The hydrogen atom in a weak magnetic field

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The approximate integral of motion $\Lambda = 4A^2 - 5A_z^2$ (**A** is the Runge-Lenz vector) is obtained for a hydrogen atom located in a weak magnetic field of intensity **H** in first-order perturbation theory in terms of H^2. The existence of this invariant makes the atom's variables in ellipsoidal-cylindrical coordinates on a sphere in four-dimensional momentum space separable, accurate to H^4. The phenomenon, recently found in experimental and theoretical investigations, whereby the level energy splitting at the points of quasi-intersection decreases exponentially as the principal quantum number increases is explained. A new classification of the states of the hydrogen atom in a weak magnetic field is proposed.

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1. INTRODUCTION

The problem of the hydrogen atom in a magnetic field is of general theoretical interest, and has been the subject of a large number of papers. It has important applications in astrophysics and solid state physics (excitons in a magnetic field). Recently there has been a significant upsurge in interest in this problem as a result of the discovery of the exponential decrease with increasing principal quantum number n of the level energy splitting at the points of quasi-intersection. This behavior of the splitting was discovered both theoretically (in a numerical computation),[1] and experimentally.[2] To explain this phenomenon, Zimmerman *et al.*[1] and Delande and Gay[2] postulated the existence of an approximate hidden symmetry. In Refs. 3 and 4 an attempt is made to find this symmetry by analogy with the already known approximate symmetry of alkali atoms in an electric field.[5] A consistent description of the approximate symmetry and an explanation of the exponential decrease of the splitting are presented in Ref. 6, where there is obtained in first order perturbation theory in terms of H^2 (H is the magnetic field intensity) the approximate integral of motion $\Lambda = 4A^2 - 5A_z^2$ (A is the Runge–Lenz vector), the existence of which makes the variables for the hydrogen atom in the magnetic field separable within an accuracy of H^4 in the ellipsoidal-cylindrical coordinates on a sphere in four-dimensional momentum space. This symmetry, which indeed obtains in the problem of the hydrogen atom in a weak magnetic field, differs essentially from the symmetries considered in Refs. 3 and 4.

In the present paper we carry out a systematic investigation of the problem of the hydrogen atom in a weak magnetic field. A preliminary report dealing with some of the results of this investigation has already been published.[6] In the second section we find the integral of motion Λ with the aid of classical perturbation theory, and also discuss the character of the perturbed classical trajectories. In the third section we formulate the Bohr-Sommerfeld quantization conditions for these trajectories, and derive approximate expressions for the quadratic—in H—corrections to the energy. The fourth section is devoted to a quantum-mechanical treatment of the problem, and it is shown there that the operator $\hat{\Lambda}$ commutes with the total Hamiltonian of the system in the subspace of the hydrogenic wave functions with a fixed principal quantum number value, this result being valid for any n, and not just in the quasiclassical region, which corresponds to large n values. In the fifth section we discuss the exponential decrease of the energy level splitting, which is most simply explained in the quasiclassical approximation. The existence of the approximate symmetry gives rise to a new classification of the states of the hydrogen atom in a weak magnetic field and to approximate selection rules. These questions are also considered in the fifth section.

2. THE CLASSICAL PERTURBATION THEORY

A hydrogen atom located in a homogeneous magnetic field H is invariant under rotations about the z axis, along which the magnetic field is oriented. Arising from this symmetry is the conservation of the z component of the angular momentum l. The existence of the integral of motion l_z allows us to reduce the three-dimensional problem to a two-dimensional one. Further simplification is possible only in certain limiting cases. Below this problem is considered in the limit of weak magnetic fields.

In the Hamiltonian

$$\mathcal{H} = p^2/2 - 1/r + \omega^2\rho^2/2 + i\omega l_z, \tag{1}$$

($\rho^2 = x^2 + y^2$, $m = e = h = 1$) describing the hydrogen atom in a magnetic field, the last term, which is connected with the linear Zeeman effect, can be eliminated by going over to the coordinate system rotating about the z axis with frequency $\omega = H/2c$ (c is the velocity of light). The resulting Hamiltonian $\mathcal{H}'$ contains only a potential interaction, which splits up into the Coulomb interaction with the nucleus and a diamagnetic interaction [the third term in (1)]. The difference between the energy in the new coordinate system and the energy in the original system is equal to $m\omega$ ($l_z = m$; $m = 0, \pm 1, \pm 2, \ldots$), and this exhausts the contribution of the magnetic field in terms of the azimuthal variable φ. Below we shall consider only the nontrivial part of the interaction with the magnetic field: the diamagnetic interaction.

