are illustrated with a numerical computation of the eigenvalues of the TRR (7) as functions of β for $n = 20$, $m = 0$ (see Fig. 6). The mean value of the electron's z coordinate was computed at the same time as functions of β in the stationary states of the system (Fig. 7); this quantity coincides to within algebraic sign with the dipole moment $\bar{d}_z$ of the perturbed atom.

We should, depending on the relative field strengths, distinguish three cases[5]: $0 < \beta < 1/5$, $1/5 < \beta < 1$, and $\beta > 1$.

a) For $0 < \beta < 1/5$ there exists a potential barrier formed by the maximum of the function U_k^- (Fig. 8a). Accordingly, we can distinguish three groups of levels (I, II, III), to which correspond the states localized in the regions I, II, and III in Fig. 8a.

The first group of levels is located in the energy interval

$$\min U_k^- = -10n^2\beta < \varepsilon < \max U_k^- = n^2(1 + 25\beta^2). \tag{27}$$

The states of this group are localized in k space to the left of the potential barrier, mostly in the region of negative k. Since the TRR (7) was derived in a parabolic basis, with

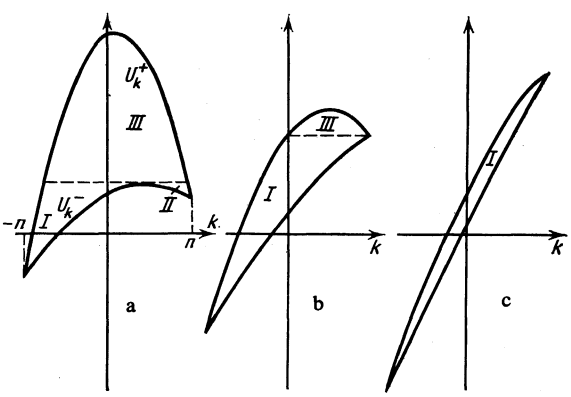

FIG. 8. The potential curves of the TRR (7): a) for $0 < \beta < 1/5$, b) for $1/5 < \beta < 1$, and c) for $\beta > 1$.

$k = n_1 - n_2$, the group-I states have a positive dipole moment. On the eigenvalue curve, to these states correspond the levels that slope downwards as β increases, and lie below the potential-barrier top (the position of which is indicated by dots in Fig. 6).

The lower levels of group I are given by the approximate formula ($N = 0,1,...$)

$$\varepsilon_N \approx -10n^2\beta + (N+1/2)\,4\sqrt{5}\,n[(1+\beta)(1+5\beta)]^{1/2} - 12(N+1/2)^2\left[1 - \frac{2\beta}{(1+\beta)(1+5\beta)}\right]. \quad (28)$$

The coefficient attached to $N + \frac{1}{2}$ coincides with the classical harmonic frequency[1] (17). The dipole moment of the lower states is close to the highest possible value of $3/2n(n-1)$, and is almost field-independent even for very small β values (see Fig. 7, in which the lower lines, which are almost parallel to the abscissa axis, correspond to these states). This evidently corresponds to the linear Stark effect.

The second group of levels lies in the energy region

$$U_n^- = 10n^2\beta < \varepsilon < \max U_k^-.$$

The states of this group are localized in k space to the right of the potential barrier, which corresponds to a negative dipole moment. In Fig. 6 the levels of this group lie below the vertex of the potential barrier, and slope upwards; in the $\bar{z}$ curve (Fig. 7) they correspond to the upper lines that are almost parallel to the abscissa axis. The formula for the lower levels of group II are given by (28) with β replaced by $-\beta$.

The third group of energy levels lies above the potential barrier in the interval

$$\max U_k^- < \varepsilon < \max U_k^+ = 5n^2(1+\beta^2).$$

Here we have the only classically admissible region, which, for small β, is almost symmetric about the point $k = 0$; this indicates that the group-III states have a relatively small dipole moment. For $\beta = 0$ these levels are nondegenerate, so that the quadratic Stark effect obtains in their case.

