Symmetries of highly excited atomic hydrogen: Quadratic Zeeman splitting distorted by fine-structure effects

D. A. Arbatsky* and P. A. Braun†
Department of Theoretical Physics, Institute of Physics, St. Petersburg State University, St. Petersburg 198904, Russia
(Received 20 January 1998)

Using the classical mechanical perturbation approach and semiclassical quantization rules we explain the spectrum of atomic hydrogen in a weak magnetic field in which fine structure of levels cannot be neglected. The general pattern of the spectrum turns out to be very different from the nonrelativistic scheme. In particular, we point out the presence of another type of ''exponentially narrow'' doublet. [S1050-2947(98)07609-4]

PACS number(s): 31.15.Gy, 31.15.Md, 31.30.Jv, 32.60.+i

INTRODUCTION

The presence of discrete symmetry in a quantum system often leads to the appearance of extremely narrow multiplets in the energy spectrum. The usual example is two symmetric communicating wells when the lower part of the spectrum consists of ''exponentially narrow'' doublets. In the semiclassical approach it can be attributed to the presence of two symmetric phase trajectories of the corresponding classical system.

A more interesting case is the highly excited hydrogen atom in a magnetic field of suitable strength. The specific properties of this problem have been discovered in experiments on hydrogenlike spectra of alkali-metal atoms [1,2] and on hydrogen proper [3,4], and in numerical calculations [5–7]. A semiclassical theory underlying the observed effects is described in [8–13]; for details and complete bibliography, see the reviews [14–18]. The phase space of this system possesses symmetry that also leads to exponentially narrow doublets in the so-called ''vibrational part'' of the spectrum.

In this paper we consider the same system. But the magnetic field is assumed to be weaker so that the diamagnetic splitting is comparable with the fine structure of the unperturbed atom. Relativistic effects conserve the above-mentioned symmetry and it seems unlikely that they will lead to essentially new effects.

Nevertheless, we will show that the hydrogen atom in magnetic field possesses yet another symmetry. The latter does not lead to any interesting phenomena in the nonrelativistic situation. However, when the relativistic effects are present it gives birth to another type of doublet. Here we analyze the dynamical symmetry origin of these doublets and other peculiar relativistic distortions of the quadratic Zeeman spectra in the atomic hydrogen. We give a physical explanation of the earlier results of [19] where the discrete Wentzel-Kramers-Brillouin-Jeffreys (WKBJ) method was used to solve the quantum perturbation theory equations of the problem.

*Electronic address: arbatsky@snoopy.phys.spbu.ru
†Electronic address: braun@niif.spb.su

I. BASIC ASSUMPTIONS

The Hamiltonian of the system can be written as

$$H = H^{(0)} + \frac{\gamma}{2}(L_z + \sigma_z) + V_{\rm dia} + V_{\rm rel}. \tag{1}$$

Here $V_{\rm dia} = (\gamma^2/8)(x^2+y^2)$ is the diamagnetic interaction, γ is the magnetic field in atomic units ($\gamma = 1$ corresponds to $B = 2.35\times 10^5$ T), σ_z is the z component of the doubled spin operator $\boldsymbol{\sigma}$, and $V_{\rm rel}$ is the Pauli operator of the relativistic corrections comprising ''the mass on velocity dependence,'' the spin-orbit interaction, and the Darwin contact interaction:

$$V_{\rm rel} = V_{\rm mass} + V_{\rm so} + V_{\rm Darw},$$

$$V_{\rm mass} = -\frac{(E-U)^2}{2c^2} = -\frac{(E+1/r)^2}{2c^2},$$

$$V_{\rm so} = \frac{1}{4c^2 r}\frac{\partial U}{\partial r}(\boldsymbol{\sigma}\cdot\mathbf{L}) = -\frac{1}{4c^2 r^3}(\boldsymbol{\sigma}\cdot\mathbf{L}),$$

$$V_{\rm Darw} = \frac{1}{8c^2}\nabla^2 U = \frac{\pi}{2c^2}\delta(\mathbf{r}).$$

There are three perturbations present in Eq. (1); their relative impact depends on the field strength and the extent of the atomic excitation. We will make the following assumptions.