The quasiclassical perturbation theory in terms of

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the small parameter ω^2 for the discrete spectrum of the Hamiltonian

$$\mathcal{H}'=\mathcal{H}_0+V,\quad \mathcal{H}_0=p^2/2-1/r,\quad V=\omega^2\rho^2/2$$

splits up into two parts: the first part consists in the computation of the evolution of the classical Coulomb trajectories under the action of the magnetic field; the second, the formulation of the Bohr–Sommerfeld quantization rules for the trajectories obtained, the determination of the parameter values at which the trajectories satisfy the quantization conditions, and the computation of the energy spectrum.

In the unperturbed problem the electron moves along elliptic trajectories that are the solution to the Kepler problem. To compute the change that occurs in these trajectories under the action of the diamagnetic interaction V, we use the method of secular perturbations,[7] which was actively used in the old Bohr theory. In the method of secular perturbations the electron motion splits up into motion along an unperturbed elliptic trajectory and a slow variation of the parameters of the ellipse under the action of the perturbation. Let us choose as the parameters specifying the shape and orientation of the ellipse the angular momentum $\mathbf{l}=\mathbf{r}\times\mathbf{p}$ and the Runge-Lenz vector $\mathbf{A}=[\mathbf{pl}]-\mathbf{r}/r$. The radius vector of the electron can be represented in terms of these parameters as follows:

$$\mathbf{r}=x_0(t)\mathbf{A}/A+y_0(t)[\mathbf{l}\times\mathbf{A}]/lA, \tag{2}$$

where

$$x_0(t)=a(\cos\xi-e),\quad y_0(t)=a(1-e^2)^{1/2}\sin\xi \tag{3}$$

is the solution to the Kepler problem in the X_0Y_0 plane, with the X_0 axis directed along the Runge-Lenz vector[8] $\mathbf{A}$, a is the semimajor axis of the ellipse, and e is the eccentricity. The dependence of the coordimates on the time is realized through the Kepler anomaly ξ, which is connected with the time by the relation[8]

$$t=a^{3/2}(\xi-e\sin\xi).$$

Differentiating $\mathbf{l}$ and $\mathbf{A}$ with respect to the time, we obtain the equations of motion for these quantities ($\rho=\mathbf{x}+\mathbf{y}$):

$$\frac{d\mathbf{l}}{dt}=-\omega^2[\mathbf{r}\times\rho],\quad \frac{d\mathbf{A}}{dt}=-\omega^2\{[\mathbf{p}\times[\mathbf{r}\times\rho]]+[\rho\times[\mathbf{r}\times\mathbf{p}]]\}. \tag{4}$$

As $\omega^2\to 0$, the changes that occur in $\mathbf{l}$ and $\mathbf{A}$ over a period of rotation of the electron along the ellipse tend to zero; therefore, we can average the right members of the equations (4) over the period, assuming in the first approximation that $\mathbf{l}$ and $\mathbf{A}$ are constants. It is the replacement of the right members of the equations of motion by their values averaged over the period that forms the basis of the method of secular perturbations. Using (2) and (3), we obtain, after the averaging, a closed system of equations describing the variation of the parameters of the ellipse in time under the action of the diamagnetic interaction:

$$\frac{d\mathbf{l}}{dt}=\frac{\omega^2a^2}{8}\left\{(4A^2+1)\frac{A_z[\mathbf{A}\times\mathbf{k}]}{A^2}+\frac{(1-A^2)(\mathbf{k}\times[\mathbf{l}\times\mathbf{A}])[[\mathbf{l}\times\mathbf{A}]\times\mathbf{k}]}{l^2A^2}\right\},$$
$$\frac{d\mathbf{A}}{dt}=-\frac{\omega^2a^{3/2}}{8lA^2}(1-A^2)^{1/2}\{(3A^2-4A_z^2)[\mathbf{l}\times\mathbf{A}]+(A^2\mathbf{k}+A_z\mathbf{A})(\mathbf{k}[\mathbf{l}\times\mathbf{A}])\}. \tag{5}$$

Here $\mathbf{k}$ is the unit vector along the z axis. At first glance the system of equations (5) appears to be quite complicated, but it can be verified that the following three independent integrals of motion follow from it:

$$l_z,\quad Q=l^2/(1-A^2),\quad \Lambda=4A^2-5A_z^2. \tag{6}$$

Here l_z is the above-indicated exact integral of motion for a hydrogen atom in a magnetic field, while Q and Λ are approximate integrals of motion, which are conserved within an accuracy of ω^4. The quantity $Q=-1/2E_0$ is equal to the semimajor axis of the ellipse, and its conservation reflects the fact that in the first approximation the particle wanders the set of ellipses corresponding to the unperturbed energy value. This property is a natural one, and it is analogous to a well-known fact from perturbation theory for the degenerate case in quantum mechanics, where the wave function of the particle is constructed in the first-order theory from the set of wave functions corresponding to the unperturbed energy value.

