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The hydrogen atom in an external magnetic field

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Abstract. A quantitative analysis of two sets of excited states of hydrogen atom in an arbitrary constant magnetic field is carried out for the first time. A 'nonlinearisation' method was used. Perturbational terms up to $\mathcal{H}^6$ are calculated. It is shown that the domain of applicability of the perturbation theory is contracted sharply with increase in the atom excitation degree. The range of this domain is estimated. Functional structure of arbitrary correction to the wavefunction is investigated and some of its substructures are found explicitly. Detailed calculations are performed for magnetic fields of arbitrary strengths. The accuracy of the calculations is estimated. Crossovers of the levels in the region of fields $\gtrsim 10^8$ G are discussed. Possible experimental consequences are considered.

1. Introduction

The problem of the description of the hydrogen atom in external fields is one of the oldest problems in quantum mechanics. Its importance is due to the fact that it arises in various domains of physics, in particular in semiconductor physics and in astrophysics. In the former case, excitons are hydrogen-like quasi-atoms with a small effective mass and a large dielectric constant. A description of the problem with weak fields may be found in any textbook on quantum mechanics (see e.g. Landau and Lifshitz 1974), so one might suppose that the problem is solved exhaustively in this simple case. Actually, the situation is not so clear; a brief review of the present state of the problem is given below.

1. The Stark effect ($\mathcal{E} \neq 0, \mathcal{H} = 0$)

It is known that in this case the state classification is done by means of the parabolic and magnetic quantum numbers (e.g. Landau and Lifshitz 1974) since variables are separated into the parabolic coordinates. At present, the exact coefficients of the perturbation theory (PT) series are known up to $\mathcal{E}^{17}$ for any state (Silverstone 1978), so the problem for weak electric fields is solved completely (a review is given in Damburg and Kolosov 1980).

In the case of strong fields (for the ground state the domain of strong fields is $\mathcal{E} \gtrsim 0.15$ au, see Dolgov and Turbiner 1980) the situation is quite indefinite; only the case of the ground state is investigated (see Dolgov and Turbiner (1980) and references therein).

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2. The Zeeman effect ($\mathscr{E}=0, \mathscr{H}\neq 0$)

There is no general solution to the state classification problem. It is known only that the states

$$n_r=0, \qquad m=\pm l, \tag{1a}$$

$$n_r=0, \qquad m=\pm(l-1), \tag{1b}$$

$$n_r=1, \qquad m=\pm l, \tag{1c}$$

are not degenerate (Avron 1981), and they are described in terms of the Coulomb quantum numbers; here n_r is the radial quantum number, l is the angular momentum and m is the magnetic quantum number. For weak fields, besides the term linear in the field and describing the linear Zeeman effect, the coefficient at the field squared is known for these states (a discussion is given in Garstang 1977). The asymptotics of the PT coefficients in the field magnitude is also known (Avron 1981). 100 coefficients of the PT series are found for the ground state (Avron *et al* 1979), and first three coefficients (up to the term $\mathscr{H}^6$) are known for lower excited states with the principal quantum number $n=2$ (Galindo and Pascual 1976). Since the PT series has zero convergence radius (Avron *et al* 1977, 1979, Avron 1981), the domain of applicability of the perturbation theory is restricted, and it is not clear now, how ample it is. Thus even in the case of weak fields the information on the excited state spectrum of hydrogen atom in a constant magnetic field is rather scant.

In the case of strong fields, the states with $n\leqslant 3$ were investigated. However, only the calculations of the ground state, presented in Kaschiev *et al* (1980) can be considered as reliable indeed; these calculations were performed with a high accuracy throughout the whole range of the magnetic field intensities, for which the non-relativistic treating is applicable. In fact, almost all other calculations (see Galindo and Pascual (1976) and references therein) have a restricted domain applicability and differ sometimes even in the first(!) significant digit. Besides, the accuracy was not controlled in those works, as a rule. No calculations for highly excited states were done until now.

In the present work we consider the behaviour of the hydrogen atom in constant magnetic fields. We deal with the states of the types (1*a*) and (1*b*) for arbitrary fields. Our present aim is not to attain an extremal precision, but to pay special attention to the qualitative aspects of the problem.

It is remarkable that the problem attracts a considerable interest at present (Simola and Viztamo 1978, Kara and McDowell 1980, Ruder *et al* 1981, Patil 1981, Cohen and Hermann 1981) in view of its spectrum. Another important aspect of the subject is the discovery of an approximate integral of motion in this problem, that reveals a possiblity of an approximate classification of highly excited states (Zimmerman *et al* 1980, Robnik 1981, Solovyev 1981).

The paper is organised as follows. In § 3 we present a brief description of the "nonlinearisation method' which is a basis for our approach. The Zeeman effect is discussed in § 4.

The case of arbitrary constant magnetic fields is concerned in § 5, the results calculated for highly excited states are presented; the level crossover is subject to a special discussion. Section 6 contains conclusions.

