On the theory of the quadratic Zeeman effect for the highly excited states of the hydrogen atom

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The quadratic Zeeman effect for the hydrogen atom in a highly excited state is investigated with the aid of a discrete analog of the WKB method. This method is applied to a three-term recurrence formula obtained by expanding the zeroth-order wave function in terms of the basis eigenfunctions of the unperturbed Hamiltonian for the hydrogen atom in parabolic coordinates. Approximate analytical expressions are found for the energy levels and the inversion level splitting in the case when the mixing of states from different shells can be neglected.

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The spectrum of the highly-excited Rydberg states of atoms located in a magnetic field exhibits a number of distinctive and incompletely explained features.[1,2] In this connection, Zeeman effect calculations have been performed for the hydrogen atom in states with high principal quantum numbers n.[3–7] The only true integral of the motion (besides the energy) in a homogeneous magnetic field is the angular momentum component m along the direction of the field. This means that atomic levels with the same m cannot be degenerate in any nonzero magnetic field. Numerical computations have, however, shown that:

a) in weak magnetic fields $\mathscr{H}$, when we can neglect the mixing of wave functions from different shells (i.e., when we need consider only the l-mixing regime), some of the levels are grouped in close doublets. The separation between the doublet components tends exponentially rapidly to zero with increasing n. Thus, for $n = 20$, $m = 0$ the separation between the components of the doublet with the lowest energy is approximately 10^7 times smaller than the distance between neighboring doublets;

b) upon further increase of $\mathscr{H}$ (i.e., in the n-mixing regime), the levels derived from neighboring shells undergo quasi-crossing. If n is large, then this quasi-crossing is extremely small, and also tends exponentially to zero as $n \to \infty$.

A qualitative explanation of these results was found in Refs. 8 and 9 by Solov'ev on the basis of an investigation of the motion of a classical particle in the Coulomb and weak magnetic fields. In these papers Solov'ev also derived a quasiclassical quantization rule and classified the states of the hydrogen atom in a magnetic field. He was, however, unable to compute the magnitudes of the exponentially small splittings.

In the present paper we find an approximate analytical expression for the magnitude of the doublet splitting of the Zeeman spectrum of the hydrogen atom under the conditions of l mixing. We also derive an approximate expression for the correct zeroth-order wave function, which is necessary for the computation of the quasi-crossings under the conditions of n mixing. The results are compared with the results obtained in a numerical calculation.

1. RECURRENCE FORMULA FOR THE COEFFICIENTS IN THE WAVE FUNCTION EXPANSION

The nonrelativistic Hamiltonian for the hydrogen atom in a magnetic field has the form

$$H = -{}^1/_2\Delta - 1/r + \omega_L L_z + {}^1/_2\omega_L{}^2 V, \tag{1}$$

where

$$\omega_L = \mathscr{H}/2c, \quad V = x^2 + y^2 \tag{2}$$

[in the expression (1) we neglect the spin and use the atomic system of units: $\hbar = |e| = m_e = 1$]. The operator (1) contains terms of both first and second order in the field. We, however, have $[H, L_z] = 0$, and we can allow for the $\omega_L L_z$ term exactly (this term leads to the trivial effect whereby the levels with magnetic quantum number m get shifted through a distance of $m\omega_L$). Therefore, the perturbation operator is just $\omega_L^2 V/2$, while the perturbation parameter is the square of the magnetic field.

We shall limit the analysis to fields in which we can neglect the mixing of states from different shells, i.e., for which it is sufficient to consider the first order in ω_L^2 in the expression for the energy. To do this, it is, in its turn, sufficient that the quadratic Zeeman splitting (estimates of which are given below) be much smaller than the distance between neighboring shells; for $m = 0$, for example, this leads to the inequality $5n^4\omega_L^2/4 \ll n^{-3}$. In fact, many Zeeman sublevels are well described by the formulas of first-order perturbation theory, and in much stronger fields. This circumstance is directly connected with the nature of the quasicrossings of levels from neighboring shells, and requires special treatment (cf. the analogous situation in the case of the Stark effect for the Rydberg states of the alkali metals[10]).

In order to compute the Zeeman effect to second order in the magnetic field, we must diagonalize the matrix of the operator V in the basis of the unperturbed eigenfunctions belonging to the shell with the given n. We shall use the basis obtained by separating the variables in the parabolic coordinates $\xi = r + z$, $\eta = r - z$, and φ (Ref. 11, §37):

$$\psi_{n_1 n_2 m} = (\sqrt{2}/n^2) f_{n_1 m}(\xi/n) f_{n_2 m}(\eta/n) \exp(im\varphi)/\sqrt{2\pi}, \tag{3}$$

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where

$$f_{n_1 m}(x)=[n_1!/(n_1+|m|)!]^{1/2}L_{n_1}^{m}(x)\exp(-x^2/2)x^{|m|/2}.$$

The quantum numbers n_1 and n_2 are connected with the principal quantum number n and the magnetic quantum number m by the relation

$$n_1+n_2=n-|m|-1\equiv 2a. \tag{4}$$

The wave function in the zeroth-order approximation can be written in the form

$$\Psi=\sum_{n_1=0}^{2a} C_{n_1}\psi_{n_1,2a-n_1,m}. \tag{5}$$

The coefficients C_{n_1} are the elements of the eigenvector of the perturbation-operator matrix

$$V_{n_1 n_1'}=\langle\psi_{n_1,\,2a-n_1,\,m}|x^2+y^2|\psi_{n_1',\,2a-n_1',\,m}\rangle. \tag{6}$$

The matrix elements $V_{n_1 n_1'}$ are easily computed; it turns out that $V_{n_1 n_1'}=0$ when $|n_1-n_1'|\geqslant 2$. Consequently, the equation for the C_{n_1} is a three-term recurrence formula (TRF); it can be written in the form

$$p_{n_1}C_{n_1-1}+(w_{n_1}-\varepsilon)C_{n_1}+p_{n_1+1}C_{n_1+1}=0 \tag{7}$$

($0\leqslant n_1\leqslant 2a$). Here

$$\begin{aligned} w_{n_1}&\equiv(2/n^2)V_{n_1 n_1}=3n^2-m^2+1-12(a-n_1)^2,\\ p_{n_1}&\equiv(2/n^2)V_{n_1,\,n_1-1}\\ &=4[n_1(n_1+|m|)(2a-n_1+1)(2a-n_1+|m|+1)]^{1/2}. \end{aligned} \tag{8}$$

The eigenvalues ε of the TRF (7) are connected with the eigenvalues of the Hamiltonian (1) by the formula

$$E=-(1/2n^2)+\omega_L m+{}^1/_4\omega_L^2 n^2\varepsilon+O(\omega_L^4). \tag{9}$$

Below we shall, for brevity, sometimes call the eigenvalues ε energy levels.

