Rydberg atoms in weak magnetic fields

A. P. Kazantsev and V. L. Pokrovsky
Landau Institute for Theoretical Physics, 142432 Chernogolovka, Moscow Region, Union of Soviet Socialist Republics

J. Bergou
Central Research Institute for Physics, P.O. Box 49, H-1525 Budapest, Hungary and Max-Planck-Institut für Quantenoptik, D-8046 Garching, P.O. Box 1513, Federal Republic of Germany†*

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The quadratic Zeeman effect of Rydberg atoms is treated with the help of first-order perturbation theory and a special WKB approximation. The Bohr-Sommerfeld quantization leads to complete elliptic integrals. As a result we found that the spectrum is doubly degenerate if $n^2/m^2 > 5$, this part exhibiting a linear Stark effect in an additional weak electric field; the rest of the spectrum ($n^2/m^2 < 5$) is nondegenerate, exhibiting a quadratic Stark effect in an additional weak electric field.

The remarkable interest recently shown towards Rydberg atoms is motivated mainly by the improved experimental possibilities of investigating them in atomic beams using highly selective excitation methods.[1,2] Earlier experimental investigations were carried out with interstellar atoms (see, e.g., Ref. 3). Theoretical treatment of the spectrum of a Rydberg atom in external fields is therefore desirable. Exact analysis of the hydrogen atom spectrum in a constant electric field (dc Stark effect) is possible since the variables can be separated in the parabolic coordinate system.[4] Even though the governing equations are relatively simple the magnetic interactions are less well understood. This is connected with the fact that in a constant magnetic field the variables cannot be separated. The present state of the art is described, for example, in Ref. 5. The experimentally discovered approximate symmetry of the hydrogen atom in a constant magnetic field[1] called special attention to this problem in recent years. Recent works in the field provided either a classical analysis of the problem[6-8] or a quantum-mechanical analysis based on group-theoretical considerations.[9] Our purpose here is to present an entirely quantum-mechanical treatment based on the—conceptually simpler and more natural for the weak field—perturbation theory. At the same time the method of solving the secular equation exploits the analogy between the classical and quantum-mechanical behaviors of highly excited states.

The entire region of variation of the magnetic field H can be separated into three subregions, viz., weak, intermediate, and strong magnetic fields. The contribution of the quadratic Zeeman effect to the energy of the nth level will be shown to be proportional to $\omega_c^2 n^4$ (ω_c is the cyclotron frequency in atomic units). We shall consider a magnetic field as weak if this contribution is smaller than the energy separation (which is proportional to n^{-3}), i.e., if $\omega_c^2 < n^{-7}$ holds. In the intermediate case this contribution is more than the interlevel separation but less than the Coulomb energy ($\sim n^{-2}$), that is, $n^{-7} < \omega_c^2 < n^{-6}$. Finally, the magnetic field is strong if its contribution is larger than the Coulomb energy, $\omega_c^2 > n^{-6}$.

In the present paper we deal with the weak-field case. For a weak field, the usual first-order perturbation theory applies, where the nontrivial part of the interaction V is the diamagnetic interaction

$$V = \tfrac{1}{8}\omega_c^2 \rho^2 \ . \tag{1}$$

Here $\rho^2 = x^2 + y^2$, and the magnetic field H is directed along the z axis. The main difficulty in perturbational treatment is due to the n^2-fold degeneracy of the nth Rydberg level. This high degeneracy makes the exact solution of the secular equation hopeless. For the approximate solution of the secular equation we use a special modification of the quasiclassical approximation which is elaborated for the solution of three-term recurrence equations, and it is especially well suited to highly degenerate states.[10,11] The approximation is justifiable because of the large value of n. As a result we obtain the Bohr-Sommerfeld quantization equations in terms of elliptic integrals.

To obtain the matrix elements of the perturbation we use the unperturbed Coulomb wave functions in parabolic coordinates. The quantum numbers characterizing the nth Rydberg state are n_1, n_2, and m, where m is the usual magnetic quantum number and $n = n_1 + n_2 + |m| + 1$. The difference $n_1 - n_2 = k$ is proportional to the z component of the Runge-Lenz vector,[12] which is a symmetry operation of the unperturbed Coulomb problem. Since in our problem m and n are fixed it is convenient to use k to label the unperturbed wave functions. The perturbed wave function can be looked for in the form of linear superposition of the unperturbed ones. Starting from the Schrödinger equation we obtain for the coefficients c_k of this expansion (to first order in V)

$$(V_{kk} - \epsilon) c_k + V_{k,k+2} c_{k+2} + V_{k,k-2} c_{k-2} = 0 \ , \tag{2}$$

where V_{kk} are the diagonal matrix elements of V,

$$V_{kk} = \frac{n^2}{2}[3n^2 - m^2 + 1 - 3k^2] \ . \tag{3a}$$

The only nonvanishing nondiagonal elements are

$$V_{k,k\pm 2} = \frac{n^2}{2}\{[n + |m| + (k \pm 1)][n + |m| - (k \pm 1)][n - |m| + (k \pm 1)][n - |m| - (k \pm 1)]\}^{1/2} \ . \tag{3b}$$

ϵ is the energy shift in $\frac{1}{8}\omega_c^2$ units. The above matrix elements have been calculated by Clark,[13] though in a different notation, viz., in terms of n_1 and n_2.

