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The Zeeman effect for the 'anistropic hydrogen atom' in the complex WKB approximation: I. Quantization of closed orbits for the Pauli operator with spin–orbit interaction

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Abstract. Using the complex WKB method, new semiclassical spectral series for perturbed states of an 'anisotropic' hydrogen atom, taking into account the electron's spin polarization in a homogeneous magnetic field (the anomalous Zeeman effect) are constructed. They are valid uniformly for all values of the field's magnitude. These series correspond to families (stable in the linear approximation) of periodic and conditionally periodic motions of a classical electron in the plane orthogonal to the direction of the field. The corresponding semiclassical wavefunctions have the property of quantum 'superscaring' in the coordinate space near these classical trajectories of motion. We obtain the limit cases of our semiclassical energy levels for strong and weak magnetic fields. We compare them with the only known approximations, i.e. for the hydrogen atom.

1. Introduction

We consider the following spectral problem

$$\hat{H}_{\mathrm{p}}\Psi = E\Psi \qquad \Psi \in L_2(\mathbb{R}^3_{x,y,z}) \times \mathbb{C}^2 \qquad \Psi = {}^t(\Psi_1, \Psi_2) \tag{1}$$

where the quantum Hamiltonian $\hat{H}_{\mathrm{p}}$ has the form

$$\begin{aligned} &\hat{H}_{\mathrm{p}} = \hat{H}_{\mathrm{s}} + \hat{H}_{\mathrm{s-f}} \\ &\hat{H}_{\mathrm{s}} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}A\right)^2 + V_\gamma(x,y,z) \qquad V_\gamma = -\frac{e^2}{\sqrt{x^2+y^2+\gamma z^2}} \\ &\hat{V}_{\mathrm{s-f}} = -\frac{e\hbar}{2mc}\langle\sigma, H\rangle - \frac{e\hbar}{4m^2c^2}\left\langle\sigma, E\times\left(-i\hbar\nabla - \frac{e}{c}A\right)\right\rangle. \end{aligned} \tag{2}$$

Here $\gamma > 0$ is the parameter of anisotropy of the scalar potential $V_\gamma(q)$, $q = (x, y, z)$, $A = \frac{1}{2}H_0(-y, x, 0)$ is the vector potential of a homogeneous magnetic field, $\hat{V}_{\mathrm{s-f}}$ is the operator of interaction between the spin and the external field, $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ are the Pauli matrices; $eE = -\nabla V_\gamma(q)$, $H = \nabla \times A$. When $\gamma = 1$ the problem (1)–(2) is known as the *anomalous Zeeman effect* problem [1].

The exact solution of (1)–(2) is known only in two cases: when there is no magnetic field and $\gamma = 1$, i.e. when the operator $\hat{H}_{\mathrm{p}}$ is the Hamiltonian of the hydrogen atom, and when $V_\gamma = 0$, i.e. in a purely homogeneous magnetic field. For the electron without spin ($\hat{V}_{\mathrm{s-f}} = 0$), $\gamma = 1$ and $H_0 \neq 0$ (1)–(2) is one of the oldest and most difficult problems of

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quantum mechanics: the problem of calculating the splitting of atomic energy levels in a homogeneous magnetic field (the *Zeeman effect*) [1]. When $H_0 = 0$, $\gamma \neq 1$, problem (1)–(2) is the quantum analogue of the *anisotropic Kepler problem* (AKP). This model, which arose in solid state theory, became popular in connection with the study of the chaotic behaviour of classically non-integrable systems and their quantum analogues (see [2]).

For the Zeeman effect, well known approximation methods, such as regular perturbations [3–7], the averaging method [8], or adiabatic approximation [9, 10] give quite good results, either for weak or strong magnetic fields (see, e.g., the surveys [11–14]). For all these methods the intermediate domain of magnetic field, $H_0 \sim 10^8$–10^{10} G, is the most difficult for analysis because, in this domain, magnetic and Coulomb interactions are of the same order. In the general case, when $H_0 \neq 0$, $\gamma \neq 1$, it is not clear how to use perturbation theory. For example, in a weak magnetic field, the quantum unperturbed system (for $H_0 = 0$) is also non-integrable. Nevertheless, in this general case we obtain, in this paper, concrete information about the spectrum.

The main result of this first part is the following: we give new quite effective formulae for subsequences of asymptotic as $\hbar \to 0$ eigenfunctions $\Psi_{n,\zeta}(q,\hbar)$, (n, ζ are quantum numbers, $n = (n_1, n_2, n_3)$, $n_i \in \mathbb{Z}$; $i = 1, 2, 3$, $\zeta = \pm 1$—the spin of the electron) and eigenvalues $E_{n,\zeta}(\hbar)$ of problem (1) in the most general case ($H_0 \neq 0$, $\gamma \neq 1$, both of arbitrary magnitude and $V_{s-f} \neq 0$), in other words, we construct semiclassical spectral series $(\Psi_{n,\zeta}(q,\hbar), E_{n,\zeta}(\hbar))$, related to some special regular types of motion of the corresponding non-integrable classical system

$$\dot{p} = -H_q \qquad \dot{q} = H_p \qquad q = (x, y, z) \qquad p = (p_x, p_y, p_z)$$

$$H(p,q) = H_s(p,q) = \frac{1}{2m}\left(p - \frac{e}{2c}[H,q]\right)^2 - e^2 \Big/ \sqrt{x^2 + y^2 + \gamma z^2}. \quad (3)$$

The semiclassical approximation we use is based on a new general approach founded on *Maslov's complex germ theory* [15]. This method is called the *complex WKB method* ([29–32]). The semiclassical approximation ($\hbar \to 0$) based on the traditional multidimensional WKB method ([16–24]) is not applicable, because the associated classical system is non-integrable (in the sense of Liouville), and therefore does not possess a family of three-dimensional invariant Lagrangian tori.