The third integral of motion Λ is nontrivial. Taking into account the fact that $0\leq A^2\leq 1$, we obtain the range of Λ values: $-1\leq\Lambda\leq 4$. The possibility of Λ's having positive and negative values leads to an interesting property for the perturbed trajectories. Let us choose as the generalized coordinate the angle ϑ between the Runge-Lenz vector and the z axis. Then we can write Λ in the form

$$\Lambda=A^2(4-5\cos^2\vartheta).$$

For $\Lambda=0$ the Runge-Lenz vector lies on the surface of the double cone Ω specified by the condition $\cot\vartheta_0=2$. For $\Lambda\neq 0$ all the trajectories split up into two classes: the trajectories with $\Lambda<0$ librate inside the double cone Ω ($0\leq\vartheta\leq\vartheta_0$ or $\pi-\vartheta_0<\vartheta<\pi$) and the trajectories with $\Lambda>0$ librate outside this cone ($\vartheta_0\leq\vartheta\leq\pi-\vartheta_0$). Thus, all the states are localized in the two nonoverlapping ϑ domains, the boundary between which is a universal boundary, not dependent on the energy of the particle. This unique property leads to a number of qualitative results, a consequence of which is the effect discovered by Zimmerman *et al.*[1] and Delande and Gay.[2]

3. THE BOHR-SOMMERFELD RULES

The existence of the three independent integrals of motion (l_z, Q, Λ) allows an analytic description of the caustic and the formulation of the Bohr-Sommerfeld quantization rules. Two of the three quantization rules give the obvious results: $l_z=m$ (m is the azimuthal quantum number) and the unperturbed energy value $E_0=-1/2n^2$ ($n=Q^{1/2}$ is the principal quantum number). The third quantization rule, from which the value of the integral of motion Λ can be determined, is nontrivial. It is convenient, in formulating this quantization rule, to choose from among the topologically equivalent contours lying on the invariant torus the contour that depends on the generalized coordinate ϑ, the angle between the Runge-Lenz vector and the z axis. The generalized momentum conjugate to this coordinate is the angular momentum component $l_\perp$ perpendicular to the plane passing through the z axis and the Runge-Lenz vector $\mathbf{A}$. Using the condition

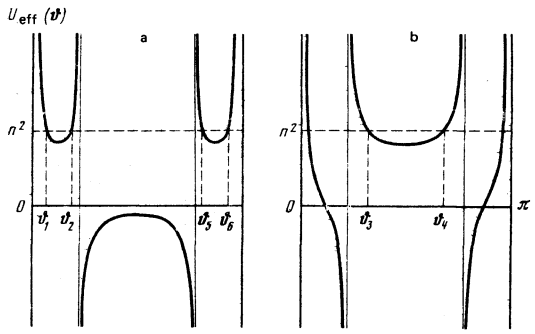

FIG. 1. The effective potential $U_{\text{eff}}(\vartheta)$: $l_\perp(\vartheta) = (n^2 - U_{\text{eff}}(\vartheta))^{1/2}$; a) for the case $\Lambda < 0$; b) for the case $\Lambda > 0$.

$$Al = A_\parallel l_\parallel + A_z l_z = 0,$$

($A^2 = A_\parallel^2 + A_z^2$ and $l^2 = l_\parallel^2 + l_\perp^2 + l_z^2$), we express $l_\perp$ in terms of the integrals of motion (6) and the angle ϑ:

$$l_\perp(\vartheta) = \left[l^2 - l_z^2 - \frac{A_z^2}{A_\parallel^2} l_z^2 \right]^{1/2} = \left[n^2 \left(1 + \frac{\Lambda}{1 - 5\sin^2\vartheta} \right) - \frac{m^2}{\sin^2\vartheta} \right]^{1/2}. \quad (7)$$

The expression under the radical sign in (7) has two first-order poles at $\vartheta = \vartheta_0$ and $\vartheta = \pi - \vartheta_0$, which specify the double cone Ω, whose role was discussed at the end of the preceding section.