2. THE DISCRETE WKB APPROXIMATION

For large $n-|m|$ and far from the boundaries of the interval $[0,2a]$, the relative change that occurs in the coefficients w_{n_1} and p_{n_1} in the TRF (7) when the subscript n_1 is changed by unity turns out to be small. An approximate solution to the TRF with slowly varying coefficients can be obtained with the aid of a discrete analog of the WKB method.[12-18] Following Refs. 16 and 18, let us set forth some minimum amount of information, necessary for the understanding of the subsequent computations, about this method.

Let us consider the Hermitian TRF

$$p_k C_{k-1}+(w_k-\varepsilon)C_k+p_{k+1}C_{k+1}=0, \tag{10}$$

whose coefficients are slowly varying functions of the subscript k; this implies that they can be represented in the form

$$p_k=P(\lambda k),\quad w_k=W(\lambda k), \tag{11}$$

where λ is a small parameter and $P(x)$ and $W(x)$ are smooth functions of their arguments, with $P(x)>0$. From the condition (11) it follows that the coefficients w_k and p_k are also defined for noninteger k, and that

$$\partial w_k/\partial k=O(\lambda),\quad \partial p_k/\partial k=O(\lambda).$$

Let us go over from the C_k to a new unknown sequence μ_k by setting

$$C_k=\prod_{s=k_0}^{k}\mu_s. \tag{12}$$

Then for the μ_k we obtain the relation

$$p_k+(w_k-\varepsilon)\mu_k+p_{k+1}\mu_k\mu_{k+1}=0. \tag{13}$$

It is well known that the solution to Eq. (13) in the trivial particular case in which the coefficients w_k and p_k do not depend on k can be obtained by setting $\mu_k=\mu_{k+1}=\mu$. Then (13) goes over into a quadratic equation, the two roots of which give two particular solutions of the original TRF (10); a linear combination of these particular solutions will be the general solution to the TRF with constant coefficients.[19] In the case of the TRF with slowly varying coefficients, we can assume that the successive elements μ_k, μ_{k+1}, though not equal, will be close to each other. Setting $\mu_{k+1}\approx\mu_k$ in (13), we arrive at the quadratic equation

$$p_k+(w_k-\varepsilon)\mu_k+p_{k+1}\mu_k^2=0. \tag{14}$$

Let us, taking into account the fact that according to the condition (11)

$$p_k p_{k+1}=p_{k+1/2}^2+O(\lambda^2),$$

write the discriminant of Eq. (14) in the form

$$D_k\approx(U_k^+-\varepsilon)(U_k^--\varepsilon),$$

where the quantities

$$U_k^+\equiv w_k+2p_{k+1/2},\quad U_k^-\equiv w_k-2p_{k+1/2} \tag{15}$$

are functions of the subscript k. The functions $U^{\pm}$ play for the TRF a role similar to that played by the potential energy in the Schrödinger equation, and determine the character of the solutions of the TRF. Thus, if

$$U_k^-<\varepsilon<U_k^+, \tag{16}$$

then $D_k<0$. The roots of the quadratic equation will be purely imaginary and close in absolute value to unity; they can be written in the form

$$\mu_k^{\pm}\approx B_k\pm i(1-B_k^2)^{1/2}=\exp(\pm i\arccos B_k), \tag{17}$$

$$B_k\equiv(\varepsilon-w_k)/2p_{k+1/2}. \tag{18}$$

Substituting (17) into (12), we obtain two particular solutions to the TRF:

$$C_k^{\pm}\sim\exp\Big(\pm i\sum_{s=k_0}^{k}\arccos B_s\Big)\sim\exp\Big(\pm i\int_{k_0}^{k}\arccos B_s ds\Big). \tag{19}$$

The formula (19) is the lowest approximation of the WKB method. Allowance for the next order in λ gives the pre-exponential factor; in this order the real linear combination of the solutions to the TRF can be written in the form[16]

$$C_k=A(-D_k)^{-1/4}\cos\Big(\int_{k_0}^{k}\arccos B_s ds+\vartheta_0\Big) \tag{20}$$

(A and ϑ_0 are arbitrary constants). It is clear that the range of k values over which the inequalities (16) are satisfied is the

analog of the classically allowed region (CAR) in the coordinate representation.

If $\varepsilon > U_k^+$, then the roots of Eq. (14) are real and positive. They can be represented in the form

$$\mu_k^{\pm} \approx B_k \pm (B_k^2-1)^{1/2} = \exp(\pm \operatorname{arch} B_k). \tag{21}$$

The fundamental particular solutions of the TRF with allowance for the pre-exponential factor then have the form

$$C_k^{\pm} = C^{\pm} D_k^{-1/4} \exp\left(\pm \int_{k_0}^{k} \operatorname{arch} B_s ds\right) \tag{22}$$

(the $C^{\pm}$ are arbitrary constants). The solution C_k^+ increases exponentially with increasing k, while the solution C_k^- exponentially decreases. Thus, the condition $\varepsilon > U_k^+$ determines the classically forbidden region.

The solutions of the TRF have a special character if $\varepsilon < U_k^-$. Then the roots of Eq. (14) are real and negative:

$$\mu_k^{\pm} \approx B_k \pm (B_k^2-1)^{1/2} = -\exp[\mp \operatorname{arch}(-B_k)]. \tag{23}$$

The particular solutions of the TRF have the form

$$C_k^{\pm} = C^{\pm} D_k^{-1/4} (-1)^k \exp\left[\mp \int_{k_0}^{k} \operatorname{arch}(-B_s) ds\right]. \tag{24}$$

The absolute value of the solution C_k^- increases exponentially with increasing k, while that of the solution C_k^+ exponentially decreases; this means that the range of values where $\varepsilon < U_k^-$ is a classically forbidden region. Here, however, neighboring elements C_k and C_{k+1} of each of the particular solutions (24) have opposite signs.