Moreover, as has been shown (see surveys [11, 12, 25]), in special cases, namely, for the AKP ($H_0 = 0$, $\gamma \neq 1$) and the Zeeman effect, there exists a region of parameters (energy E and projection of the orbital momentum I) for which the motion of the classical system in phase space is completely chaotic (hard chaos).

For the AKP, Gutzwiller was the first [26, 27] to discover hard chaos in the neighbourhood of $I = 0$ (see [2]). The hydrogen atom in a magnetic field ($\gamma = 1$) is a real classically non-integrable system with soft chaos This fact was considered in several places (see surveys [11, 25]). In particular, a detailed classification of regular and irregular types of motion of the electron, in accordance with the value of the integrals E and I, is performed, on the basis of numerical methods, in [28].

In the present paper we obtain information about the behaviour of sequences of individual eigenfunctions and eigenvalues (spectral series) for problem (1)–(2) *under the condition* $|I| \neq 0$ within the frame of the complex WKB method†. This method, developed in [29–32] is based, as we stated above, on the general complex germ theory [15, 29]. Essentially, it is a simplified construction of the Maslov canonical operator with complex phase. This construction is adapted to the solution of spectral problems for scalar and matrix

† For the quantum AKP ($\gamma = \text{const} \neq 1$, $H_0 = 0$) and the hydrogen atom in a magnetic field the semiclassical spectral series were constructed in [33, 34] respectively.

(pseudo) differential operators (see [32]) corresponding to both classically integrable and *non-integrable* Hamiltonian systems.

In the semiclassical approach to spectral problems, one can construct only partial spectral series in a certain domain of the energy spectrum, dependent on $\hbar$ ($\hbar \to 0$). In complex germ theory the classification of semiclassical spectral series is based on geometrical objects in phase space, generated by solutions of the classical equations of motion. These objects are known as isotropic (Lagrangian of less than full dimension) manifolds of dimension $k, 0 \leqslant k < n$, where n is the dimension of the configuration space of the classical system. If the motion of the system takes place in a bounded domain, they are isotropic (small-dimensional) tori.

A fundamental difference between quantization of full dimensional tori and tori of less than full dimension Λ^k, $k \leqslant n$, is that the last must be stable in the linear approximation. So conditions are imposed on the solutions of the Hamiltonian linear system in variations along Λ^k. The geometric object formed with these *complex* solutions is called the *complex germ*. It is a vector bundle with a basis on Λ^k. In particular, when $k = 1$ and Λ^1 is a closed phase curve, the existence of the complex germ is equivalent to the stability of Λ^1 in the linear approximation, i.e. the phase curve Λ^1 is of elliptic type.

For the AKP in a homogeneous magnetic field (non-integrable Hamiltonian system with one cycle variable) we construct the semiclassical spectral series corresponding to families of isotropic tori of dimension $k = 1$ (part I) and $k = 2$ (part II). They are generated by the motion of the classical electron in the plane ($z = 0$) perpendicular to the direction of the magnetic field $\boldsymbol{H}_0$.

Finally, we note that, in contrast to the real multidimensional WKB method, the phase S of the semiclassical germ asymptotics of wavefunctions $\Psi_E \sim \exp(\mathrm{i}S/\hbar)\varphi$ is complex, and $\operatorname{Im} S \geqslant 0$. Due to this fact, the functions $\Psi_E(x, \hbar)$ have the following typical property in the limit (as $\hbar \to 0$): they are located in a small (of order $\sqrt{\hbar}$) neighbourhood of the domain of light D_x^k, where $\operatorname{Im} S(x) = 0$. This domain is the projection of the family of phase trajectories forming the isotropic tori Λ^k on the configuration space. The dimension k of D_x^k is less than the dimension n of the configuration space R_x^n. Having in mind this property of semiclassical wavefunctions in spectral problems, we use the term 'superscar' near D_x^k following the pioneer work [35]. In [35] Heller discovered the 'scarring' phenomenon for *isolated* unstable periodic orbits in the stadium potential and introduced the notion of 'superscar' ([35] p 1517) for the wavefunctions corresponding to *non-isolated* (neutrally stable) periodic orbits. The power of the quantum superscarring depends on the geometry of the projection D_x^k and can have singularities with respect to $\hbar$, $\hbar \to 0$, in the vicinity of the focal points and caustics lying in D_x^k (see the details in [30, 32] and in part II of this work).

For closed phase curves Λ^1 without focal points, WKB asymptotics with complex phases can be constructed by means of Gaussian packets (or squeezed states)

$$\Psi_E \sim C(t) \exp\left(\frac{\mathrm{i}}{\hbar} S_{\mathrm{cl}}(t)\right) \exp\left(-\frac{1}{2\hbar}\langle D(t)(x - x_{\mathrm{cl}}), x - x_{\mathrm{cl}}\rangle\right) \exp\left(\frac{\mathrm{i}}{\hbar}\langle p_{\mathrm{cl}}(t), x - x_{\mathrm{cl}}\rangle\right) (*).$$

Here t is the 'intrinsic time' along the trajectory $\Lambda^1 = (x, p : x = x_{\mathrm{cl}}(t), p = p_{\mathrm{cl}}(t))$, $\operatorname{Re} D(t) > 0$, and the amplitude $C(t)$ has no singularities.

This ansatz was proposed in [36, 37] for the case of closed geodesics. The construction of localized states in the vicinity of closed phase curves is also discussed in [38–41]. In the general case for isotropic tori Λ^k, $k \geqslant 1$, with focal points, the localized states ansatz generalizing (*) was proposed in [30].