To formulate the Bohr-Sommerfeld rules, we must analyze the roots of $l_\perp(\vartheta)$. Let us first discuss the case $m \neq 0$. Figure 1 shows the effective potential in which the ϑ motion occurs. Let us denote by ϑ_1, ϑ_2, ϑ_5, and ϑ_6 the $l_\perp(\vartheta)$ roots corresponding to the negative values of Λ and by ϑ_3 and ϑ_4 the roots for positive Λ. The roots lie in the interval $[0, \pi]$ in the following order:

$$0 < \vartheta_1 < \vartheta_2 < \vartheta_0 < \vartheta_3 < \vartheta_4 < \pi - \vartheta_0 < \vartheta_5 < \vartheta_6 < \pi$$

and are symmetric about the value $\vartheta = \pi/2$:

$$\vartheta_6 = \pi - \vartheta_1, \quad \vartheta_5 = \pi - \vartheta_2, \quad \vartheta_4 = \pi - \vartheta_3.$$

To determine the domain where the ϑ motion is classically allowed, we must take into account the sign of the quantity Λ besides the fact that $l_\perp(\vartheta)$ is real.

For negative values of Λ, the motion in the intervals $[\vartheta_1, \vartheta_2]$ and $[\vartheta_5, \vartheta_6]$ is classically allowed. Classical motion in the interval $[\vartheta_0, \pi - \vartheta_0]$ is impossible, although $l_\perp(\vartheta)$ is real there (see Fig. 1). The exclusion is due to the fact that the integral of motion Λ cannot, by definition, assume negative values in this interval. Thus, we obtain for negative Λ two alternative quantization rules corresponding to the two potential wells in the intervals $[0, \vartheta_0]$ and $[\pi - \vartheta_0, \pi]$:

$$I_1(\Lambda) = \int_{\vartheta_1}^{\vartheta_2} l_\perp(\vartheta)\, d\vartheta = \pi(k + 1/2), \quad (8)$$

$$I_2(\Lambda) = \int_{\vartheta_5}^{\vartheta_6} l_\perp(\vartheta)\, d\vartheta = \pi(k + 1/2), \quad k = 0, 1, 2, \ldots. \quad (9)$$

The exact wave functions of a hydrogen atom in a magnetic field have a definite parity with respect to the XY plane. Let us follow how the states with a definite parity arise in the present case. Since the potential wells in (8) and (9) are identical, the Λ values turn out to be doubly degenerate (see Fig. 1). The first quantization condition describes a state localized in the upper part of the double cone Ω ($0 < \vartheta < \vartheta_0$); the second, a state with the same Λ value in the lower part of the cone ($\pi - \vartheta_0 < \vartheta < \pi$). Owing to the degeneracy, we can construct from these states a quasiclassical wave function that is symmetric or antisymmetric with respect to the XY plane. The analysis of the roots of the function $l_\perp(\vartheta)$ shows that the states with $\Lambda < 0$ exist only when $m < n/\sqrt{5}$.

When $\Lambda > 0$, the region of classically allowed motion is the interval $[\vartheta_3, \vartheta_4]$. Classical motion with positive Λ is impossible in the intervals $[0, \vartheta_0]$ and $[\pi - \vartheta_0, \pi]$. The Λ values in this case are nondegenerate, and can be determined from the quantization conditions

$$I_3(\Lambda) = \int_{\vartheta_3}^{\vartheta_4} l_\perp(\vartheta)\, d\vartheta = \pi(k + 1/2), \quad k = 0, 1, 2, \ldots. \quad (10)$$

These states are localized outside the double cone Ω ($\vartheta_0 < \vartheta < \pi - \vartheta_0$), and their parity with respect to the XY plane is equal to $(-1)^k$.

The situation with $m = 0$ is somewhat different from the above-analyzed situation. In this case the roots ϑ_1 and ϑ_6 do not occur, and, instead of them, we must consider the singular points at $\vartheta = 0$ and $\vartheta = \pi$, which are due to the geometry of the problem. For $m = 0$ the trajectory of the electron lies in the fixed plane passing through the z axis, and characterized by the azimuthal angle φ_0. The quasiclassical state is represented by an ensemble of trajectories with an equiprobable φ_0 distribution; therefore, all the trajectories of the ensemble in question intersect on the z axis, and the z axis is a caustic. The crowding of the trajectories on the z axis has a geometric character, and reflects the crowding of the coordinate surfaces of the azimuthal angle in spherical coordinates. This is the cause of the singularities of the Lamé coefficients of the Laplace operator, that arise when the three-dimensional problem is reduced to a two-dimensional problem in spherical coordinates. The role of such singular points in the formulation of the quantization conditions is considered in, for example, Ref. 9 (§49), where it is shown that they are characterized by the same Morse index that characterizes an ordinary reversal point. Therefore, the quantization conditions for $m = 0$, $\Lambda < 0$ are formally obtained from the quantization conditions (8) and (9) by setting $\vartheta_1 = 0$ and $\vartheta_6 = \pi$. The quantization conditions for positive Λ remain unchanged.