The approximate WKB-type solutions lose meaning in the neighborhood of the "turning points" k_t, the roots of the equations $\varepsilon = U_k^+$ and $\varepsilon = U_k^-$. The matching of the solutions obtained in the different regions can be accomplished, using, for example, the standard TRF for the Bessel functions.[16] We shall give here the matching condition for the case in which the classically allowed region, which is bounded by the turning points k_t and k_t' ($k_t < k_t'$), lies to the right of the region where $\varepsilon < U_k^-$. Then that solution to the TRF which decays exponentially into the interior of the left classically forbidden region has the form

$$C_k = A(-D_k)^{-1/4} \cos\left(\int_{k_t}^{k} \arccos B_s ds + k_t\pi + \frac{\pi}{4}\right) \tag{25}$$

for $k_t < k < k_t'$ and

$$C_k = \frac{A}{2} D_k^{-1/4} (-1)^k \exp\left[-\int_{k}^{k_t} \operatorname{arch}(-B_s) ds\right] \tag{26}$$

for $k < k_t$.

The normalization constant A in (25) and (26) is determined from the condition

$$1 = \sum C_k^2 \approx \int_{k_t}^{k_t'} C_k^2 dk \approx \frac{A^2}{2} \int_{k_t}^{k_t'} (-D_k)^{-1/2} dk. \tag{27}$$

Requiring that the solution be damped in both the $k < k_t$ and the $k > k_t'$ regions, we obtain the quantization rule–the analog of the Bohr-Sommerfeld quantization rule:

$$\int_{k_t}^{k_t'} \left(s+\frac{1}{2}\right) \frac{dB_s}{ds} \frac{ds}{(1-B_s^2)^{1/2}} = \left(N+\frac{1}{2}\right)\pi, \tag{28}$$

where N is a whole number.

In the problems of quantum mechanics the role of the small parameter λ responsible for the slowness of the variation of the coefficients in the TRF is usually played by the Planck constant $\hbar$ [Eq. (7) is no exception; this becomes evident when it is written with the dimensional factors retained]. Let us show that the formulas of the discrete quasiclassical approach are simply connected with the equations of classical mechanics. Let us assume that the TRF (10) is a Schrödinger equation for some mechanical system in the $\hat{K}$ representation, where $\hat{K}$ is a Hermitian operator whose eigenvalues are successive whole numbers. This means that the elements C_k of the solution to the TRF are the coefficients in the expansion

$$\Psi = \sum_k C_k f_k \tag{29}$$

of the eigenfunction Ψ of the Hamiltonian of the system in terms of the eigenfunctions f_k of the operator $\hat{K}$:

$$\hat{K} f_k = k f_k. \tag{30}$$

In the classical limit $\hbar \to 0$ the subscript k has the meaning of a dynamical variable that satisfies a classical equation of motion (just as the independent variable x of the one-dimensional Schrödinger equation acquires the meaning of a particle coordinate in the classical limit). Let us find this equation. According to (20), the role of the classical momentum, conjugate to the variable k, is played by the quantity

$$\Pi = \arccos[(\varepsilon - w_k)/2p_{k+1/2}]. \tag{31}$$

From this it follows that the classical Hamiltonian of the system in question has, in the canonical variables k and Π, the form

$$H = \varepsilon(k, \Pi) = w_k + 2p_{k+1/2}\cos\Pi. \tag{32}$$

This leads to the canonical equations

$$\frac{d\Pi}{dt} = -\frac{dw_k}{dk} - 2\cos\Pi \frac{dp_{k+1/2}}{dk}, \qquad \frac{dk}{dt} = -2p_{k+1/2}\sin\Pi. \tag{33}$$

According to (32),

$$\sin\Pi = \pm\{1-[(\varepsilon-w_k)/2p_{k+1/2}]^2\}^{1/2}.$$

Therefore, the sought equation has the form

$$dk/dt = \pm[4p_{k+1/2}^2 - (\varepsilon-w_k)^2]^{1/2} = \pm[(U_k^+-\varepsilon)(\varepsilon-U_k^-)]^{1/2} \tag{34a}$$

(cf. the equation $\dot{x} = \pm\{2/m)[\varepsilon - U(x)]\}^{1/2}$ for the coordinate x). The integration of (34a) leads to the formula

$$t + C = \pm \int_{k_0}^{k} \frac{ds}{[(U_s^+-\varepsilon)(\varepsilon-U_s^-)]^{1/2}}. \tag{34b}$$

Thus, to each TRF with slowly varying coefficients correspond the equations (34) of classical mechanics. The boundaries of the domain of variation of the variable k are deter-

mined by the roots of the expression under the square-root sign, i.e., by the turning points k_t. The motion described by Eqs. (34a) and (34b) can occur only when the classical energy ε satisfies the inequalities

$$\min U_k^- < \varepsilon < \max U_k^+. \tag{35}$$

It is therefore natural to expect that the energy spectrum for the quantum problem (10) lies wholly in the interval $[\min U_k^-, \max U_k^+]$; this statement can be rigorously proved.

Let us give a simple example that, as will be seen below, has a direct bearing on the problem of the quadratic Zeeman effect for the hydrogen atom. Let us consider the free quantum-mechanical asymmetrical top with rotational constants a_i ($a_1 > a_2 > a_3$) and in a state with prescribed total-angular-momentum squared $J(J+1)$ and energy ε values. The expansion of the wave function of the top in terms of the generalized spherical functions leads to the TRF (Ref. 11, §103)

$$p_{J_3} C_{J_3-2} + (w_{J_3} - \varepsilon) C_{J_3} + p_{J_3+2} C_{J_3+2} = 0, \tag{36}$$

where J_3 is the angular momentum component along the axis of inertia of a top with rotational constant a_3;

$$w_{J_3} = {}^1/_2 \{(a_1+a_2)[J(J+1) - J_3^2] + 2a_3 J_3^2\},$$
$$p_{J_3} = {}^1/_4 (a_1 - a_2)[(J-J_3+2)(J-J_3+1)(J+J_3)(J+J_3-1)]^{1/2}. \tag{37}$$

The role of the variable k, which changes by 1 at each step of the TRF, is played here by $J_3/2$. Neglecting the corrections that are unimportant at large J and J_3 values, we find that

$$U^+(J_3) \approx a_1 J^2 - (a_1 - a_3) J_3^2, \quad U^-(J_3) \approx a_2 J^2 - (a_2 - a_3) J_3^2. \tag{38}$$

Equation (34a) therefore assumes the form

$${}^1/_2 dJ_3/dt = \pm \{[a_1 J^2 - (a_1 - a_3) J_3^2 - \varepsilon][\varepsilon - a_2 J^2 + (a_2 - a_3) J_3^2]\}^{1/2}. \tag{39}$$

As was to be expected, it coincides with the equation, well known in classical mechanics, of motion of the free asymmetrical top [see Ref. 20, Eq. (37.7)].