From the point of view of obtaining specific numerical results from our formulae for *scalar* Hamiltonians, our method reduces the computation of the perturbed energy level spectrum, in the entire range of the magnetic field, to the investigation of two systems of differential equations: the Hamiltonian system and its system in variations. (We find particular solutions that generate isotropic tori with projections onto $\mathbb{R}^3_x$ lying in the plane $z = 0$). In this part of the work we consider a special family $\Lambda^1(I)$ of closed phase trajectories, namely circles, being stationary motions or the relative equilibria. For the family $\Lambda^1(I)$ we must solve one algebraic equation of the fourth degree with respect to the equilibrium radius $R_0(I)$, and the equations in variations are reduced to a system with constant coefficients†. To apply the complex WKB method to spectral problems with *matrix* Hamiltonians such as (1)–(2), we have to integrate a third system of differential equations for the spin correction (the polarization equation). In [42, 43] families of closed orbits and two-dimensional Lagrangian (isotropic) tori for the system of Dirac equations were quantized by this method. Also in those papers, the polarization equation for the spin of a relativistic electron is deduced. In the (non-relativistic) problem we consider here, the equation of polarization is a limit of the polarization equation from [42, 43] with respect to the relativity parameter v/c, with v the speed of the electron. In particular, for $\Lambda^1(E)$ this equation is reduced to a system of two linear ordinary differential equations with constant coefficients.

It is essential to note that our formulae for the semiclassical spectral series are valid for all values of the magnetic field, including those from the intermediate domain and for all values of parameter γ. We obtain formulae for the semiclassical energy levels and wavefunctions for problem (1)–(2), simple enough for its analysis, in the two limit cases of weak ($H_0 \to 0$) and strong ($H_0 \to \infty$) magnetic fields. This is the second (practical) result of the present paper.

The complex WKB method formulae, as well as the formulae of any other method of semiclassical ($\hbar \to 0$) approximation of quantum mechanics, have a non-perturbative character with respect to other classical parameters within the systems; in our case with respect to the parameters H_0 and γ. Consequently, if in a neighbourhood of any characteristic value of such parameters there is no bifurcation in the classical equations (Newton equation, equations in variations and the electron's spin polarization equation) that define the semiclassical asymptotics of problem (1)–(2)‡, then the semiclassical formulae for the spectrum and wavefunctions will regularly (smoothly) depend on these classical parameters.

The structure of the paper is as follows. In section 2 we give a rigorous statement of the problem. In sections 3–5 we quantize the family of closed phase curves $\Lambda^1(I)$ and give the results of calculation. In sections 6 and 7 we study the behaviour of the semiclassical energy levels in the limit cases of weak and strong magnetic fields. In section 8 a comparison is given between these limit cases of our formulae for $\gamma = 1$ and previously known results.

2. General statement of the problem

The complex WKB method allows us to associate the semiclassical spectral series $(E_{n,\zeta}, \Psi_{n,\zeta})$ of the quantum matrix problem (1), with families of invariant (orbitally stable)

† The more complicated case of two-dimensional isotropic tori Λ^2 requires some auxiliary constructions and will be considered in part II of this work.

‡ In particular Λ^1 lies beyond a neighbourhood of separatrices (independent of $\hbar$), and the system in variations is strongly stable in the sense of the Gelfand–Krein–Lidskii theory [44] (all the eigenvalues of the reduced monodromy matrix are different and lie on the unit circle).

isotropic tori $\Lambda^k(\omega)$, $0 \leqslant k < 3$, of the corresponding classical system. In the case under consideration this classical system is

$$\dot{p} = -\nabla_q H_s(p,q) \qquad \dot{p} = \nabla_p H_s(p,q)$$
$$(p = (p_x, p_y, p_z) \in \mathbb{R}^3_p \; q = (x,y,z) \in \mathbb{R}^3_q) \tag{4}$$

with the Hamiltonian

$$H = H_s(p,q) = \frac{1}{2m}\left(p - \frac{e}{c}A\right)^2 + V_\gamma(q). \tag{5}$$

A rigorous statement of the problem; for problem (1) we construct semiclassical series for the spectrum and for the asymptotic eigenfunctions, i.e. spectral series; this means the following. Let $E = E^{\mathrm{cl}}$ be a fixed value of the spectral parameter E, and suppose that the energy level $M_{E^{\mathrm{cl}}}$ of the Hamiltonian function (5) corresponding to the operator $\hat{H}_s$, $M_{E^{\mathrm{cl}}} = \{(p,q), H_s(p,q) = E^{\mathrm{cl}}\}$, contains a k-dimensional isotropic torus $\Lambda^k(E^{\mathrm{cl}})$ invariant with respect to phase flow $g^t_H : \Lambda^k(E_0) = g^t_H \Lambda^k(E_0, t \in \mathbb{R}^1$. This means that the entire trajectory

$$\{r_t(p_0,q_0) = (p = p(t,p_0,q_0), q = q(t,p_0,q_0)) \; t \in \mathbb{R}^1 \; (p_0,q_0) \in \mathbb{R}^3_p \times \mathbb{R}^3_q\}$$

of the Hamiltonian system (4), starting from an arbitrary point $r_0 = (p_0, q_0)$ on $\Lambda^k(E^{\mathrm{cl}})$, lies on $\Lambda^k(E^{\mathrm{cl}})$, i.e., $r_t(p_0,q_0) = g^t_H(r_0) \in \Lambda^k(E^{\mathrm{cl}})$, $t \in \mathbb{R}^1$. In other words, the phase flow g^t_H leaves the invariant torus $\Lambda^k(E^{\mathrm{cl}})$ in its place, and shifts the points of the phase space $\mathbb{R}^3_p \times \mathbb{R}^3_q$ that lie on $\Lambda^k(E^{\mathrm{cl}})$ along the trajectories of (4).