With the above matrix elements (2) is still a complicated difference equation for the determination of c_k. The secular equation is equivalent to the vanishing of the determinant of a tridiagonal matrix of rank $2n-2|m|-1$; thus, in general, it leads to a high-order equation for ϵ whose roots cannot be given in a simple analytic form. Instead of the exact solution we introduce some simplifying approximations based on the large value of n compared to unity. In this case the small change between $V_{k,k-2}$ and $V_{k,k+2}$ can be neglected and we introduce the notations $V_{k,k\pm2}\equiv M_k$ and $V_{kk}=D_k$. With these notations, (2) can be written as

$$(D_k-\epsilon)c_k+M_k(c_{k-2}+c_{k+2})=0 \quad . \tag{4}$$

Let us assume that the ratio $c_{k-2}/c_k=z_k$ is a slowly varying function of k. Then from (4)

$$z_k+z_k^{-1}=2f_k;\quad f_k\equiv\frac{\epsilon-D_k}{2M_k} \quad . \tag{5}$$

The solution of (5) for z_k is

$$z_k=f_k\pm(f_k^2-1)^{1/2} \quad , \tag{6a}$$

which for $f_k^2<1$ can be written as

$$z_k=e^{\pm i\phi_k};\quad \phi_k=\cos^{-1}f_k \quad , \tag{6b}$$

that is, z_k is a phase factor ($0\leq\phi_k\leq\pi$). From here we obtain the solution for c_k:

$$c_{k,1}=A\exp\left[+i\sum_{k'<k}\phi_{k'}\right];\quad c_{k,2}=B\exp\left[-i\sum_{k'<k}\phi_{k'}\right] \quad . \tag{7}$$

These solutions are very much like the usual quasiclassical wave functions and are, in fact, those in k representation. The turning points k_i can be found from the following equation:

$$f_{k_i}=\pm1 \quad \text{or} \quad \phi_{k_i}=0,\pi \quad . \tag{8}$$

Equation (8) is a fourth-order equation for the determination of k_i.

In the regions of real ϕ_k, the wave function exhibits an oscillatory behavior, whereas outside these regions the wave function is purely exponential.

To satisfy the matching condition between these two types of regions we have to investigate the Schrödinger equation (2) near the turning point. Since $f_k\approx z_k\approx1$ if the upper sign holds in (8), the coefficients c_k are slowly varying functions of k in the vicinity of a turning point k_i and the difference Eq. (4) can be approximated by the differential equation

$$c_k''-\tfrac{1}{2}f'(k_i)(k-k_i)c_k=0 \quad . \tag{9}$$

Here we made use of the expansion of $f(k)$ around the turning point: $f_k-1=f'(k_i)(k-k_i)$. Equation (9) can be recognized as the Airy equation. Following the well-known procedure of the quasiclassical approximation, one has to compare the asymptotic forms of the Airy function valid to the left and to the right of the turning point. From this comparison it follows that

$$\tfrac{1}{2}\int_{k_i}^{k_i+1}\phi_k dk=(s+\tfrac{1}{2})\pi \quad \text{or} \quad \sum_{k_i}^{k_i+1}\phi_k=(s+\tfrac{1}{2})\pi \tag{10a}$$

must hold, i.e., we are led to the quasiclassical or Bohr-Sommerfeld quantization rule. Here k_i, k_{i+1} are a pair of adjacent turning points such that ϕ_k is real between these points.

If the functions f_k and, consequently, z_k are equal to -1 in the turning points, a special consideration is necessary. In this case the quantity c_k cannot be regarded as a slowly changing function of k. We separate the alternating factor so that the remaining function $\tilde{c}_k=(-1)^{k/2}c_k$ is a slowly varying function. All the previous considerations can now be applied to the function $\tilde{c}_k$. Hence, the Bohr-Sommerfeld quantization condition can be reformulated for this case as follows:

$$\sum_{k_i}^{k_{i+1}}(\pi-\phi_k)=(s+\tfrac{1}{2})\pi \quad . \tag{10b}$$

The consideration of the next approximation over the power of $1/n$ leads to the following form of c_k inside the regions of positive ϕ_k:

$$c_k=\frac{1}{(M_k\sin\phi_k)^{1/2}}\exp\left[\tfrac{1}{2}i\left(\int^k\phi_{k'}dk'+\phi_k\right)\right] \quad . \tag{11}$$

The contribution to the phase $\frac{1}{2}\phi_k$ does not change the quantization condition (10a) and (10b) since $\phi_{k_i}=0$ or π. It can be important, however, together with the amplitude factor for the calculation of quasiclassical transition probabilities.