The integrals entering into the quantization conditions (8), (9), and (10) cannot be computed analytically, but certain approximate expressions can be derived which provide a practically complete picture. Let us, to begin with, compute the number of states obtainable from the quantization conditions (8), (9), and (10) for fixed values of n and m. The number N of states is determined by the highest value of the variables $I_i(\Lambda)$ that is attained at $\Lambda = 0$ for all $I_i(\Lambda)$. The integrals in this case can be evaluated without difficulty, and we find as a result that

$$N = \frac{1}{\pi}[I_1(0) + I_2(0) + I_3(0)] = n - m.$$

This value coincides with the exact number of states

with given n and m, but we must take into account the fact that this number is distributed among the three quantization conditions, and instead of I_i we should take the integral part of $[I_i+\frac{1}{2}]$; therefore, we actually have $N=n-m, n-m\pm1$. The deviation by one of the number of states from the exact value is due to the fact that the states localized inside the cone Ω are doubly degenerate, and, therefore, when n is increased by one, new states of this type either do not appear at all, or they appear in pairs. The number of states will apparently turn out to be the correct one if we take into account the degeneracy-lifting exchange interaction between states with the same value of $\Lambda<0$.

The energy in first order perturbation theory can be expressed in terms of the value of ρ^2 averaged over the orbital period of the electron. Using (2) and (3), we obtain

$$E=E_0+\frac{\omega^2}{2}\overline{\rho^2}=-\frac{1}{2n^2}+\frac{\omega^2n^2}{4}(n^2+m^2+n^2\Lambda_k). \tag{11}$$

The Λ_k values are determined from the quantization conditions. The energy levels fan out from the unperturbed value as the magnetic field intensity is increased. Of greatest interest are the outermost levels in a given nm multiplet, since they are the first to undergo quasi-intersection in the course of the approach to each other of two neighboring multiplets. These energy levels correspond to the lowest levels in the effective potential wells in the quantization conditions (8), (9), and (10). For the levels lying at the bottom of a well, we can use the parabolic approximation for the effective potential. For $m=0$ the minimum of the effective potentials is attained for the quantization conditions (8), (9), and (10) at values of ϑ equal respectively to 0, π, and $\pi/2$. Computing Λ_k in this approximation, and substituting the result into (11), we obtain for the lowest energy levels in the multiplet ($\Lambda_k<0$ and the levels are doubly degenerate) the expression

$$E=-\frac{1}{2n^2}+\omega^2n^2\sqrt{5}\left(k+\frac{1}{2}\right)$$

$$\times[(5(2k+1)^2+n^2)^{1/2}-\sqrt{5}(2k+1)],\quad k=0,1,2,\ldots.$$

For the upper energy levels in the multiplet ($\Lambda_k>0$ and the levels are nondegenerate) we obtain the following approximate expression:

$$E=-\frac{1}{2n^2}+\frac{\omega^2n^2}{8}[5(2k'+1)^2+10n^2$$

$$-\sqrt{5}(2k'+1)(5(2k'+1)^2+16n^2)^{1/2}],\quad k'=0,1,2,\ldots.$$

The boundary between the degenerate and nondegenerate energy levels in the quasiclassical approximation is the value of E for $\Lambda=0$:

$$E=-1/2n^2+\omega^2n^4/4.$$

It is not possible to compute analytically the negative values of Λ_k for $m\neq0$ in this approximation.

4. THE QUANTUM PERTURBATION THEORY

The integral of motion Λ was obtained above in first order quasiclassical perturbation theory in terms of H^2. The equivalent procedure in quantum mechanics is to prove the assertion that the operator $\hat{\Lambda}=4\hat{A}^2-5\hat{A}_z^2$ commutes with the total Hamiltonian of the system in the subspace of hydrogenic wave functions with a fixed n value for highly excited states. But, as will be shown below, a stronger assertion is valid, namely, the operator $\hat{\Lambda}$ commutes with the total Hamiltonian of the system in an n-layer for any n. For this purpose it is sufficient to prove that the operator $\hat{\Lambda}$ commutes with the operator $\hat{\rho}^2$ in an n-layer, since the operator $\hat{\Lambda}$ is an exact integral of motion for the hydrogen atom in the absence of a magnetic field.