A sequence of values $E_{n,\zeta} = E_{n,\zeta}(\hbar)$, where the number $n = (n_1, n_2, n_3)$, in general, can depend on $\hbar(\zeta = \pm 1)$, and a sequence of functions $\Psi_{E_{n,\zeta}(\hbar)}(q,\hbar) \in L_2(\mathbb{R}^3_q) \times \mathbb{C}^2$, $\hbar \in (0,1]$ are called *semiclassical spectral series* for problem (1)–(2), corresponding to the k-dimensional isotropic torus $\Lambda^k(E^{\mathrm{cl}})$ as $\hbar \to 0$, if the following conditions hold.

(i) $E_{n,\zeta}(\hbar) \to E^{\mathrm{cl}}$ as $\hbar \to 0$ (correspondence of the semiclassical spectral series $E_{n,\zeta}(\hbar)$ to classical motion on the level E^{cl});

(ii) $\Psi_{E_{n,\zeta}(\hbar)}(q,\hbar) = O(1)$ for almost all† $q \in D^k_q(E^{\mathrm{cl}})$ and $\Psi_{E_{n,\zeta}(\hbar)}(q,\hbar) = O(\hbar^\infty)$ for $q \notin D^k_q(E^{\mathrm{cl}})$ where $D^k_q(E^{\mathrm{cl}})$ is the projection of $\Lambda^k(E^{\mathrm{cl}})$ on the configuration space R^3_q (correspondence of the semiclassical series for the (asymptotic) eigenfunctions $\Psi_{E_{n,\zeta}(\hbar)}(q,\hbar)$ to the isotropic torus $\Lambda^k(E^{\mathrm{cl}})$);

(iii) $\|(\hat{H} - E_{n,\zeta}(\hbar))\Psi_{E_{n,\zeta}(\hbar)}(q,\hbar)\|_{L_2(\mathbb{R}^3_q)\times\mathbb{C}^2} = O(\hbar^{3/2})$ as $\hbar \to 0$ (formal asymptotics condition).

In broad outlines, for problem (1) the orbital ($q = (x,y,z)$) and spin ($\zeta = \pm 1$) variables can be separated up to $O(\hbar^2)$ in the semiclassical approximation ($\hbar \to 0$). Namely, the semiclassical spectral series of the initial spectral problem has the following structure outside neighbourhoods of focal points:

$$\Psi_{n,\zeta}(q,\hbar) = \Psi_n(q,\hbar) f_\zeta(q) \qquad E_{n,\zeta}(\hbar) = E_n(\hbar) + \hbar\mu_\zeta + O(\hbar^2). \tag{6}$$

Here $(E_n(\hbar), \Psi_n(q,\hbar))$ is the semiclassical spectral series of the scalar Schrödinger operator $\hat{H}_s$:

$$\hat{H}_s \Psi_E(q,\hbar) = E\Psi_E(q,\hbar) \qquad \Psi_E(q,\hbar) \in L_2(\mathbb{R}^3_q) \tag{7}$$

$$\hat{H}_s = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{2c}[H,q]\right)^2 - \frac{e^2}{\sqrt{x^2+y^2+\gamma z^2}} \qquad q = (x,y,z) \tag{8}$$

† Except for focal points or points lying on caustics. At such points the solution is singular in $\hbar$ as $\hbar \to 0$ (for details, see [31,32]).

(E is the spectral parameter), and μ_ζ, $f_\zeta(q)$ are a solution of the spectral problem for the polarization equation on Λ^k:

$$-\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}f_\zeta + \Pi|_{\Lambda^k} f_\zeta = \mu_\zeta f_\zeta \qquad f_\zeta : \Lambda^k \to \mathbb{C}^2 \tag{9}$$

where the polarization matrix Π has the form

$$\Pi = -\frac{e}{2mc}\left\langle \sigma, \boldsymbol{H}(q) - \frac{1}{2mc}[\boldsymbol{E}(q) \times p]\right\rangle \tag{10}$$

and $\mathrm{d}/\mathrm{d}t$ means differentiation along the trajectories of system (4).

Remark. The correction μ_ζ, $\zeta = \pm 1$ to the spectrum of the scalar particle is analogous to the Berry phase correction [46]. In contrast to the scalar problem (7), the spectral problem (9) on the invariant torus Λ^k has a smooth solution for the spin contribution f_ζ of the wavefunction, in particular in the vicinity of the focal points (in the orbital variables), where branching of the scalar part $\Psi_n(q, \hbar)$ of the semiclassical wavefunction $\Psi_{n,\zeta}(q, \hbar)$ occurs.

3. Semiclassical spectral series of the Schrödinger operator

Here we construct semiclassical spectral series for the spectral problem (7)–(8). In section 4 we will find the solution for the spectral problem for the polarization (9). With these two results we write down in section 5 the general semiclassical formulae. Since operator $\hat{H}_s$ is invariant with respect to the rotation about the axis 0z, parallel to the field $\boldsymbol{H} = (0, 0, H_0)$, the classical system possesses a motion integral p_φ—the projection of the orbital momentum on the axis 0z. Let us pass to cylindrical coordinates ρ, z, φ. The classical Hamiltonian for operator (8) is

$$H = H_s(p, p_\varphi, q) = \frac{p_\rho^2}{2m} + \frac{p_z^2}{2m} + \frac{p_\varphi^2}{2m\rho^2} + \tfrac{1}{8}m\omega_H^2\rho^2 - \frac{e_0^2}{(\rho^2 + \gamma z^2)^{1/2}} + \tfrac{1}{2}\omega_H p_\varphi \tag{11}$$

where the variables p_ρ, p_z and p_φ are canonically conjugate to the variables ρ, z, $\varphi(\mathrm{mod}\, 2\pi)$, $p = (p_\rho, p_z)$, $\omega_H = e_0 H_0/mc$ is the cyclotron frequency, $e = -e_0$, $e_0 > 0$, is the charge and m is the mass of the electron.