The upper group-III levels are approximately equidistant, and are given by the formula ($N' = 0,1,2,...$)

$$\varepsilon_{N'} \approx 5n^2(1+\beta^2) - \left(N' + \frac{1}{2}\right)4\sqrt{5}\,n(1-\beta^2)^{1/2} + \left(N' + \frac{1}{2}\right)^2\left(\frac{9}{2} + \frac{6\beta^2}{1-\beta^2}\right). \quad (29)$$

We can, using (29) and (8) and the relation $\bar{d}_z = -\partial E/\partial F$, find the dipole moment of the upper states. In this case the dipole moment turns out to be proportional to F, which corresponds to the quadratic Stark effect. For the highest state, which is localized in the vicinity of the maximum of the U_k^+ curve with $k = k_0^+ = n\beta$, the dipole moment can be estimated directly from the relation

$$\bar{d}_z = -\frac{3}{2}n\bar{k} \approx -\frac{3}{2}nk_0^+ = -\frac{18}{5}\frac{c^2F}{H^2}.$$

The relative number of levels in each group depends on the electric-field strength. For $\beta = 0$ we have

$$(2n/\pi)\arcsin(2/\sqrt{5}) \approx 0{,}7n$$

levels in group III and $0.15n$ doublet levels. Following the switching on of the electric field, each doubly degenerate level produces one group-I level and one group-II level. As the field intensity increases, the number of group-I levels increases, while the numbers of group-II and group-III levels decrease. Using the quantization rule (A3), we can show that

$$N_{III}^{tot} = \frac{2n}{\pi}\left[\arcsin\frac{2}{[5(1-5\beta^2)]^{1/2}} - \sqrt{5}\,\beta\arcsin\frac{2\sqrt{5}\,\beta}{(1-5\beta^2)^{1/2}}\right], \quad (30)$$

$$N_I^{tot} = \frac{n}{2} + \frac{n\sqrt{5}}{2}\beta - \frac{1}{2}N_{III}^{tot},$$

$$N_{II}^{tot} = \frac{n}{2} - \frac{n\sqrt{5}}{2}\beta - \frac{1}{2}N_{III}^{tot},$$

where N_I^{tot}, N_{II}^{tot}, and N_{III}^{tot} are the numbers of levels in groups I, II, and III.

It follows from the formulas (30) that, as the electric-field intensity increases, there occurs

1) an "overflow" of states from group II into group I at a constant—in β—rate of $n\sqrt{5}/2$;

2) an "outflow" of states from group III into groups I and II at equal rates. This effect is noticeable only when β is close to 1/5.

As can be seen from Fig. 6, the transformation of group-II states into group-I states is realized in the vicinity of the vertex of the potential barrier. A group-II level sloping upwards undergoes here a quasicrossing with a lower group-III level, being "reflected" from it. After this the dipole moment of the group-II state changes sign, and the term begins to slope downwards, which is a result of the transformation of the level into a group-I level. Successive reflections from a lower group-III level of levels that go from the right well into the left well leads to a situation in which this level behaves nonmonotonically, and its dipole moment oscillates sharply (the curve α in Figs. 6 and 7).

Figure 6 shows, besides the above-mentioned quasicrossings, numerous narrow quasicrossings of the group-I and group-II levels. They are similar to the well-studied quasicrossings in the problem with two nonsymmetric potential wells when the parameters of the Hamiltonian are varied.[2] In the quasicrossing region the wave functions of the pair of states go over into each other. This is accompanied by a practically abrupt exchange of dipole-moment values between these states (the vertical lines in Fig. 7).