The matrix elements of the operator $\hat{\rho}^2$ in the basis of hydrogenic wave functions are given in, for example, Ref. 10. In spherical coordinates the nonzero matrix elements are the diagonal elements and the elements connecting states that differ in their orbital quantum numbers l by two[10]:

$$\langle nlm|\hat{\rho}^2|nlm\rangle=\frac{n^2[5n^2+1-3l(l+1)](l^2+l-1+m^2)}{(2l-1)(2l+3)}, \tag{12}$$

$$\langle nlm|\hat{\rho}^2|nl-2m\rangle=-\frac{5}{2}n^2\left\{\frac{(n^2-l^2)(l^2-m^2)[n^2-(l-1)^2][(l-1)^2-m^2]}{(2l+1)(2l-1)^2(2l-3)}\right\}^{1/2}.$$

For the computation of the matrix elements of the operator $\hat{A}^2$ let us use the operational equation[11]:

$$\hat{A}^2=1+2\hat{\mathscr{H}}_0(\hat{l}^2+1), \tag{13}$$

whence we find that the only nonzero matrix elements in the spherical basis are the diagonal elements, which are equal to

$$\langle nlm|\hat{A}^2|nlm\rangle=1-[l(l+1)+1]/n^2. \tag{14}$$

It is convenient to compute the matrix elements of the operator $\hat{A}_z^2$ first in parabolic coordinates, in which this operator is diagonal, and then go over to spherical coordinates. The coupling between the hydrogenic wave functions in spherical and parabolic coordinates is realized through the Clebsch-Gordan coefficients, and are given in, for example, Refs. 9 and 11. The information about the Clebsch-Gordan coefficients that is necessary for the computations can be found in Ref. 12. In spherical coordinates the matrix elements that are nonzero for the operator $\hat{A}_z^2$ turn out to be the same matrix elements that are nonzero for the operator $\hat{\rho}^2$. After simple computations, we obtain

$$\langle nlm|\hat{A}_z^2|nlm\rangle=\frac{1}{n^2}\left[\frac{(l^2-m^2)(n^2-l^2)}{(2l+1)(2l-1)}+\frac{[(l+1)^2-m^2][n^2-(l-1)^2]}{(2l+1)(2l+3)}\right], \tag{15}$$

$$\langle nlm|\hat{A}_z^2|nl-2m\rangle=\frac{1}{n^2}\left\{\frac{(n^2-l^2)(l^2-m^2)[n^2-(l-1)^2][(l-1)^2-m^2]}{(2l+1)(2l-1)^2(2l-3)}\right\}^{1/2}.$$

By gathering (12), (14), and (15) together, we can easily verify the following operational equation:

$$\hat{\rho}^2=n^2[n^2+m^2+3+n^2\hat{\Lambda}]/2, \tag{16}$$

which is satisfied in the subspace of hydrogenic wave functions with a fixed value of n. This relation differs from the quasiclassical relation (11) by a constant term. The appearance of such a discrepancy when we go over from classical to quantum mechanics is normal; for example, the equation (13) is obtained from the corresponding classical equation by formally replacing l^2 by $\hat{l}^2+1$. It is evident that the relation (16) is violated in the complete basis, since the matrix elements connecting hydrogenic states with different principal quan-

tum numbers are nonzero in the case of the operator $\hat{p}^2$, but zero in the case of the operator $\hat{\Lambda}$. The equation (16) is similar to the well-known operational equation in an n-layer $\mathrm{r}=-\frac{3}{2}n\hat{\mathrm{A}}$, which allows us to choose $\hat{l}_z$ and $\hat{A}_z$ as the independent integrals of motion in the solution of the problem of the hydrogen atom in a homogeneous electric field and separate the variables in parabolic coordinates. The operational equation (16) leads to a similar result. In Ref. 13, which is devoted to the separation of the variables for the hydrogen atom, among the various alternatives considered is one in which the independent integrals of motion are $\hat{l}_z$ and an operator that is quadratic in the components of the Runge-Lenz vector, a particular case of which is the operator $\hat{\Lambda}$. Using the results of that paper, we find that the Schrödinger equation for the hydrogen atom in a magnetic field admits of the separation of the variables accurate to H^4 in ellipsoidal-cylindrical coordinates on a sphere in four-dimensional momentum space.