(i) The spin and the orbital movements are uncoupled. This means that the first-order Zeeman splitting induced by the operator $H^{(1)} \equiv (\gamma/2)(L_z+\sigma_z)$ is much larger than the fine structure, or

$$\frac{\gamma}{2} \gg \frac{\alpha^2}{n^3},$$

where α is the fine-structure constant; n is the principal quantum number of the atomic state under consideration ($n \gg 1$).

(ii) The first-order (paramagnetic) Zeeman splitting is large compared with the second order (diamagnetic) one, or

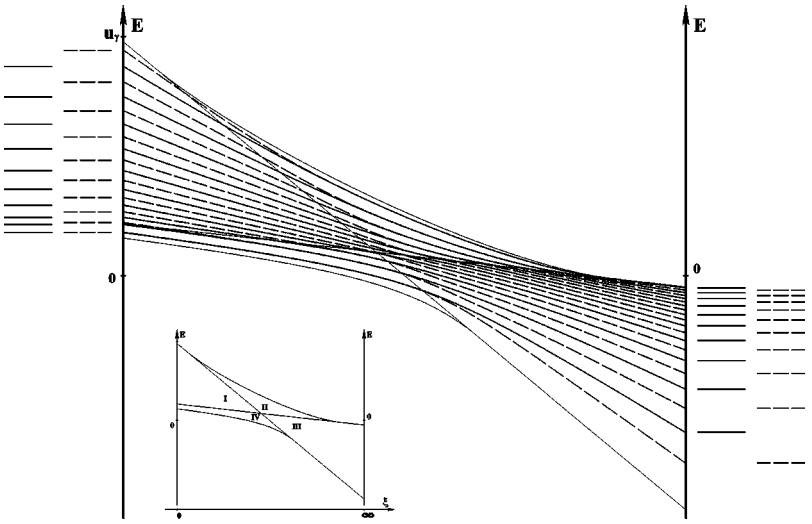

FIG. 1. Spectrum of the Hamiltonian as a function of parameter $\xi \equiv 32E^4/c^2\omega_L^2$ for $n=25$, $m=5$, $\sigma_z=1$. Left-hand side corresponds to $\xi=0$, right-hand side corresponds to $\xi=+\infty$. The case $\xi=+\infty$ is, of course, unattainable in reality (see Sec. I). Solid and dashed thick lines correspond to even and odd levels. Thin lines border regions with different symmetry and topology of level surfaces of a classical Hamiltonian.

$$\frac{\gamma}{2} \gg u_\gamma \equiv \frac{5\gamma^2 n^4}{16}.$$

(iii) The diamagnetic splitting is much smaller than the energy interval between adjacent shells in the unperturbed atom, or

$$u_\gamma \ll \frac{1}{n^3}.$$

(iv) The diamagnetic splitting is comparable with the fine structure, or

$$u_\gamma \sim \frac{\alpha^2}{n^3}. \tag{2}$$

The first and the second of these assumptions guarantee that the orbital angular momentum component L_z is conserved. The third assumption means that mixing between different shells of the atom can be neglected and n is a good quantum number. Finally, Eq. (2) means that the magnetic field is weaker than that usually considered in the theory of the second-order Zeeman effect; in such fields the relativistic effects compete with the field-induced splitting completely modifying it in some cases (see below).

II. QUANTUM PERTURBATION THEORY

The paramagnetic operator splits the level $E_n^{(0)}=-1/2n^2$ of the nonrelativistic unperturbed atom into a set of equidistant levels with the spacing $\gamma/2$:

$$E_{m\sigma_z}^{(1)} = \frac{\gamma}{2}(m+\sigma_z), \tag{3}$$

where $\sigma_z=\pm 1$ is the spin quantum number. These levels are still degenerate.