The locations of the quasicrossing points of the group-I and group-II levels can be found analytically with the aid of the formulas of the discrete WKB method. Let us consider the difference $N_I - N_{II}$ (where N_I and N_{II} are the quantum numbers of the levels participating in a given quasicrossing). Let us express the N_I and N_{II} in this difference in terms of the integrals of the quantization rules (A3). Then this difference can be computed analytically in terms of the residue of the integrand at infinity. As a result, we obtain the quasicrossing condition

$$\sqrt{5}\beta n = N_{II} - N_I = \Delta N, \quad (31)$$

where ΔN is a whole number. It is remarkable that all the group-II levels undergo, according to (31), quasicrossing at the same time.[3]

b) The region $1/5 < \beta < 1$. For $\beta > 1/5$, there is no potential barrier, and there is a single classically admissible region at all energies. In this case, however, there exists a singularity, called in Sec. 3 a quasibarrier [the intersection of the potential curves U_k^+ and U_k^- in the case when the derivatives $(U_k^+)'$ and $(U_k^-)'$ have different signs at the intersection point $k = n$]; see the plot in Fig. 8b. The position of the top of the quasibarrier for $\beta > 1/5$ is indicated in Fig. 6 by dots (when $\beta = 1/5$, the potential barrier undergoes a continuous transformation into a quasibarrier).

Of the three groups of levels that occur when $\beta < 1/5$, only group I (the lower levels lying below the quasibarrier) remain here; the group III (the upper levels lying above the quasibarrier) remain here; the group II disappears. As the electric-field intensity is increased, the levels go over one by one from the upper into the lower group. During the crossing of the quasibarrier, the dipole moment of the states attains its minimum value (correspondingly, the quantity $\bar{z}$ has its maximum value). From the classical standpoint this is explained by the fact that the system gets stuck for a long time in the vicinity of the quasibarrier at $k \approx n$ (i.e., at the maximum value of the Runge-Lenz-vector z component that determines the dipole moment of the state). It follows from the minimality of $\bar{d}_z$ that the quasibarrier is the locus of the points of inflection of the energy levels, since here

$$\partial^2 E/\partial F^2 = -\partial \bar{d}_z/\partial F = 0.$$

For the upper and lower levels we respectively have as before the approximate formulas (29) and (28).

c) The region $\beta > 1$. In this case the diamagnetic interaction can be considered to be weak in comparison with the interaction with the electric field. Both of the potential curves are monotonic (Fig. 8c), and there is no quasibarrier. Consequently, there are no group-III levels; the energy levels and the dipole moment of the stationary states vary monotonically as β increases, and tend, as $\beta \to \infty$, to values corresponding to the linear Stark effect. The lower levels are given by the formula (28); the upper levels, by the formula ($N' = 0,1,...$)

$$\varepsilon_{N'} \approx 10n^2\beta - \left(N' + \frac{1}{2}\right) 4\sqrt{5}\, n[(\beta-1)(5\beta-1)]^{1/2} - 12\left(N' + \frac{1}{2}\right)^2 \left[1 + \frac{2\beta}{(\beta-1)(5\beta-1)}\right]. \quad (32)$$

As $\beta \to \infty$ (i.e., as $H \to 0$), the formulas (28) and (32) with allowance for the relation (8) go over into the same expression for the linear Stark splitting, an expression which coincides with the exact formula.

For $m \neq 0$ the behavior of the levels is qualitatively similar to the behavior investigated above. It should only be emphasized that, for $m > n/\sqrt{5}$, the second group of levels does not occur at all values of β; as a result, only the quadratic Stark effect is observed in weak electric fields, and none of the quasicrossings given by the formula (31) occurs.

6. CONCLUSION

In the present paper we have investigated practically all the nontrivial situations where allowance must be made for the diamagnetic interaction in the determination of the correct functions of the zeroth approximation. The case of parallel fields considered in the preceding section in fact includes the variant in which the diamagnetic interaction and the interaction with the electric field have the same order of magnitude and the alignment of the fields is arbitrary. In this case only that component of the electric field which is directed along the magnetic field should be taken into consideration. This is due to the fact that there remains, after taking the interaction $\mathbf{H} \cdot \mathbf{L}$ into account, the degeneracy in the subspace of the hydrogen wave functions with a fixed value of m, a subspace in which all the matrix elements of the electric-field component perpendicular to $\mathbf{H}$ are equal to zero.