3. QUASICLASSICAL SOLUTIONS TO THE TRF DESCRIBING THE HYDROGEN ATOM IN A MAGNETIC FIELD

According to the formulas (8) and (15), the potential functions for the TRF (7) have the form

$$U_{n_1}^{\pm} = 3n^2 - m^2 + 1 - 12(a - n_1)^2 \pm 8\{[(a+{}^1/_2)^2 - (a-n_1)^2][(a+|m|+{}^1/_2)^2 - (a-n_1)^2]\}^{1/2}. \tag{40}$$

Notice that

$$U_{2a-n_1}^{\pm} = U_{n_1}^{\pm}. \tag{41}$$

This means that the plots of the functions $U_{n_1}^{\pm}$ are symmetrical about the straight line $n_1 = a$. The condition (41) is a consequence of the evenness of the Hamiltonian (1). Indeed, the parabolic coordinates ξ and η transform into each other under inversion. The quantum numbers n_1 and n_2 then change places, which, according to (4), corresponds to the substitution $n_1 \to 2a - n_1$.

The basis functions ψ_{n_1}, $2a - n_1, m$ are the eigenfunctions of the z component of the Runge-Lenz operator $\hat{\mathbf{A}}$ (Ref. 11, §37):

$$\hat{A}_z \psi_{n_1,\, 2a-n_1,\, m} = (2/n)(n_1 - a) \psi_{n_1,\, 2a-n_1,\, m}. \tag{42}$$

Consequently, the role of the operator $\hat{K}$ in Eq. (30) is played by the operator $(n/2)\hat{\mathbf{A}}_z + a$, and Eq. (34), as applied to the TRF (7), determines the evolution of the z component of the Runge-Lenz vector in the classical problem of the motion, perturbed by a weak magnetic field, of a particle in the Coulomb field. As is well known, the vector $\mathbf{A}$ for a particle in the Coulomb field is oriented along the semimajor axis of the elliptic orbit and is, in absolute value, equal to the eccentricity of the orbit; the perturbation by the magnetic field leads to the periodic variation of $\mathbf{A}$ in magnitude and direction. Allowing for the factor $\omega_L^2 n^2/4$, which relates the matrix of the TRF (7) to the perturbation operator in the Hamiltonian (1), we find that

$$\frac{n}{2}\frac{dA_z}{dt} = \pm \frac{\omega_L^2 n^2}{4} \{[U^+(A_z) - \varepsilon][\varepsilon - U^-(A_z)]\}^{1/2}. \tag{43}$$

Here $U^+(A_z)$ and $U^-(A_z)$ are the functions (40) in which we have set $n_1 = a + nA_z/2$.

Let us now consider particular cases corresponding to different relations between the quantum numbers n and m.

a) $m = 0$. The potential curves are then parabolas, since

$$U_{n_1}^+ \approx 5n^2 - 20(n_1 - a)^2, \quad U_{n_1}^- \approx n^2 - 4(n_1 - a)^2 \tag{44}$$

(see Fig. 1). Equation (43) assumes the form

$$\frac{n}{2}\frac{dA_z}{dt} = \pm \frac{\omega_L^2 n^2}{4}[(5n^2 - 5n^2 A_z^2 - \varepsilon)(\varepsilon - n^2 + n^2 A_z^2)]^{1/2}. \tag{45}$$

It is not difficult to see its similarity to the Eq. (39) of motion of the asymmetrical top; these equations coincide if we set in (39)

$$a_1 = 5, \; a_2 = 1, \; a_3 = 0, \; J = n, \; J_3(t) = nA_z(t) \tag{46}$$

and carry out a scaling transformation of the independent variable.

Thus, the classical motion of a particle in the Coulomb field, perturbed by a weak magnetic field, can, in the $m = 0$ case, be simulated by the free rotation of the asymmetrical top. A number of properties of the solutions to Eq. (45) follow at once from this analogy. Thus, it is evident that, in the case of a prescribed total angular momentum J, the energy of a top with rotational constants $a_1 > a_2 > a_3$ is limited by the inequalities $a_1 J^2 \geqslant \varepsilon \geqslant a_3 J^2$. To the limiting cases $\varepsilon = a_3 J^2$ and $\varepsilon = a_1 J^2$ correspond stable steady rotations about the axes 3 (in which case $J_3 = \pm J$) and 1 ($J_3 = 0$) respectively. For $a_3 J^2 < \varepsilon < a_2 J^2$, the angular-momentum component J_3 oscillates without changing its sign; the amplitude of the oscillations increases with increasing ε. For $\varepsilon \to a_2 J^2$ the period of the J_3 oscillations tends to infinity (the top "gets stuck" in the state of unstable steady rotation about the axis 2 for which $J_2 = \pm J$ and $J_3 = 0$). Finally, for $a_2 J^2 < \varepsilon < a_1 J^2$ the angular-momentum component J_3 oscillates about zero, the amplitude of the oscillations decreasing with increasing ε.

Analysis of Eq. (45) with the aid of the potential curves and with allowance for the relations (46) leads to the same results. The possible ε values in Eq. (45) [and, hence, the eigenvalues of the TRF (7)] satisfy the inequalities