On the second stage we consider the splitting of this residual degeneracy. This can be done by diagonalizing the sum of the operators of the relativistic corrections and the diamagnetic interaction in the basis set of the spin-orbitals belonging to the level (3). The respective basis set is formed by the functions

$$|nlm\sigma_z\rangle = R_{nl}(r)Y_{lm}(\theta,\phi)u(\sigma_z)$$

with fixed n, m, σ_z, and all possible l. Here R_{nl} stands for the nonrelativistic radial wave function of the atomic hydrogen and $u(\sigma_z)$ is the spin function.

It may be argued that, since there is degeneracy of the level (3) with respect to the spin projection

$$E_{m\sigma_z}^{(1)} = E_{m+2\sigma_z,-\sigma_z}^{(1)},$$

mixing of states with $\sigma_z=1$ and $\sigma_z=-1$ must be taken into account. However, the relativistic correction operator can change the orbital angular momentum projection m by no more than 1; thus such mixing cannot take place in the first order by $V_{\rm rel}$. Thus in the first order of perturbation theory the operator of the spin-orbit interaction $V_{\rm so}$ can be replaced by a simpler operator $\tilde{V}_{\rm so}=-(1/4c^2r^3)\sigma_z L_z$, where σ_z is a c number.

The operator $\tilde{V}_{\rm so}$ has clear classical meaning. In the classical limit $n\to\infty$ it becomes a usual (not operatoral) function of dynamical variables. The operator $V_{\rm mass}$ comprising ''mass on velocity dependence'' has a clear classical meaning from the very beginning. The Darwin contact interaction $V_{\rm Darw}$ will be excluded from consideration here because it is substantial only if $L_z=0$ (the case $L_z=0$ is more complicated and will not be analyzed here). Thus we are left with three perturbations only: $V_{\rm dia}$, $V_{\rm mass}$, and $\tilde{V}_{\rm so}$.

Numerically calculated splitting produced by the relativistic and diamagnetic interactions is shown in Fig. 1.

III. CLASSICAL PERTURBATION THEORY

In the classical model the electron of the unperturbed hydrogen atom moves along a Kepler orbit. All possible Kepler orbits form a manifold later referred to as the Kepler orbit space. Each orbit is characterized by the angular momentum vector **L** and the Runge-Lenz vector **A**, which are mutually orthogonal.

Owing to the perturbing influence of the external magnetic field and the relativistic effects, **L** and **A** will no longer be constant. Their time dependence will consist of small oscillations with the period of the Kepler motion and slow

accumulating drift, which eventually leads to their large scale change (the so called secular evolution). The effective Hamiltonian determining the secular evolution (in the first order of perturbation theory) is obtained by averaging the perturbation over a period of the unperturbed Kepler movement [20]; it can be regarded as a function of **L** and **A** characterizing the unperturbed orbit.

The paramagnetic term in the perturbation can be excluded from consideration by using the frame of reference that rotates with the Larmor frequency.

Averaging $V_{\rm dia}$, $V_{\rm mass}$, and $\tilde{V}_{\rm so}$ over a period we obtain the effective Hamiltonian

$$\langle V_{\rm dia}\rangle=\frac{\omega_L^2}{2}\left[\frac{1}{8E^2}(\Lambda+1)-\frac{L_z^2}{4E}\right],$$

$$\langle V_{\rm mass}\rangle=\frac{E^2}{c^2}\left(\frac{3}{2}-\frac{2}{\sqrt{1-A^2}}\right), \tag{4}$$

$$\langle \tilde{V}_{\rm so}\rangle=\frac{2E^3\sigma_z L_z}{c^2(1-A^2)^{3/2}},$$

$$H^{(2)}=\langle V_{\rm dia}\rangle+\langle V_{\rm mass}\rangle+\langle \tilde{V}_{\rm so}\rangle,$$

where $\omega_L\equiv H/2c$ is the Larmor frequency, $\Lambda\equiv 4A^2-5A_z^2$ is the well-known Solov'ev integral [8,9], $A\equiv|\mathbf{A}|$, and A_z and L_z are z components of **A** and **L**, respectively.