In a Hamiltonian system with a cyclic (angular) variable one can always single out a special family of closed trajectories—circles, which are stationary motions or relative equilibrium states of the system in reduced phase space (cf [45]). For each value $I \in \mathbb{R}^1$ of the 'momentum' integral ($p_\varphi = I$), the curve

$$\Lambda^1(I) = \{p_\rho = 0, p_z = 0, p_\varphi = I, \rho = R_0(I), z = 0, \varphi = \omega_0(I)t + \varphi_0, t \in \mathbb{R}\} \tag{12}$$

is a closed trajectory of the Hamiltonian system (4)–(5). It lies on the energy level $E = \alpha(I)$ of the function $H_s(p, I, q)$ given by (11).

$$E = \alpha(I) = \frac{\omega_H I}{2} - \frac{e_0^2}{2R_0(I)} + \frac{m\omega_H^2 R_0^2(I)}{4}. \tag{13}$$

The frequency of rotation is

$$\omega_0(I) = \partial H/\partial p_\varphi(0, 0, I, R_0(I), 0) = \omega_H/2 + I/(mR_0^2(I)). \tag{14}$$

Here $R_0(I)$ is a critical point of the 'effective' potential

$$V_I(\rho, z) = \frac{I^2}{2m\rho^2} + \frac{m\omega_H^2\rho^2}{8} - \frac{e_0^2}{(\rho^2 + \gamma z^2)^{1/2}} \tag{15}$$

in the plane $z = 0$. Thus $R_0(I)$ is a solution of the equation

$$m^2\omega_H^2 R_0^4/4 + e_0^2 m R_0 = I^2 \qquad (\Rightarrow R_0 = R_0(I)). \tag{16}$$

The frequencies $\omega_1(I)$ of radial and $\omega_2(I)$ of axial oscillations of the Hamiltonian system linearized in a neighbourhood of the equilibrium point $p_\rho = p_z = 0$, $\rho = R_0(I)$, $z = 0$ in reduced phase space $\mathbb{R}_p^2 \times \mathbb{R}_q^2$ ($p = (p_\rho, p_z)$ and $q = (\rho, z)$) can be easily calculated:

$$\omega_1(I) = \omega_\rho = (\omega_H^2 + \gamma^{-1}\omega_z^2(I))^{1/2} \qquad \omega_2(I) = \omega_z = \left(\frac{\gamma e_0^2}{m R_0^3(I)}\right)^{1/2}. \tag{17}$$

Following [34] the quantization condition for the family $\Lambda^1(I)$ becomes

$$\frac{1}{2\pi\hbar}\oint_{\Lambda^1(I)} p\,\mathrm{d}q = \sum_{j=1}^{2}\frac{\beta_j(I)}{2\pi}(\nu_j + \tfrac{1}{2}) + l \qquad (l = \pm 1, \pm 2, \ldots\ \nu_j = 0, 1, 2, \ldots\ j = 1, 2). \tag{18}$$

The topological characteristics $\beta_j(I)$, $j = 1, 2$ of the complex germ $r^3(\Lambda^1(I))$ are related to the frequencies of rotation $\omega_0(I)$ and of radial and axial oscillations by the following relation (see [31, 32])

$$\beta_j(I)/2\pi = \omega_j(I)/\omega_0(I) \qquad j = 1, 2.$$

Notice that for this approximation the orbital quantum number $l = l(\hbar)$ is a large parameter, $|l| \gg 1$. It is connected with the parameter $\hbar$, $\hbar \to 0$ by the condition $l(\hbar)\hbar \to I^{\mathrm{cl}}$, where the orbital momentum I^{cl} corresponds to the fixed energy E^{cl} of the classical system due to relation $E^{\mathrm{cl}} = \alpha(I^{\mathrm{cl}})$ (13).

Condition (18) gives us a discrete sequence of quantized values of the orbital momentum $I = I_{l,\nu_1,\nu_2}(\hbar)$. Then the semiclassical energy levels that correspond, in the limit as $\hbar \to 0$, to the family of closed trajectories Λ^1(12) near the classical energy $E^{\mathrm{cl}} = \alpha(I^{\mathrm{cl}})$ (see introduction) are defined by the formula

$$E_{l,\nu_1,\nu_2} = H_s|_{\Lambda^1(I_{l,\nu_1,\nu_2}(\hbar))} = \alpha(I_{l,\nu_1,\nu_2}(\hbar)).$$

Using the Taylor series $E = E^0 + \hbar E^1 + \mathrm{O}(\hbar^2)$ in $\hbar \to 0$ and the well known formula $(1/2\pi)\partial/\partial E \oint_{\Lambda^1(I)} p\,\mathrm{d}q = \omega_0(I)^{-1}$ [45] it is not difficult to show that the upper formula for E_{l,ν_1,ν_2} is equivalent (up to $\mathrm{O}(\hbar^2)$, $\hbar \to 0$) to the formula for the spectrum in the 'oscillator approximation':

$$E = E_{l,\nu_1,\nu_2}(\hbar) = E_l^{(0)}(\hbar) + \hbar E_{l,\nu_1,\nu_2}^{(1)}(\hbar) + \mathrm{O}(\hbar^2). \tag{19}$$