$$\min U_{n_1}^- = 0 < \varepsilon < \max U_{n_1}^+ = 5n^2. \tag{47}$$

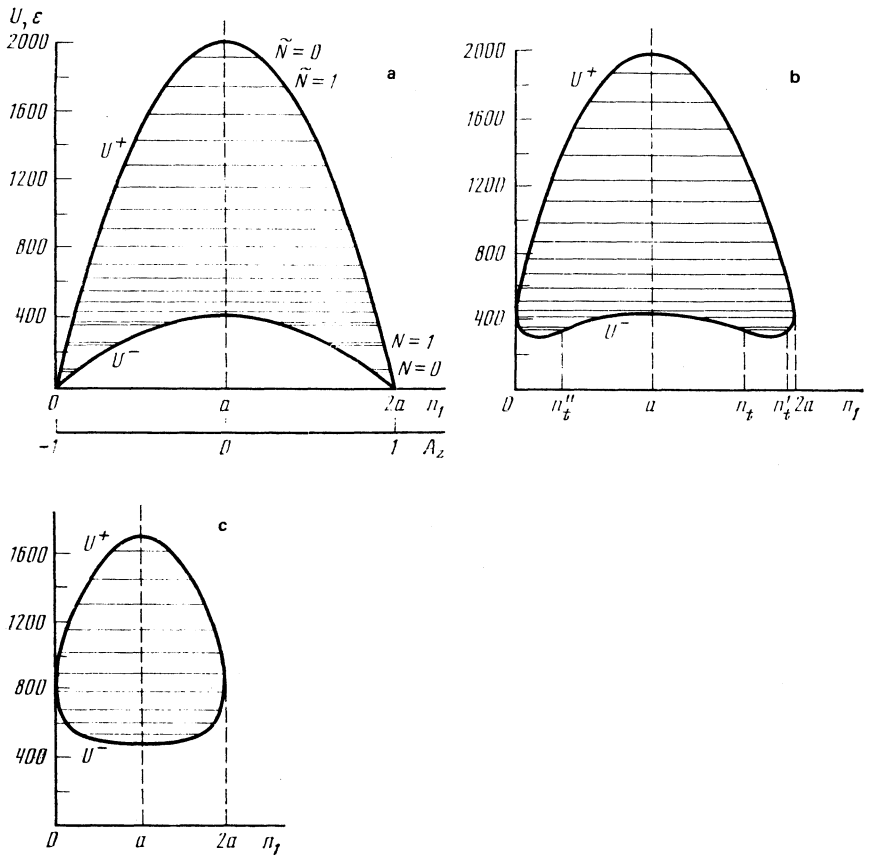

FIG. 1. The potential curves and the eigenvalues of the three-term recurrence formula (7) for $n = 20$ (the splittings of the bottom doublets are shown without regard to scale; see Tables I and II) and different values of m: a) $m = 0$; b) $m = 4$; c) $m = 10$.

As can be seen from Fig. 1a, for $\min U_{n_1}^- < \varepsilon < \max U_{n_1}^- = n^2$ the problem contains two symmetrical CAR; for $\max U_{n_1}^- < \varepsilon < \max U_{n_1}^+$, one CAR with its center at the point $n_1 = a$ (i.e., at the point where $A_z = 0$). Therefore, for $\varepsilon < \max U_{n_1}^-$ the solution to Eq. (45) oscillates without changing its sign (which is positive or negative, depending on the initial conditions); for $\varepsilon > \max U_{n_1}^-$ the functions $A_z(t)$ oscillates about zero. In the limiting cases $\varepsilon = \min U_{n_1}^-$ and $\varepsilon = \max U_{n_1}^+$ the CAR degenerates into points. The solutions to Eq. (45) will then be the constants $A_z = \pm 1$ or $A_z = 0$. For ε close to the mininum of $U_{n_1}^-$ or the maximum of $U_{n_1}^+$, the A_z oscillations will be harmonic oscillations.

We can, by finding $A_z(t)$ from Eq. (45), determine the time dependence of the elements of the elliptic orbit of a classical particle in the Coulomb and a weak magnetic field. Thus, taking account of the fact that $A_z^2 \leqslant \mathbf{A}^2 \leqslant 1$, we find that, for $\varepsilon = \min U^-$, the particle moves along a trajectory that has degenerated into a straight line oriented along (when $A_z = 1$) or against (when $A_z = -1$) the field. For other ε values the dependence of the eccentricity and the orientation of the orbit on the time can be established, using the following relation found in Ref. 8:

$$4\mathbf{A}^2 - 5A_z^2 = (\varepsilon - n^2 - m^2)/n^2.$$

The enumerated characteristics of the classical motion are directly reflected in the character of the spectrum of the TRF (7). In particular, the presence in the case when $\min U_{n_1}^- < \varepsilon < \max U_{n_1}^-$ of two symmetrical CAR separated by a potential barrier (the role of which is played by the peak of the function $U_{n_1}^-$) leads to the earlier-mentioned doublet structure of the Zeeman spectrum. Indeed, if we neglect tunneling and seek the quasiclassical solutions to the TRF in the left and right CAR independently of each other, we obtain two sets of solutions $\{C_{n_1}\}$ to the TRF. The solutions of one of the sets differ substantially from zero in the region $n_t < n_1 < n_t'$, where n_t and n_t' are the boundaries of the right CAR, and fall off exponentially outside it. To these solutions correspond those eigenfunctions of the Hamiltonian (1) which contain in their expansions mostly the basis functions $\psi_{n_1 n_2 m}$ with $n_2 = 2a - n_1 < n_1$. This indicates an asymmetry in the charge distribution with respect to the $z = 0$ plane: the greater part of the charge is located in the region $z > 0$ (Ref. 11, §37). The solutions to the TRF that belong to the other set are localized in the left CAR (the charge in the corresponding atomic states is located mostly in the $z < 0$ region). On account of the symmetry of the problem, the eigenvalues of the recurrence formula in the WKB approximation are double degenerate. They can be found from the quantization rule (28) with the integration performed over one of the CAR (the left one or the right one, it makes no difference).

The region $\max U_{n_1}^- < \varepsilon < \max U_{n_1}^+$ contains only one CAR. To the quasiclassical solutions of the TRF correspond here atomic wave functions describing a charge distribution that is symmetric about the $z = 0$ plane. Therefore, we do not have the approximate twofold degeneracy.

To the harmonic oscillation of the classical variable A_z for ε close to the minimum of $U_{n_1}^-$ or the maximum of $U_{n_1}^+$ in the quantummechanical problem corresponds the approximate equidistance of the lowest and the highest energy levels for a given n. Using the formula (68) of the Appendix, we can obtain for the lowest (doublet) levels an expansion of the form

$$\varepsilon_N=1+4n\sqrt{5}(N+{}^1/_2)-12(N+{}^1/_2)^2+\ldots, \quad (48)$$

where N is a quantum number ($N=0,1,2,\ldots$). For the upper levels we find from the formula (67b) that

$$\varepsilon_{\tilde N}=1+5n^2-4n\sqrt{5}(\tilde N+{}^1/_2)+{}^9/_2(\tilde N+{}^1/_2)^2+\ldots \quad (49)$$

($\tilde N=0,1,2,\ldots$). Let us draw attention to the fact that, as the quantum number $\tilde N$ increases, the energy of the levels described by the formula (49) decreases. Strictly speaking, the formulas (48) and (49) are applicable when $N\ll n$ and $\tilde N\ll n$; numerical examples show, however, that they are sufficiently accurate for N and $\tilde N$ comparable to n as well.