Let us point out two mathematically equivalent problems in which a special variant of the problem of the hydrogen atom in perpendicular fields arises. In collision theory the effect of an incoming heavy particle on the hydrogen atom reduces in certain cases to the effect of a uniform electric field oriented along the axis joining the heavy particle and the nucleus of the hydrogen atom (the internuclear axis). On going over to the coordinate system rotating with the internuclear axis, there appears, according to the Larmor theorem, an effective magnetic field oriented perpendicularly to the collision plane, but with no diamagnetic interaction occurring. We encounter the same Hamiltonian in the problem of the computation of the quasienergies of the hydrogen atom in the field of a circularly polarized wave.[24] The absence of the diamagnetic interaction gives rise to insignificant changes, and the expression for the energy in terms of the eigenvalues of the operator $\hat{h}$ in this case is derived in Ref. 12. The results obtained in Sec. 4 above are valid for both problems; only the dependence of the parameter b on the field intensities and the range of b values change: $b = 4(1+\gamma^2)$, $4 \leqslant b < \infty$.

The spectra of the Rydberg states in perpendicular fields can be used in astrophysical- and thermonuclear-plasma diagnostics. Here there arises (in the coordinate system fixed to the atom), as a result of the motion of the Rydberg atom in the magnetic field, an electric field perpendicular to $\mathbf{H}$, and proportional to the velocity v of the atom.[25] The presence of the electric field leads to a spectral modification, by interpreting which we can, in principle, determine the velocity v and, after that, the temperature of the plasma. The results of the present paper are especially important in the $q = 0$ case, where the first-order correction obtained in Refs. 10 and 11 vanish. The detailed analysis of the possibility of using such a diagnostics procedure constitutes a separate problem, and requires the consideration of all the processes leading to the distortion of the spectra (the collisional broadening of the lines, the Doppler effect, etc.) under the specific conditions in question.

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APPENDIX

The solutions to the TRR (9) split up into two classes: in one of them only the elements C_k with even indices k are

nonzero; in the other, only those with odd indices. Let us introduce the number

$$\begin{aligned} \nu &= 1 \quad (\text{ even } k), \\ \nu &= 0 \quad (\text{ odd } k). \end{aligned} \tag{A1}$$

Let us also introduce the following function of the variable k and the energy E:

$$B_k = \frac{E - w_k}{2p_{k+1}} = \frac{2E - U_k^+ - U_k^-}{U_k^+ - U_k^-}. \tag{A2}$$

In this notation the quantization rule found in Ref. 17 for the eigenvalues of the TRR (9) has the form

$$\frac{1}{2}\int_{k_{t_1}}^{k_{t_2}} \frac{(k+\nu)}{(1-B_k^2)^{1/2}} \frac{dB_k}{dk}\, dk = \left(N + \frac{1}{2}\right)\pi. \tag{A3}$$

Here N is an integral quantum number; the integral is taken over the classically admissible region between the turning points k_{t_1} and k_{t_2}, the roots of the equations $e = U_k^+$ or $E = U_k^-$.

According to (A2), $B_k = \pm 1$ at the ends of the integration interval. From this it follows that, in the left member of the formula (A3), the contribution proportional to ν is equal to $\pm \nu\pi/2$ in the case when one turning point lies on the U_k^+ curve and the other lies on the U_k^- one, and zero in the case when both of the turning points lie on one and the same potential curve. Consequently, it is only in the first of these cases that the quantization rules for the solutions with even and odd indices are different.

[1)]The first two terms in (28) coincide with the formula (34) in Ref. 22.
[2)]Such quasicrossings in problems with a discrete independent variable are considered in Refs. 16 and 18.
[3)]Precisely the same situation is observed for the quasienergies of an anharmonic oscillator with a quadratic anharmonicity, excited by an external resonance force (here the quasicrossings occur when the detuning is varied). Apparently, this result has hitherto not been noted, notwithstanding the numerous investigations that have been carried out (see Refs. 16, 17, 20, 21, and 23 and the references cited therein).

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