$E_l^{(0)}(\hbar)$ is the energy of the electron on the equilibrium orbit, quantized by (18):

$$E_l^{(0)}(\hbar) = \alpha(I = l\hbar) = \tfrac{1}{2}\omega_H\hbar l - \frac{e_0^2}{2R_0(l\hbar)} + \tfrac{1}{4}m\omega_H^2 R_0^2(l\hbar) \tag{20}$$

and $\hbar E_{l,\nu_1,\nu_2}^{(1)}(\hbar)$ is the energy of small oscillations with frequencies $\omega_j(I)$, $j = 1, 2$ ((17) with $I = l\hbar$) near the equilibrium point $\rho = R_0(I)$, $z = 0$,

$$E_{l,\nu_1,\nu_2}^{(1)}(\hbar) = \sum_{j=1}^{2}\omega_j(l\hbar)(\nu_j + \tfrac{1}{2}) \qquad \nu_j = 0, 1, 2\ldots\ j = 1, 2. \tag{21}$$

The corresponding semiclassical orthonormal eigenfunctions are (cf [31, 32]):

$$\Psi_{E_{l,\nu_1,\nu_2}}(q,\hbar) = \frac{\sqrt{m}(\omega_1(I)\omega_2(I))^{1/4}}{(\pi^2\hbar R_0(l\hbar)2^{\nu_1+\nu_2}\nu_1!\nu_2!)^{1/2}}\exp\{il\varphi\}$$
$$\times\left\{\exp\{-m\omega_1(I)(\rho - R_0(I))^2/2\hbar\}H_{\nu_1}\left(\sqrt{m\omega_1(I)}\frac{\rho - R_0(l\hbar)}{\sqrt{\hbar}}\right)\right.$$
$$\left.\times\exp\{-m\omega_2(I)^2z^2/2\hbar\}H_{\nu_2}\left(\sqrt{m\omega_2(I)}\frac{z}{\sqrt{\hbar}}\right)\right\}\Big|_{I=l\hbar}. \tag{22}$$

Here H_{ν_j} are the Hermite polynomials and $l(\hbar)\hbar \to I^{\mathrm{cl}}$ (as $\hbar \to 0$), where $E^{\mathrm{cl}} = \alpha(I^{\mathrm{cl}})$ is the given energy level of the classical system.

4. The polarization equation (spin correction)

The matrix of polarization (10) for the family $\Lambda^1(I)$ is a matrix with constant coefficients. Using expressions (12), (14) and (16) we obtain

$$\Pi|_{\Lambda^1(I)} = \frac{e_0}{2mc}\left(H_0 + \frac{e_0 I}{2mcR_0^3(I)}\right)\sigma_3 \tag{23}$$

where σ_3 is the Pauli matrix. Since the differentiation operator along the trajectory $\Lambda^1(I)$ is $\mathrm{d}/\mathrm{d}t|_{\Lambda^1(I)} = \omega_0(I)\partial/\partial\varphi$, the spectral problem (9) takes the form

$$\left(-\mathrm{i}\omega_0(I)\frac{\partial}{\partial\varphi} + \frac{e_0}{2mc}\left(H_0 + \frac{e_0 I}{2mcR_0^3(I)}\right)\sigma_3\right)f_\zeta = \mu_\zeta f_\zeta \tag{24}$$
$$f_\zeta(\varphi + 2\pi) = f_\zeta(\varphi) \qquad \sigma_3 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

Obviously, its solution is given by the following formula:

$$f_\zeta(\varphi, I) = \mathrm{e}^{\mathrm{i}k\varphi}v_\zeta \qquad \zeta = \pm 1 \quad v_{+1} = {}^t(1,0) \quad v_{-1} = {}^t(0,1)$$
$$\mu_\zeta = \zeta\frac{e_0}{2mc}\left(H_0 + \frac{e_0 I}{2mcR_0^3(I)}\right) + \omega_0(I)k \qquad k = 0, \pm 1, \pm 2, \ldots. \tag{25}$$

5. Semiclassical spectral series of the Pauli operator with spin–orbit interaction

Without loss of generality (see below) we can assume $k = 0$. The series of semiclassical eigenvalues of the original problem (1)–(2) is given by

$$E_{l,\nu_1,\nu_2,\zeta}(\hbar) = E_{\mathrm{cl}}(l\hbar) + \hbar\sum_{i=1}^{2}\omega_i(l\hbar)(\nu_i + \tfrac{1}{2}) + \hbar\zeta\frac{e_0}{2mc}\left(H_0 + \frac{e_0 l\hbar}{2mcR_0^3(l\hbar)}\right) + \mathrm{O}(\hbar^2)$$
$$l = 0, \pm 1, \pm 2, \ldots \quad \nu_i = 0, 1, 2, \ldots \quad \zeta = \pm 1. \tag{26}$$

The sequence of semiclassical eigenfunctions $\Psi_{l,\nu_1,\nu_2,\zeta}(\rho,\varphi,z)$ corresponding to $E_{l,\nu_1,\nu_2,\zeta}(\hbar)$ (according to (6)) has the following form:

$$\Psi_{l,\nu_1,\nu_2,\zeta}(\rho,\varphi,z,\hbar) = v_\zeta\Psi_{E_{l,\nu_1,\nu_2}}(q,\hbar) \tag{27}$$