b) Let the magnetic quantum number m be restricted by the inequalities $0<m<n/\sqrt{5}$. The graph of the potential functions for this case is shown in Fig. 1b. The function $U_{n_1}^-$ has a maximum at $n_1=a$. Therefore, for

$$\min U_{n_1}^-\approx -4m^2+2\sqrt{5}n|m|<\varepsilon<\max U_{n_1}^-\approx n^2+m^2 \quad (50)$$

we have two symmetrical CAR and an approximate twofold degeneracy of the levels; the approximate degeneracy does not occur in the region

$$\max U_{n_1}^-<\varepsilon<\max U_{n_1}^+\approx 5n^2-3m^2. \quad (51)$$

The bottom and the top levels are approximately equidistant. For them we can obtain the expansions

$$\varepsilon_N=1-4m^2+2\sqrt{5}n|m|+4(5n^2+5m^2-6\sqrt{5}|m|n)^{1/2}(N+{}^1/_2)$$
$$-12\left(1+\frac{2\sqrt{5}n|m|}{5n^2+5m^2-6\sqrt{5}n|m|}\right)\left(N+\frac{1}{2}\right)^2+\ldots, \quad (52)$$

$$\varepsilon_{\tilde N}=1-3m^2+5n^2-4(5n^2-m^2)^{1/2}\left(\tilde N+\frac{1}{2}\right)$$
$$+\frac{3}{2}\frac{15n^2+m^2}{5n^2-m^2}\left(\tilde N+\frac{1}{2}\right)^2+\ldots, \quad (53)$$

which are respectively similar to the formulas (48) and (49).

c) Let $|m|>n/\sqrt{5}$. The potential curves are shown in Fig. 1c. The function $U_{n_1}^-$ does not have a maximum in this case, so that there is only one CAR for all possible ε. There is therefore no twofold degeneracy. The upper levels are described as before by the formula (53); for the lower levels we obtain in place of (52) the expression

$$\varepsilon_N=m^2+n^2+1+4(5m^2-n^2)^{1/2}(N+{}^1/_2)$$
$$+{}^3/_2(15m^2+n^2)/(5m^2-n^2)(N+{}^1/_2)^2+\ldots \quad (54)$$

4. COMPUTATION OF THE DOUBLET g-u SPLITTING

The coefficients of the TRF (7) satisfy relations that are a consequence of the evenness of the Hamiltonian:

$$w_{n_1}=w_{2a-n_1},\quad p_{n_1}=p_{2a-n_1+1}. \quad (55)$$

Therefore, if $\mathbf{C}=\{C_{n_1}\}$ is some solution to the TRF, then $\mathbf{C}'=\{C_{n_1}'\}$, where $C_{n_1}'=C_{2a-n_1}$, will also be a solution corresponding to the same eigenvalue. From this it follows that either $\mathbf{C}'=\mathbf{C}$, or $\mathbf{C}'=-\mathbf{C}$; to the first case corresponds an even, and to the second an odd, wave function (5) if m is even (if m is odd we have the opposite situation).

We shall consider those values of the parameters for which the levels are approximately doubly degenerate, i.e., for which $|m|<n/\sqrt{5}$ and $\min U^-<\varepsilon<\max U^-$ (Figs. 1a and 1b). When allowance is made for the finite transparency of the barrier between the CAR, the doubly degenerate energy levels split. The correct solutions to the TRF in the zeroth approximation will be the even or odd combination of the WKB-type solutions localized in the left and right CAR.

The splitting calculation can be carried out in much the same way as the corresponding computations are carried out in the coordinate representation (Ref. 11, §50, problem 3) (a formula for the splitting of the eigenvalues of the TRF is given in Ref. 18 without deviation). Let us denote by $\mathbf{f}=\{f_{n_1}\}$ that solution to the TRF which is localized in the right CAR, and falls off exponentially under the barrier (for $n_1<n_t$; see Fig. 1b). We shall assume that $\mathbf{f}$ is normalized:

$$\sum_{n_1=n_t}^{n_t'} f_{n_1}^2=1.$$

Let us denote the ε value corresponding to this solution by ε_0. Let us denote the eigenvalues of the TRF that correspond to the correct linear combinations (we assume, for definiteness, that m is even)

$$C_{n_1}^g=(f_{n_1}+f_{2a-n_1})/\sqrt{2},\quad C_{n_1}^u=(f_{n_1}-f_{2a-n_1})/\sqrt{2}, \quad (56)$$

by ε_g and ε_u. Let us write out the TRF that are satisfied by the sequences f_{n_1} and $C_{n_1}^g$:

$$p_{n_1}f_{n_1-1}+(w_{n_1}-\varepsilon_0)f_{n_1}+p_{n_1+1}f_{n_1+1}=0, \quad (57)$$

$$p_{n_1}C_{n_1-1}^g+(w_{n_1}-\varepsilon_g)C_{n_1}^g+p_{n_1+1}C_{n_1+1}^g=0. \quad (58)$$

Let us introduce a whole number q that is equal to a if a is integral and $a+\frac{1}{2}$ if a is half-integral. Let us multiply the TRF (57) by $C_{n_1}^g$ and the TRF (58) by f_{n_1}, subtract one of the resulting expressions from the other, and sum over n_1 in the range from q to $2a$. Taking account of the fact that $p_{2a+1}=0$, we obtain

$$p_q(f_{q-1}C_q^g-f_qC_{q-1}^g)+(\varepsilon_g-\varepsilon_0)\sum_{n_1=q}^{2a}f_{n_1}C_{n_1}^g=0. \quad (59)$$

On account of the normalization condition, we have

$$\sum_{n_1=q}^{2a}f_{n_1}C_{n_1}^g\approx\frac{1}{\sqrt{2}}.$$

Using (56), we thus obtain

$$p_q(f_{q-1}f_{2a-q}-f_qf_{2a-q+1})+\varepsilon_g-\varepsilon_0=0. \quad (60a)$$

We can establish in an entirely similar fashion that

$$p_q(-f_{q-1}f_{2a-q}+f_qf_{2a-q+1})+\varepsilon_u-\varepsilon_0=0. \quad (60b)$$

Subtracting (60b) from (60a), we find that, for integral a

$$\varepsilon_g-\varepsilon_u=2p_qf_q(f_{q+1}-f_{q-1}); \quad (61)$$

and for half-integral a

$$\varepsilon_g-\varepsilon_u=2p_q(f_q^2-f_{q-1}^2). \tag{62}$$

Inside the barrier, $\varepsilon < U^-$, and the quasiclassical solution is given by the formula (26). Let us also take into account the fact that, according to the formulas (12) and (23),

$$f_{q+1}/f_q \approx f_q/f_{q-1}=\mu_q^-=B_q-(B_q^2-1)^{1/2}<0.$$

Consequently, for integral a

$$\varepsilon_g-\varepsilon_u \approx 2p_q f_q^2(\mu_q^- - 1/\mu_q^-) \approx -2D_q^{1/2} f_q^2<0;$$

and for half-integral a

$$\varepsilon_g-\varepsilon_u \approx 2p_q f_q f_{q-1}(\mu_q^- - 1/\mu_q^-) \approx -2D_q^{1/2} f_q f_{q-1}>0.$$

Replacing f_q and f_{q-1} by their values as given by the formula (26), and taking the symmetry of (55) into account, we finally obtain

$$\varepsilon_g-\varepsilon_u=(-1)^n \exp\left[-\int_{n_t''}^{n_t} \operatorname{arch}(-B_s)\,ds\right] \Big/ \int_{n_t}^{n_t'} (-D_s)^{-1/2}\,ds. \tag{63}$$

Here $n_t''=2a-n_t$ is the turning point at the left boundary of the barrier (see Fig. 1b). The formula (63) is valid for both even and odd magnetic quantum numbers m. The integral in the exponent is taken over the barrier; the integral in the denominator, over the right CAR. For given n and m the magnitude of the splitting is smallest for the lowest levels, and increases rapidly as the level approaches the top of the barrier.