IV. QUALITATIVE ANALYSIS OF PHASE TRAJECTORIES

Now we have three integrals of motion. They are L_z, $E\equiv H^{(0)}$, and $H^{(2)}$. The first integral is conserved exactly. The other two are conserved in the averaged system.

The integral $H^{(2)}$ can be simplified by dropping the term $\langle \tilde{V}_{\rm so}\rangle$, which is always much smaller than $\langle V_{\rm mass}\rangle$ in the semiclassical limit. Therefore, this term is negligible when analyzing the topology of the phase trajectories (however, the exact appearance of $\langle \tilde{V}_{\rm so}\rangle$ *is* essential when we state that $\langle \tilde{V}_{\rm so}\rangle$ does not violate the symmetry of $\langle V_{\rm dia}\rangle$ and $\langle V_{\rm mass}\rangle$).

The conserving property $H^{(2)}$ can be replaced by some other function of $\langle V_{\rm dia}\rangle+\langle V_{\rm mass}\rangle$, L_z, and E. We will use the integral

$$\tilde{\Lambda}\equiv 4A^2-5A_z^2-\frac{32E^4}{c^2\omega_L^2}\frac{1}{\sqrt{1-A^2}}\equiv\Lambda-\frac{32E^4}{c^2\omega_L^2}\frac{1}{\sqrt{1-A^2}}.$$

The parameter $\xi\equiv 32E^4/c^2\omega_L^2$ is a constant. Therefore we can say that $\tilde{\Lambda}$ is a function only of **A**. The typical level surfaces of $\tilde{\Lambda}$ for some intermediate value of ξ are presented in Fig. 2. $\tilde{\Lambda}$ is invariant under rotation about the z axis in the **A** space, and Fig. 2 shows a section of **A** space by an arbitrary plane containing the z axis.

All possible values of **A** are determined by the inequality

$$Z(\mathbf{A})\equiv(1-A^2)\left(1-\frac{A_z^2}{A^2}\right)-2L_z^2(-E)\geqslant 0. \tag{5}$$

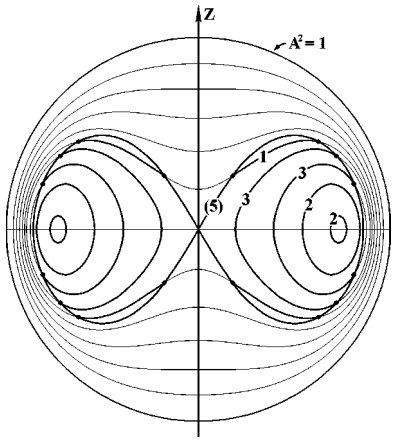

FIG. 2. Level surfaces of $\tilde{\Lambda}$ in **A** space for $\xi=5$ and $2L_z^2(-E)=0.26$. Formal expression for $\tilde{\Lambda}$ is defined for $A^2<1$ but real Kepler orbits exist only for A bounded by inequality (5). The boundary $Z(\mathbf{A})=0$ is depicted by the ∞-like bold line. The level surfaces can be classified in accordance with their topological structure and symmetry. There are three types of level surfaces of $\tilde{\Lambda}$ in **A** space: (1) *Pairs of symmetric closed strips.* In the Kepler orbit space they are represented by pairs of symmetric tori. The corresponding quantum spectrum consists of doublets in the lower part of the multiplet. (2) *Tori.* In the Kepler orbit space every such torus is represented by a pair of symmetric tori. The corresponding quantum spectrum consists of doublets in the upper part of the multiplet. (3) *Closed strips.* In the Kepler orbit space every such strip is represented by one torus that is symmetric by itself. The corresponding quantum spectrum consists of singlets.