(see $\Psi_{E_{l,\nu_1,\nu_2}}(q,\hbar)$ in (22) and v_ζ in (25)). The case $k \neq 0$ implies only a renumeration of the energy levels (26) with respect to the orbital quantum number l: $E_{l,\nu_1,\nu_2,\zeta}(\hbar) \mapsto E_{l',\nu_1,\nu_2,\zeta}(\hbar)$, $l' = l + k$. Actually, by the definition of rotation frequency: $\omega_0(I) = \partial H/\partial I|_{\Lambda^1(I)} = \partial E_{\mathrm{cl}}(I)/\partial I$, the spin correction $\hbar\omega_0(I)|_{I=l\hbar}k$, $k \neq 0$ to formula (26) means that the equality

$$E_{l,\nu_1,\nu_2,\zeta}(\hbar) + \hbar\omega_0(l\hbar)k = E_{l+k,\nu_1,\nu_2,\zeta}(\hbar) + \mathrm{O}(\hbar^2)$$

holds up to $O(\hbar^2)$. The corresponding renumeration $l \mapsto l + k$ in the wavefunctions (27) influences the term $e^{il\varphi} \mapsto e^{i(l+k)\varphi}$ only. It does not affect the final result up to $O(\hbar)$, because, for $l \gg k$, $\exp[i(l+k)\varphi] \sim \exp(il\varphi)$.

6. Semiclassical spectral series in the weak magnetic field approximation

6.1. The Schrödinger operator

Let us choose the ratio $(a_B/a_H)^4 = \varepsilon_w$ as a criterion of smallness of magnetic fields, where $a_H = (c\hbar/e_0H_0)^{1/2}$, $a_B = \hbar^2/me_0^2$. The parameter $\varepsilon_w = H_0^2(\hbar^3/cm^2e_0^3)^2$ is efficiently small up to values of the magnetic field H_0 of order 10^3 G. For this case let us find the approximate value for the solution $R_0(I)$ of equation (16) as $\varepsilon_w \to 0$, considering $I = l\hbar$, $l \neq 0$. The actual parameter q_w of the expansion is

$$q_w = \varepsilon_w l^6 = \left(\frac{l^3 H_0 \hbar^3}{cm^2 e_0^3}\right)^2 \ll 1.$$

We have

$$R_0(I = l\hbar) = a_B l^2 \sum_{j=0}^{\infty} r_j^w q_w^j. \tag{28}$$

In particular, $r_0^w = 1$, $r_1^w = -\frac{1}{4}$, $r_2^w = \frac{1}{4}$. After substituting (28) into (13), (17) and (19) we obtain the semiclassical energy levels for the electron's motion along the closed phase curves $\Lambda^1(I)$ (12) in the weak magnetic field approximation $H_0 \to 0$, in the form of the following expansion in power series of q_w:

$$E_{l,\nu_1,\nu_2}(\hbar) = \tfrac{1}{2}\hbar\omega_H l + \frac{\hbar\omega_0}{l^2} \sum_{j=0}^{\infty} C_j^w(\nu_1, \nu_2, l) q_w^j + O(\hbar^2). \tag{29}$$

ω_0 is the classical frequency of the electron's motion in a Coulomb field: $\omega_0 = me_0^4/\hbar^3$. The first four coefficients of expansion (29) look as follows:

$$\begin{aligned}
C_0^w &= -\tfrac{1}{2} + (\nu_1 + \tfrac{1}{2})/|l| + \sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/|l| \\
C_1^w &= \tfrac{1}{8} + 3\sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/8|l| + 7(\nu_1 + \tfrac{1}{2})/8|l| \\
C_2^w &= -\tfrac{1}{32} - 33\sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/128|l| - 73(\nu_1 + \tfrac{1}{2})/128|l| \\
C_3^w &= \tfrac{3}{128} + 324\sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/1024|l| + 735(\nu_1 + \tfrac{1}{2})/1024|l|.
\end{aligned} \tag{30}$$

When $\varepsilon_w = 0$ and $\gamma = 1$, assuming $n = |l| + \nu_1 + \nu_2 + 1$ (n is the main quantum number [1]), we get the exact spectrum of the electron in a hydrogen atom up to $O(\hbar^2)$.

6.2. The spin correction

Substituting the radius expansion (28) and (25) we get the following formula for the spin correction

$$\hbar\mu_\zeta^w = E_\zeta^w = \frac{\zeta\hbar\omega_H}{2} + \frac{\zeta\hbar e_0^5 m}{4c^2 l^5 \hbar^5}(1 + \tfrac{3}{4}q_w - \tfrac{3}{8}q_w^2 + O(q_w^3)). \tag{31}$$

7. Semiclassical spectral series in the strong magnetic field approximation

7.1. The Schrödinger operator

Let us consider the magnetic field to be so strong that the Larmour radius $a_H = (c\hbar/e_0H_0)^{1/2}$ is much less than the Bohr electron radius $a_B = \hbar^2/me_0^2$ [1]. Condition $a_H \ll a_B$ is efficiently executed for values of the field starting with $H_0 \sim 4.7 \times 10^9$ G. The actual dimensionless parameter of this expansion (as $l \neq 0$) is:

$$q_S = \varepsilon_S(2|l|)^{-3/2} = (2|l|)^{-3/2}a_H/a_B = [cm^2e_0^3/(8|l|^3H_0\hbar^3)]^{1/2} \ll 1.$$

From (16) the solution $R_0(I)$, determining the equilibrium radius of the electron orbit in the plane $z = 0$, can be expanded in the following way:

$$R_0(I = l\hbar) = a_H\sqrt{2|l|}\sum_{j=0}^{\infty} r_j^S q_S^j. \tag{32}$$

The first five coefficients are $r_0^S = 1$, $r_1^S = -1$, $r_2^S = -\frac{1}{2}$, $r_3^S = -\frac{1}{2}$, $r_4^S = \frac{7}{8}$. After substituting (32) into (13), (17) and (19), the semiclassical energy levels, corresponding to the electron's motion along the closed phase curves $\Lambda^1(I)$ (12) in the strong magnetic field ($H_0 \to \infty$) approximation, are obtained in the form of the following expansion:

$$E_{l,\nu_1,\nu_2}(\hbar) = \hbar\omega_H\sum_{j=0}^{\infty} C_j^S(\nu_1, \nu_2, l)\varepsilon_S^{j/2} + O(\hbar^2). \tag{33}$$