The formula obtained by us is entirely similar to the well-known expression for the magnitude of the g-u splitting in the coordinate representation. The denominator in the formula (63) is equal to one half the period of the classical motion described by the equations (34); the numerator has the meaning of a barrier factor, which gives the probability for tunneling in a single approach to the barrier. A characteristic departure from the one-dimensional coordinate case consists in the fact that the bottom level in a doublet can be either or even- or odd parity. As in the coordinate analog, the formula (63) becomes inapplicable when the level approaches the top of the barrier and the barrier factor becomes comparable to unity.

The evaluation of the integrals in the formula (63) is much simpler in the $m=0$ case. It is then found that

$$I_1 \equiv \int_{n_t''}^{n_t} \operatorname{arch}(-B_s)\,ds = n\frac{4\sigma}{(5-2\sigma)^{1/2}}[\Pi(1-2\sigma,\varkappa)-\mathbf{K}(\varkappa)],$$

$$I_2 \equiv \int_{n_t}^{n_t'} (-D_s)^{-1/2}\,ds = \frac{1}{2n(5-2\sigma)^{1/2}}\mathbf{K}(\varkappa').$$

Here $\sigma=\varepsilon/2n^2$ $(0<\sigma<0.5)$; Π and $\mathbf{K}$ are the complete elliptic integrals of the third and first kind with the parameters

$$\varkappa=[5(1-2\sigma)/(5-2\sigma)]^{1/2}, \quad \varkappa'=(1-\varkappa^2)^{1/2}.$$

For small σ, the integrals I_1 and I_2 can be expanded in series:

$$I_1=n\{-\ln[(3-\sqrt{5})/2]-(1/\sqrt{5})[\sigma+{}^3/_{10}\sigma^2+\ldots]\ln(10/\sigma)+\sigma-{}^9/_{20}\sigma^2+\ldots\},$$
$$I_2=(4n/\pi)\sqrt{5}[1-{}^3/_5\sigma+\ldots]. \tag{64}$$

Using these expansions and the formula (48), we can derive an explicit expression for the g-u splitting of the lowest (for a given n and for $m=0$) levels:

$$\varepsilon_g-\varepsilon_u \approx (-1)^n\left(\frac{3-\sqrt{5}}{2}\right)^n (20n^2)^{N+1}\frac{2}{\pi}\left(\frac{e}{2N+1}\right)^{2N+1} \times \exp\left[-\frac{3}{\sqrt{5}}\frac{2N+1}{n}-\frac{9}{4\sqrt{5}}\frac{(2N+1)^2}{n}\right], \tag{65}$$

where N is the doublet number ($N=0,1,\ldots;N\ll n$).

5. NUMERICAL EXAMPLES

Let us illustrate our results by numerical examples. In Tables Ia and Ib the "exact" eigenvalues of the TRF (7), obtained through a numerical diagonalization of the TRF matrix with $n=20$, $m=0$, are compared with the approximate eigenvalues given by the quantization rule (28) and the explicit formulas (48) and (49). Table Ia contains the energies of the levels lying below the top of the potential barrier (for $n=20$ and max $U^-=400$). The exact eigenvalues here clearly group themselves into doublets. To the two components of a doublet corresponds one and the same quantum number N (since the solutions of the TRF that correspond to them are proportional to the sum of, and the difference between, the states localized in the left and right CAR, and having one and the same quantum number). Table Ib shows the energies of the levels lying above the barrier; as can be seen, no doublet structure is exhibited have. Finally, in Table II we present the values of the g-u splitting for the levels with $m=0$ and $n=5$, 8, 20. [The eigenvalues of the TRF (7) for $n=20$, $m=0$, 4, and 10 have also been plotted in Figs. 1a, 1b, and 1c respectively.]

As can be seen from the numerical data presented, the WKB approximation guarantees a high accuracy at relatively moderate n values (states with principal quantum numbers of the order of one hundred and more are observed

TABLE I. Eigenvalues of the TRF (7) for $n=20$, $m=0$: a) Bottom group of levels.

N	Approximate value: Found from the quantization rule (28)	Approximate value: Computed from the explicit formula (48)	Exact value and parity
0	87.39	87.44	87.338848 (u) 87.338909 (g)
1	240.7	242.3	240.386532 (u) 240.449173 (g)
2	362.7	373.2	358.300624 (u) 364.944891 (g)

b) Top group of levels

$\tilde{N}$	Approximate value: Found from the quantization rule (28)	Approximate value: Compute from the explicit formula (49)	Exact value and parity
0	1912.68	1912.68	1913.802 (g)
1	1742.8	1742.8	1743.910 (u)
2	1581.9	1581.9	1583.032 (g)
.	.	.	.
.	.	.	.
.	.	.	.
12	478.9	468.0	479.401 (g)
13	424.1	405.2	431.118 (u)

TABLE II. Inversion splitting of the levels of the TRF (7) for $m = 0$.

n	N	Approximate value: Computed from the formula (63)	Approximate value: Computed from the simplified formula (65)	Exact value
5	0	4.23	4.40	3.7802
8	0	0.774	0.748	0.76506
20	0	$5.31 \cdot 10^{-5}$	$5.37 \cdot 10^{-5}$	$6.058 \cdot 10^{-5}$
	1	$6.03 \cdot 10^{-2}$	$6.88 \cdot 10^{-2}$	$6.264 \cdot 10^{-2}$
	2	6.64	13.7	6.644

in experiment). The accuracy of the quantization rule (28) decreases regularly as the level approaches the top of the barrier (see the level with $\tilde{N} = 13$ in Table Ib). The high accuracy of the simplest explicit formulas (48) and (49) and the applicability of the WKB formulas for the states with $N = 0$ and $\tilde{N} = 0$ seem somewhat surprising. The applicability of the WKB formulas for the states with $N = 0$ and $\tilde{N} = 0$ is due to the fact that the quantization formula (28), like the Bohr-Sommerfeld quantization rule, gives the exact level-energy values for the harmonic oscillator.[16] The WKB approximation is, strictly speaking, inapplicable when N is close to zero, but the quasiclassical quantization rule nevertheless gives the correct result, since the harmonic approximation begins to operate. At the same time, the quasiclassical wave functions for $N = 0$ become unsatisfactory. This leads, in particular, to a marked decrease, at $N = 0$, in the accuracy of the computation of the preexponential factor in the formula (63) and to an increase in the error that is made in the calculation of the g-u splitting (see the computed values for $n = 20$ and different N in Table II).