It follows from the non-negativity of the Gram determinant of the vectors **A**, **L**, and $\mathbf{e}_z$, and from the relations

$$(\mathbf{A}\cdot\mathbf{L})=0,$$

$$L^2=\frac{1-A^2}{2(-E)}. \tag{6}$$

Equation (5) becomes equality if **A**, **L**, and $\mathbf{e}_z$ are coplanar.

For values of $\tilde{\Lambda}$ in the vicinity of minimum ($\tilde{\Lambda}\approx\tilde{\Lambda}_{\rm min}$) we have two unconnected surfaces symmetrical with respect to the xy plane in the **A** space and two types of phase trajectories, with $A_z>0$ and with $A_z<0$. This is, of course, well known [8–10], and relativistic effects do not lead to anything essentially new in this case. The result is the presence of the extremely narrow doublets of levels of opposite parity in the lower part of the spectrum (see Fig. 1) provided the relativistic distortion of the quadratic Zeeman spectrum is not too strong (ξ is not too large).

Figure 1 also shows that if relativistic effects are not too *small*, there is also a doublet structure in the *upper* part of the multiplet. Corresponding level surfaces of $\tilde{\Lambda}$ in Fig. 2 are tori. Every torus is, of course, a connected set and the presence of the doublet structure looks a little puzzling.

The explanation is that every Kepler orbit is defined not only by the vector **A** but also by the vector **L**. It is elementary to show (see Fig. 3) that, for a generic **A**, there exist two vectors **L** with the same z projection L_z satisfying Eqs. (6).

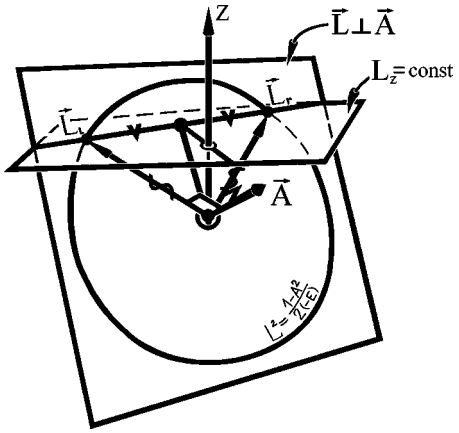

FIG. 3. Two symmetric locations of vector **L** are possible when vector **A** is fixed. This may lead to the appearance of a doublet structure in the upper part of the quantum spectrum.

These two vectors are symmetrical with respect to the $z\mathbf{A}$ plane; they merge in the exceptional case when the relation (5) turns into equality.

Thus, each level surface of $\tilde{\Lambda}$ in the **A** space that does not reach the boundary $Z(\mathbf{A})=0$ gives rise to two isolated symmetrical tori in the Kepler orbit space. Hence the doublet structure in the upper part of the multiplet.

We should also mention the third type of level surfaces of $\tilde{\Lambda}$ corresponding to its middle values. They cross the boundary $Z(\mathbf{A})=0$ where the two branches of **L** merge. Consequently there is just one torus in the Kepler orbit space corresponding to such a surface. Every such torus is symmetric by itself and does not have a partner. Therefore, the corresponding part of the quantum spectrum consists of singlets.

In the nonrelativistic case the $\tilde{\Lambda}$ level surfaces are hyperboloids that always cross the boundary $Z(\mathbf{A})=0$. Only the first and the third types of level surfaces are present. When relativistic corrections gradually grow, the maximum of $\tilde{\Lambda}$ shifts to the allowed region bounded by inequality (5), and every surface of the third type becomes a surface of the second type as soon as it is *wholly* enclosed in the allowed region.