The first six coefficients of this expansion are:

$$\begin{aligned}
&C_j^S(\nu_1, \nu_2, l) = C_j(\nu_1, \nu_2, l)(2|l|)^{-3j/4} && j = 0, 1, \ldots, 5 \\
&C_0 = \nu_1 + (l + |l|)/2 + \tfrac{1}{2} && C_1 = \sqrt{\gamma}(\nu_2 + \tfrac{1}{2}) \\
&C_2 = -2|l| + (\nu_1 + \tfrac{1}{2})/2 && C_3 = 3\sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/2 \\
&C_4 = -|l| + 11(\nu_1 + \tfrac{1}{2})/8 && C_5 = 2l\sqrt{\gamma}(\nu_2 + \tfrac{1}{2})/8.
\end{aligned} \tag{34}$$

If we identify the sum of the spectral quantum numbers $\nu_1 + (l + |l|)/2$ with the number N of a rather high ($N \gg 1$) Landau level [1] then, for $\gamma = 1$, formula (33) gives us the exact spectrum of a non-relativistic electron in a homogeneous magnetic field for $\varepsilon_S = 0$.

7.2. The spin correction

As in the previous section, using (32) and (25) we obtain the spin correction E_ζ^S in the form of the following expression:

$$\hbar\mu_\zeta^S = E_\zeta^S = \frac{\zeta\hbar\omega_H}{2}\left(1 + \frac{e_0^{5/2}H_0^{1/2}l}{4\sqrt{2m^2c^5\hbar|l|^3}}(1 + 3q_S + \tfrac{15}{2}q_S^2 + \tfrac{35}{2}q_S^3 + O(q_S^4))\right). \tag{35}$$

8. Discussion of the results

Our formulae for the semiclassical spectral series of the Schrödinger operator for $\Lambda^1(I)$ when $H_0 = 0$, $\gamma \neq 1$ pass into the corresponding spectral series for the quantum AKP [33]. Let us compare the obtained formulae for the semiclassical spectral series of the Schrödinger operator (8), with the results of other papers in the limiting cases of strong and weak magnetic fields when $\gamma = 1$ (Zeeman effect).

(i) Strong field ($H_0 \to \infty$). If we use formulae (33) and (34), and take into account only the first three expansion coefficients, we obtain for $\gamma = 1$

$$E_{k_l,\nu_1,\nu_2}(h) = h\omega_H \left[(\nu_1 + k_l + \tfrac{1}{2}) + \frac{\sqrt{\varepsilon_S}(\nu_2 + \frac{1}{2})}{(2|k_l|)^{3/4}} - \varepsilon_S \frac{[2k_l - \frac{1}{2}(\nu_1 + \frac{1}{2})]}{(2|k_l|)^{3/2}} \right]$$
$$\nu_1, \nu_2 = 0, 1, 2, \ldots \qquad |k_l| \gg 1 \; k_l = (l + |l|)/2. \tag{36}$$

The quantum numbers ν_1, $\nu_2 = 0, 1, 2 \ldots$ enumerate the modes of radial (along ρ) and axial (along z) oscillations of the wavepacket Ψ_{l,ν_1,ν_2}, in a neighbourhood of the equilibrium circle $\rho = R_0(I)$ that lies in the plane $z = 0$; l is the orbital quantum number. This number determines the level of excitation of the hydrogen atom due to the quick rotation of the electron in the plane transversal to the field H_0. If we identify the sum of the spectral quantum numbers ν_1 and k_l with the number N of a rather high ($N \gg 1$) Landau level [1], $N = \nu_1 + k_l$, then (36) gives us the exact spectrum of a non-relativistic charge in a homogeneous magnetic field for $\varepsilon_S = 0$. For $\varepsilon_S \neq 0$, the spectral series complements the results obtained by the adiabatic method in [10] when $l = 0$. Nonetheless, it is interesting to mention that taking into account the two former expansion coefficients in (33), for $\nu_2 = n$ the semiclassical spectrum (36) coincides with the energy spectrum from [10] up to $O(\varepsilon_S)$, $\varepsilon_S \to 0$, $n = 0, 1, 2, \ldots$; N is the quantum number that appears in the adiabatic method of 'separation of variables'.

(ii) Weak field ($H_0 \to 0$). For this case the majority of results obtained by perturbation theory methods is related to calculating lowly-perturbed states of hydrogen atoms (see, e.g., [5–8] and references therein). To calculate highly-perturbed states considered in the semiclassical complex WKB approximation with perturbation theory and its modifications, one meets the problem of constructing the oscillation functions in the zero approximation. It is especially interesting that the coefficients of the semiclassical spectra expansion (30), coincide with the coefficients of the perturbation theory series for energy (cf [6]) up to terms of order H_0^6 inclusive if they are extrapolated to the domain of large quantum numbers $N \gg 1$. $N = l + 1$ is the main quantum number for the extreme components of a Coulomb multiplet with zero radial quantum number $n_\rho = 0$, $m = \pm l$. Here the coincidence is exact in the zero and first orders of the field, and approximate with accuracy up to 2% in the terms of order H_0^2, H_0^4, H_0^6.

For $\varepsilon_w = 0$, assuming $n = |l| + \nu_1 + \nu_2 + 1$, n the main quantum number, we obtain the exact spectrum of a hydrogen atom from formula (29).

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