The ellipsoidal-cylindrical coordinates on a sphere S_3 $(x_1^2+x_2^2+x_3^2+x_4^2=1)$ in momentum space are specified as follows:

$$\begin{aligned} &x_1=\mathrm{sn}\,\alpha\,\mathrm{dn}\,\beta\cos\varphi, \quad x_2=\mathrm{sn}\,\alpha\,\mathrm{dn}\,\beta\sin\varphi,\\ &x_3=\mathrm{dn}\,\alpha\,\mathrm{sn}\,\beta, \quad x_4=\mathrm{cn}\,\alpha\,\mathrm{cn}\,\beta,\\ &0\leqslant\alpha\leqslant 2K, \quad -K'\leqslant\beta\leqslant K', \quad 0\leqslant\varphi\leqslant 2\pi. \end{aligned} \tag{17}$$

When the operator $\hat{\Lambda}$ is chosen as an independent integral of motion, the elliptic Jacobi functions of the variables α and β have the moduli $k=1/\sqrt{5}$ and $k'=2/\sqrt{5}$ respectively. The real and imaginary periods of the Jacobi functions with modulus k are denoted by $4K$ and $4iK'$. As is well known, the Schrödinger equation for the hydrogen atom reduces in momentum space to an equation for the eigenfunctions of the angular part of the four-dimensional Laplacian. Representing the eigenfunctions of the Laplacian on the sphere S_3 in the form

$$\Psi=A(\alpha)B(\beta)e^{im\varphi},$$

we obtain the following equations for the functions $A(\alpha)$ and $B(\beta)$[13]:

$$\frac{1}{\mathrm{sn}\,\alpha}\frac{d}{d\alpha}\mathrm{sn}\,\alpha\frac{dA}{d\alpha}+\left[-\frac{1}{5}(n^2-1)\mathrm{sn}^2\alpha-\frac{m^2}{\mathrm{sn}^2\alpha}+b\right]A=0, \tag{18}$$

$$\frac{1}{\mathrm{dn}\,\beta}\frac{d}{d\beta}dn^2\beta\frac{dB}{d\beta}+\left[(n^2-1)dn^2\beta+\frac{m^2}{5\,\mathrm{dn}^2\beta}-b\right]B=0, \tag{19}$$

where b is the eigenvalue of the operator

$$\hat{M}=k^2n^2\hat{\Lambda}+m^2+k^2(n^2-1).$$

Equations (18) and (19) can be reduced to the Lamé equations, and the solution of these equations is analyzed in detail in Ref. 13. We can, by going over to the new variable by setting $\alpha=K+iK'+ia$, easily verify that Eq. (18) coincides with Eq. (19), and therefore the eigenfunctions Ψ have the form[13]

$$\Psi_{nms}=F_{nm}^{s}(\mathrm{dn}\,\beta)F_{nm}^{s}(k\,\mathrm{sn}\,\alpha)e^{im\varphi}, \tag{20}$$

where $F_{nm}^{s}(x)$ is a polynomial of degree s in x. The eigenfunctions Ψ_{nms} are the correct wave functions in the zeroth approximation for the hydrogen atom in a weak magnetic field.

5. CONCLUSION

In Refs. 1 and 2 the exponential decrease of the energy level splitting at the points of quasi-intersection is related to the existence of an approximate symmetry, but it should be noted that the presence of an approximate symmetry *per se* cannot yet explain such behavior of the splitting. For example, the problem of the Stark effect for the alkali atoms also possesses an approximate symmetry, which is used in Ref. 5 to compute the energy level splitting at the quasi-intersection points, but in this case the splitting behaves like n^{-3}. The exponential decrease of the splitting in the problem of the hydrogen atom in a magnetic field is caused by the separation, peculiar to the present problem, of the states into two classes ($\Lambda_k<0$ and $\Lambda_k>0$) localized in the quasiclassical approximation in two nonoverlapping regions, and therefore the splitting is determined by the product of wave functions in a classically forbidden region, where they are exponentially small. This situation is similar to the quasi-intersection in the one-dimensional problem of two energy levels corresponding to states localized in different potential wells, which problem is characterized by the exponential dependence of the splitting on its parameters. If we consider two states belonging to the same class (i.e., with the same sign of Λ), then in this case the splitting should decrease in a power-law fashion with increasing n (apparently like n^{-3}). It is evident that any matrix element connecting states from different classes will be exponentially small. This pertains, for example, to oscillator strengths, for which there thus arise additional approximate selection rules.