V. DISCUSSION

(i) We described two symmetries of the classical system: the reflection in **A** space ($\mathbf{A}\rightarrow-\mathbf{A}$) and the symmetry shown in Fig. 3. Let us unify the two symmetries into a group that consists of four elements. This unified group includes the group of space reflection parity as a subgroup [the space reflection $P\equiv(\{\mathbf{r},\mathbf{p}\}\rightarrow\{-\mathbf{r},-\mathbf{p}\})$ in the Kepler orbit space operates as $P=(\{\mathbf{A},\mathbf{L}\}\rightarrow\{-\mathbf{A},\mathbf{L}\})$]. On the one hand, the operation P changes **A** to $-\mathbf{A}$ and therefore it describes the doublet structure in the lower part of the spectrum. On the other hand, P also changes the mutual orientation of the three vectors $(\mathbf{A},\mathbf{L},\mathbf{e_z})$ and therefore it describes the doublet structure in the upper part of the spectrum. So, both types of doublets can be described in terms of the group consisting of *two* elements.

(ii) But this is not always sufficient. Let us add to the system a weak electric field **E** parallel to the magnetic field **B**. To obtain the approximate integral of motion in this case one must add to $\tilde{\Lambda}$ the term that is proportional to A_z. This term will violate the space reflection symmetry and the doublets in the lower part of the spectrum will be destroyed. But the symmetry shown in Fig. 3 will remain and the doublet structure in the upper part of the spectrum will be conserved.

[1] D. Delande and J. C. Gay, Phys. Lett. **82A**, 393 (1981).
[2] D. Delande and J. C. Gay, Phys. Lett. **82A**, 399 (1981).
[3] A. Holle, B. Hager, and K. H. Welge, in *Proceedings of II European Conference on Atomic and Molecular Physics*, edited by A. E. de Vries and M. J. van der Wiel (European Physical Society, Amsterdam, 1985), Book of Abstracts, p. 6.
[4] D. Wintgen, A. Holle, G. Wiebusch, J. Main, H. Friedrich, and K. H. Welge, J. Phys. B **19**, L557 (1986).
[5] M. L. Zimmerman, M. M. Kash, and D. Kleppner, Phys. Rev. Lett. **45**, 1092 (1980).
[6] Ch. W. Clark, Phys. Rev. A **24**, 605 (1981).
[7] Ch. W. Clark and K. T. Taylor, J. Phys. B **13**, L737 (1980).
[8] E. A. Solov'ev, Pis'ma Zh. Éksp. Teor. Fiz. **34**, 278 (1981) [JETP Lett. **34**, 265 (1981)].
[9] E. A. Solov'ev, Zh. Éksp. Teor. Fiz. **82**, 1762 (1982) [Sov. Phys. JETP **55**, 1017 (1982)].
[10] D. Herrick, Phys. Rev. A **26**, 323 (1982).
[11] J. C. Gay and D. Delande, Comments At. Mol. Phys. **13**, 275 (1983).
[12] P. A. Braun, Zh. Éksp. Teor. Fiz. **84**, 850 (1983) [Sov. Phys. JETP **57**, 492 (1983)].
[13] J. B. Delos, S. K. Knudson, and D. W. Noid, Phys. Rev. A **28**, 7 (1983).
[14] H. Hasegawa, M. Robnik, and G. Wunner, Prog. Theor. Phys. Suppl. **98**, 198 (1989).
[15] P. A. Braun, Rev. Mod. Phys. **65**, 115 (1993).
[16] *The Hydrogen Atom*, edited by G. F. Bassani, M. Inguscio, and T. W. Hänsch (Springer, Berlin, 1989).
[17] J. C. Gay, in *Photophysics and Photochemistry in the Vacuum Ultraviolet*, edited by S. P. McGlynn, G. L. Findley, and R. H. Huebner (Reidel, Dordrecht, 1985).
[18] J. C. Gay, in *Atoms in Unusual Situations*, edited by J. P. Briand (Plenum, New York, 1986).
[19] D. A. Arbatsky and P. A. Braun, in *Atoms and Molecules in Strong External Fields*, edited by P. Schmelcher and W. Schweizer (Plenum, New York, 1998).
[20] V. I. Arnold, *Matematicheskie Metody Classicheskoy Mekhaniki*, 3rd ed. (Nauka, Moscow, 1989), Chap. 10.