Let us turn our attention to the quantization condition (10a). It is convenient at this stage to integrate the left-hand side of (10a) by parts:

$$\tfrac{1}{2}\int_{k_i}^{k_i+1}\phi_k dk=\tfrac{1}{2}\phi_k k\Big|_{k_i}^{k_i+1}-\tfrac{1}{2}\int_{k_i}^{k_i+1}k\frac{d\phi_k}{dk}dk \quad . \tag{12}$$

The first term on the right-hand side disappears since $\phi_{k_i}=\phi_{k_i+1}=0$. The second term can be brought to an explicit form by introducing ϕ_k from (6b). Thus, we obtain

$$\tfrac{1}{2}\int_{k_i}^{k_i+1}k\frac{df_k/dk}{(1-f_k^2)^{-1/2}}dk=(s+\tfrac{1}{2})\pi \quad . \tag{13}$$

For the turning points, we have to solve the equation

$$k^4+\tfrac{8}{5}k^2[\tfrac{3}{2}\epsilon'+(n^2+m^2)]-\tfrac{4}{5}[(n^2-m^2)^2-\epsilon'^2]=0 \quad ; \tag{14}$$

$$\epsilon=\frac{n^2}{2}[2\epsilon'+3n^2-m^2+1] \text{ or } \epsilon'=\frac{1}{n^2}\epsilon-\tfrac{3}{2}n^2+\tfrac{1}{2}m^2-\tfrac{1}{2} \quad .$$

Depending on the sign and magnitude of ϵ', we have one of the following possibilities:

(i) There are two real ($\pm k_0$) and two imaginary ($\pm iK_0$) roots of (14); ϕ_k is positive between $-k_0$ and k_0. For this case the quantization condition (13) can be written in the form

$$\frac{2Aq_1K_+^2}{k_0(1+K_+^2)}\left[\Pi\left(\frac{\pi}{2};q_1^2(1+K_+^2);q_1\right)-K(q_1)\right]+\frac{2Bq_1K_-^2}{k_0(1+K_-^2)}\left[\Pi\left(\frac{\pi}{2};q_1^2(1+K_-^2);q_1\right)-K(q_1)\right]=(s+\tfrac{1}{2})\pi \ ; \tag{15a}$$

$$K_\pm=\frac{K_0}{n\pm|m|};\quad q_1=\frac{k_0}{\sqrt{K_0^2+k_0^2}} \ .$$

(ii) There are four real roots ($\pm k_1$, $\pm k_2$; $0\leq k_1<k_2$) of (14) (k_1 and $-k_1$ may coincide); ϕ_k is positive between $-k_2$ and $-k_1$ and also between k_1 and k_2. For this case the quantization condition (13) reads as

$$\frac{Ak_+^2}{k_2[1-k_+^2]}\left[\Pi\left(\frac{\pi}{2};\frac{q_2^2}{1-k_+^2};q_2\right)\right]+\frac{Bk_-^2}{k_2(1-k_-^2)}\left[\Pi\left(\frac{\pi}{2};\frac{q_2^2}{1-k_-^2};q_2\right)\right]=(s+\tfrac{1}{2})\pi \ ;\quad k_\pm=\frac{k_1}{n\pm|m|};\quad q_2=\frac{(k_2^2-k_1^2)^{1/2}}{k_2} \ . \tag{15b}$$

In (15a) and (15b), $K(q)$ and $\Pi(\frac{1}{2}\pi,n,q)$ are complete elliptic integrals of the first and third kind, respectively.[14] The coefficients A and B are defined as follows:

$$A=5^{-1/2}[\epsilon'+\tfrac{3}{2}(n+|m|)^2] \ ;$$
$$B=5^{-1/2}[\epsilon'+\tfrac{3}{2}(n-|m|)^2] \ . \tag{16}$$

Due to the rapid convergence of the elliptic integrals, the expressions (15a) and (15b) are appropriate for a numerical study of the spectrum. This numerical study is in progress and is the subject of a future publication.

However, even without a detailed numerical study of the spectrum a few conclusions can be drawn from the analytical form of the solution. From the requirement $|f_k|<1$ the value of ϵ' is limited by the following inequalities:

$$U_-<\epsilon'<U_+;\quad U_\pm=-\tfrac{3}{2}k^2\pm\{[n+|m|)^2-k^2][(n-|m|)^2-k^2]\}^{1/2} \ . \tag{17}$$

The graphs of the "effective potentials" $U_\pm$ are schematically represented in Fig. 1.