The results obtained indicate that, besides the well-known separation of states with a fixed m according to parity, there exists an approximate separation connected with the sign of Λ. Thus, it is natural to distinguish four classes of states: ψ^{+}_{mg}, ψ^{-}_{mg}, ψ^{+}_{mu}, and ψ^{-}_{mu} [the subscripts g and u specify, as usual, the parity of the states, while the superscripts (±) specify the sign of Λ]. If the subscripts of two states are different, then, as is well known, quasi-intersection becomes exact intersection for these states. For states that differ only in their superscripts, the splitting is exponentially small when the parameter n is large. And, finally, when all the three indices coincide, the splitting is a power function of n.

The results obtained in the present paper allow us to qualitatively explain the exponential decrease, reported in Refs. 1 and 2, of the energy level splitting, but it is at present not clear how the magnitude of this splitting can be analytically estimated. To obtain such estimates in the quasiclassical approximation, we must distinguish the effective barrier separating the states localized inside and outside the cone Ω, and compute the subbarrier factor, but there arises in this procedure an unusual situation in which under the quantization conditions (8) and (9) motion in the region $\vartheta_0<\vartheta<\pi-\vartheta_0$ is, on the one hand, classically allowed on the basis of the requirement that $l_\perp(\vartheta)$ be real (see Fig. 1), and, on the other, impossible for a chosen sign of Λ. A similar picture is obtained in the case of the quantization condition (10).

The quantum perturbation theory also does not provide us with a natural procedure by which the splitting can be analytically estimated. The point is that states localized in different regions are obtained not in momentum space, in which Eqs. (18) and (19) are written, but for the generalized coordinate ϑ. Thus, we have left the possibility of a numerical computation of the splitting in terms of the total Hamiltonian's matrix element connecting correct wave functions (20) of the zeroth approximation. In fact, such a computation is performed in Ref. 1. It yields a result that is in good agreement with the experimental data.[2]

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[1]M. L. Zimmerman, M. M. Kash, and D. Kleppner, Phys. Rev. Lett. **45**, 1092 (1980).
[2]D. Delande and J. C. Gay, Phys. Lett. A **82**, 393 (1981).
[3]J.-J. Labarthe, J. Phys. B **14**, L467 (1981).
[4]C. W. Clark, Phys. Rev. A **24**, 605 (1981).
[5]I. V. Komarov, T. P. Grozdanov, and R. K. Janev, J. Phys. B **13**, L573 (1980).
[6]E. A. Solov'ev, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 278 (1981) [JETP Lett. **34**, 265 (1981)].
[7]W. Pauli, Trudy po kvantovoĭ teorii (Collected Works on Quantum Mechanics), Nauka, Moscow, 1975.
[8]L. D. Landau and E. M. Lifshitz, Mekhanika (Mechanics), Nauka, Moscow, 1965 (Eng. Transl., Pergamon Press, Oxford, 1969).
[9]L. D. Landau and E. M. Lifshitz, Kvantovaya Mekhanika (Quantum Mechanics), Nauka, Moscow, 1974 (Eng. Transl., Pergamon Press, Oxford, 1977).
[10]R. H. Garstang, Rep. Prog. Phys. **40**, 105 (1977).
[11]A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, Rasseyanie, reaktsii i raspady v nerelyativistskoĭ kvantovoĭ mekhanike (Scattering, Reactions, and Decay in Nonrelativistic Quantum Mechanics), Nauka, Moscow, 1971 (Eng. Transl., Wiley, New York, 1969).
[12]D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, Kvantovaya teoriya uglovogo momenta (Quantum Theory of Angular Momenta), Nauka, Moscow, 1975.
[13]E. G. Kalnins, W. Miller, and P. Winternitz, Siam. J. Appl. Math. **30**, 630 (1976).

Note added in proof (27 *March* 1982). As analysis of the Schrödinger equation in ellipsoidal-cylindrical coordinates shows, the energy level splitting at a quasi-intersection point can be computed as the subbarrier factor in the effective potential shown in Fig. 1. The subbarrier factor should be computed in the interval $0<\vartheta<\vartheta_0$ with $\Lambda=-1$ and in the interval $\vartheta_0<\vartheta<\pi/2$ with $\Lambda=4$. We then obtain for the splitting the estimate

$$\Delta E\approx\exp\{-n\ln[(\sqrt{5}+2)(\sqrt{5}+1)/2]\}\approx\exp(-1.92n),$$

which is in good agreement with the results of the numerical computation and the experimental data.[1,2]

A convincing demonstration of the existence of the approximate symmetry is contained in Clark and Taylor's papers. [J. Phys. B **13**, L737 (1980); Nature (London) **292**, 437 (1981)], in which the oscillator strengths of hydrogen in a magnetic field are computed. The author is deeply grateful to C. W. Clark for the communication concerning these papers.

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