6. CONCLUSION

The discrete quasiclassical method allows us to investigate the essentially two-dimensional problem of the quadratic Zeeman effect for the hydrogen atom with a degree of clearness characteristic of one-dimensional quantum-mechanical problems. Our results pertained to the l-mixing regime, but we can draw more general conclusions from them. It can be shown, in particular, that in the n-mixing regime the quasicrossing between the top level of a shell with principal quantum number $n^{\mathrm{I}} = n$ and the bottom level of the higher-lying shell with $n^{\mathrm{II}} = n + 1$ will be extremely close if $|m| < n/\sqrt{5}$. This follows from the fact that, for $|m| < n/\sqrt{5}$, the CAR for those solutions of the TRF (7) which correspond to the top and bottom (for given n and m) levels do not intersect, as well as from the fact that the operator $(\omega_L^2/2)(x^2 + y^2)$ in the representation of the functions (3) is almost localized (i.e., the matrix elements

$$\langle \psi_{n_1,\, 2n^{\mathrm{I}}-n_1,\, m} | x^2+y^2 | \psi_{n_1',\, 2n^{\mathrm{II}}-n_1',\, m} \rangle$$

decrease rapidly with increasing $|n_1 - n_1'|$).

The method developed in the paper can be applied to certain related problems as well. Thus, the results of the paper can easily be generalized to the case of level-splitting calculations for the hydrogen atom in parallel electric $\mathscr{E}$ and magnetic $\mathscr{H}$ fields if $\mathscr{E}$ and $\mathscr{H}$ are such that the mixing of states from different shells can be neglected (this means that the level energies are computed up to first order in $\mathscr{E}$ and second order in $\mathscr{H}$. In the basis (3), this problem reduces to the problem of a TRF differing from (7) only in that it has in place of the coefficient w_{n_1} the expression $w_{n_1} + 20n(n_1 - a)\beta$, where $\beta \equiv 12c^2\mathscr{E}/5\mathscr{H}^2n^2$. The potential functions lose their symmetry when $\mathscr{E} \neq 0$, which leads to the disappearance of the doublet structure of the spectrum. The spectral patterns for $0 < \beta < \frac{1}{5}$ (when we can speak of an electric-field-distorted quadratic Zeeman effect), $\beta > 1$ (when we can speak of a magnetic-field-distorted linear Stark effect), and in the intermediate region $\frac{1}{5} < \beta < 1$ are found to differ significantly from each other.

Another possible generalization is connected with the investigation of the quadratic Zeeman splitting of the Rydberg states of nonhydrogenic atoms in the quantum-defect approximation. If the Zeeman splitting is small in comparison with the spacing between neighboring shells, but comparable to the l splitting in zero field, then this problem also reduces to the problem of a TRF (if we use the basis set obtained by separating the variables in spherical coordinates). Its solution is of considerable interest in connection with the available experimental data.[2]

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APPENDIX

The eigenvalue spectrum of a TRF at points not far from the minimum of the potential function U_k^- or the maximum of U_k^+ has an approximately equidistant character. The effective frequency and anharmonicity constant can be expressed in terms of the coefficients of the Taylor expansions of the potential functions.[18] Let the functions U_k^+ and U_k^- have in the neighborhood of the point k_0 (where k_0 is not necessarily a whole number) the expansions

$$U_k^+ = \sum_{s \geqslant 0} a_s (k-k_0)^s, \qquad U_k^- = \sum_{s \geqslant 0} b_s (k-k_0)^s. \tag{66}$$

If then: a) k_0 is the minimum point of the function U_k^- ($b_1 = 0$, $b_2 > 0$), we have

$$\varepsilon_N \approx b_0 + (N+{}^1/_2)\,[b_2(a_0-b_0)]^{1/2} - (N+{}^1/_2)^2[{}^1/_4 b_2 - {}^1/_8 a_2 + {}^3/_{32} a_1^2/(a_0-b_0) + {}^3/_{16} a_1 b_3/b_2 - {}^3/_8 (a_0-b_0)\,(b_4/b_2 - {}^5/_4 b_3^2/b_2^2)], \tag{67a}$$

where $N = 0, 1, 2, \ldots$;

b) k_0 is the maximum point of the function U_k^+, the oscillator level series is "inverted" in comparison with the normal situation, and is given by the formula

$$\varepsilon_N \approx a_0 - (N+{}^1/_2)\,[-a_2(a_0-b_0)]^{1/2} - (N+{}^1/_2)^2[{}^1/_4 a_2 - {}^1/_8 b_2 + {}^3/_{32} b_1^2/(b_0-a_0) + {}^3/_{16} b_1 a_3/a_2 - {}^3/_8 (b_0-a_0)\,(a_4/a_2 - {}^5/_4 a_3^2/a_2^2)] \tag{67b}$$

$$(N = 0, 1, 2 \ldots).$$

Eigenvalue expansions similar to the formulas (67) can be written down also in the case when the U_k^+ and U_k^- curves intersect at the point k_0 at an acute, nonzero angle.[1)] Thus, let the potential functions in the vicinity of k_0 be represented by the expansions (66) in which $a_0 = b_0 \equiv U_0$, $a_1 > b_1 > 0$, and the domain of definition of the TRF lies in the region $k > k_0$. Then

$$\varepsilon_N \approx U_0 + (a_1 b_1)^{1/2}(N - \{k_0\} + 1) + (N - \{k_0\} + 1)^2 \times {}^1/_8 [(3b_1/a_1 + 1)a_2 + (3a_1/b_1 + 1)b_2], \quad (68)$$

where $N = 0,1,2,\ldots$ and $\{k_0\}$ denotes the rational part of k_0.

[1)]This indicates that k_0 is a singular point of the TRF.

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