The analytical expression for $U_\pm$, Eq. (17), shows that there are two different situations depending on the value of $n/|m|$. At $n/|m|<\sqrt{5}$ both of the branches of the effective potentials have only one extremum while at $n/|m|>\sqrt{5}$ the lower branch U_- has two minima and one maximum. The turning points are always symmetrically displaced around $k=0$ for $n/|m|<\sqrt{5}$ and they remain to be symmetric also at $n/|m|>\sqrt{5}$ provided $\epsilon'>-n^2+m^2$. The corresponding wave function is symmetric in k space and, consequently, in real space, too. This is reflection symmetry with respect to the Coulomb center. The situation described thus far corresponds to case (i). We see that no additional degeneracy remains in the problem in this case. At $n/|m|>\sqrt{5}$ and $\epsilon'<-n^2+m^2$, however, there are two pairs of turning points. The pairs are symmetric around $k=0$ and each pair leads to the same energy eigenvalue. Thus the eigenvalues are doubly degenerate. The turning points within one pair are no more symmetric around $k=0$ (they both fall on one side). The corresponding degenerate wave functions are asymmetric in k space and also in real space, thus possessing a constant dipole moment. This situation corresponds to case (ii). In other words, there is a breakdown of symmetry with the change of energy at fixed values of n and m. This leads to an interesting physical effect. If, in addition to the magnetic field, we introduce a weak electric field, two different types of behavior will be observed. In the degenerate and asymmetric case the Rydberg atoms manifest a linear Stark effect whereas in the nondegenerate symmetric case the Stark effect will be quadratic. Of course, if the electric field is strong (the Stark splitting is larger than the Zeeman splitting), the effect will be linear.

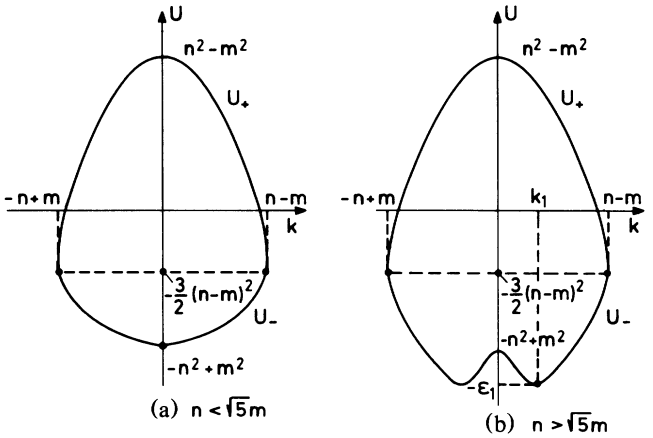

FIG. 1. The branches of the effective potential as functions of k (schematic drawing). For the energy ϵ' between $-n^2+m^2$ and n^2-m^2 the turning points and the wave function are symmetric with respect to the $k=0$ axis. In the region $n>\sqrt{5}|m|$ and $-\epsilon_1<\epsilon'<-n^2+m^2$, where $\epsilon_1=\frac{3}{2}(n^2+m^2)-\sqrt{5}nm$, the states are asymmetric and twofold degenerate.

The upper and lower branches of the effective potential energy do not overlap but intersect at $k_0=n-|m|$. The energy at the intersection is $\epsilon'=-\frac{3}{2}(n-|m|)^2$. The number of states corresponding to upper and lower branches can be found by substituting $\epsilon'=-\frac{3}{2}(n-|m|)^2$ and $k=n-|m|$ into Eqs. (10a) and (10b). It can be easily seen that the total number of states is $n-|m|$ in agreement with the well-known figure for the pure Coulomb problem.

In a recent work[6] Soloviev reported a similar double well behavior in the classical mean motion (i.e., after averaging over fast variables). His subsequent quantization rule is, however, less explicit and is formulated in terms of variables which are different from ours. A more detailed classi-

cal analysis is carried out by Richards[7] and by Delos, Knudson, and Noid.[8] The qualitative conclusions of all these works are in a general agreement; our numerics seem to best agree with Ref. 7. Along the lines of the quantum-mechanical analysis Herrick[9] succeeded in showing that the known O(4) symmetry of the hydrogen-atom bound states remains an approximate symmetry in the presence of a weak magnetic field. On this basis, he gave a complete classification of the resulting term scheme. Concerning the energy splitting we arrived at essentially the same conclusions through a completely different quantum-mechanical approach. In addition, our method has some further advantage, namely, that it provides an explicit expression for the wave function [Eq. (11)]; thus it is best suited to the calculation of other quantum-mechanical quantities (oscillator strengths, transition probabilities, etc.).

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*Permanent address.

†Present address.

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