3. The method

The problem to be investigated is the Coulomb system perturbed by a multipole interaction. The problem will be considered from two points of view: the perturbation theory in the field intensity is applied to the region of small fields, and the case of arbitrary field is investigated by means of a convergent perturbational approach. The method enabling one to look at the problem from both sides was developed previously and is based upon a "nonlinearisation" procedure (Turbiner 1979, 1980, 1981a, 1982). In the framework of this method the conventional PT expansion in the field is a purely algebraical routine: some simple recursive relations are to be solved (Turbiner 1981b).

Recall the idea of the method. Write the wavefunction in the form

$$\psi(x) = f(x) \exp\{-\phi(x)\} \tag{2}$$

assuming that the functions f and ϕ have no singularities in the real space R^k, where k is the dimensionality of the configuration space. Of course, the representation (2) is not unambiguous. In order to fix the decomposition we require that the variation of f be minimal in a sense: it must contain only information on the nodal surfaces of the wavefunction. The exact meaning of this requirement will be elucidated in the following.

Put the wavefunction (2) into the Schrödinger equation

$$\Delta\psi + (E - V)\psi = 0. \tag{3}$$

The result is the following nonlinear equation

$$\Delta\phi - (\nabla\phi)^2 + (2\nabla\phi\nabla f - \Delta f)/f = E - V. \tag{4}$$

The PT expansions will be written on the basis of this equation. Suppose the potential is

$$V = V_0 + \lambda V_1 \tag{5}$$

where λ is a parameter. The functions f and ϕ, and the energy eigenvalue E are represented by formal series in λ:

$$\phi = \sum_{n=0}^{\infty} \lambda^n \phi_n \qquad f = \sum_{n=0}^{\infty} \lambda^n f_n \qquad E = \sum_{n=0}^{\infty} \lambda^n E_n. \tag{6a, b, c}$$

For the nth term of the series we get a linear equation (Turbiner 1980, 1982),

$$\Delta\phi_n - 2\nabla\phi_0\nabla\phi_n + (2\nabla f_0\nabla\phi_n - \Delta f_n + 2\nabla\phi_0\nabla f_n)/f_0 = E_n - \tilde{Q}_n \tag{7}$$

where $\tilde{Q}_1 \equiv V_1$; a general expression for $\tilde{Q}_n$ was given in (Turbiner 1979, 1980, 1982), it is not written here explicitly because it is rather cumbersome. Any reader can reconstruct it easily, it is written in terms of preceding terms of the expansions. In particular, if the position of the nodal surfaces is known *a priori* owing to some arguments, so that $f_n = 0$ for $n \geqslant 1$, then

$$\tilde{Q}_n \equiv Q_n = -\sum_{i=1}^{n-1} (\nabla\phi_i)(\nabla\phi_{n-i}). \tag{8}$$

Note that $\tilde{Q}_n$ plays the role of the perturbation potential, since the problem for the nth correction is identical to that for the first correction with $\tilde{Q}_n$ in place of $\tilde{Q}_1 = V_1$.

The boundary condition for the equation (7) is

$$|\psi_0^2 \nabla \phi_n| \to 0 \qquad \text{at } |x| \to \infty \tag{9}$$

where ψ_0 is the unperturbed wavefunction. In view of this condition, any correction to the energy is (cf Turbiner 1979, 1980, 1981a, 1982)

$$E_n = \int \tilde{Q}_n \psi_0^2 \, dx \Big/ \int \psi_0^2 \, dx. \tag{10}$$

Some details relevant to deformations of the nodal surfaces, f_n, may be found in Turbiner (1982); this aspect is beyond the purpose of the present work.

A theorem on the algebraisation was formulated in Turbiner (1981b) and its proof given in Turbiner (1982)†.

Theorem. If V_0 is the Coulomb interaction potential, and V_1 is a perturbation containing a finite number of spherical harmonics with coefficients which are polynomials‡ in r, then the PT procedure in the present method is purely algebraical: some simple recursive relations are to be solved.

This theorem will be used in § 4, where the PT expansion in the field is constructed. Now we are in a position to approach physical problems. Some information on converging PT expansions and the relation to the variational principle will be given in § 5.

4. Hydrogen atom in weak fields. The Zeeman effect

Let us consider hydrogen atom in a weak magnetic field in the case of the states $(1a)$, $(1b)$. We shall calculate the corrections up to $\mathscr{H}^6$ inclusive. It is a platitude to say that at small fields the energy shift is linear in the field (the linear Zeeman effect). It is not clear, however, what is the domain of small fields. We shall show that with increase in the excitation of the atom the domain where the linear Zeeman effect does work, as well as the PT in the whole, is sharply shrinking. In fact we shall elucidate the meaning of the term 'weak field'.

It was mentioned in the introduction that no classification scheme is known for states of the system under review. Therefore we restrict ourselves to the non-mixing states, specified by the Coulomb quantum numbers $(1a)$, $(1b)$. Note also that the construction of the standard Rayleigh-Schrödiner PT is rather complicated from the technical point of view (a discussion is given in Garstang (1977)), both in the calculation of the transition matrix elements and in the calculation of sums over the intermediate states. Such complications do not arise in the present approach, and the matrix elements are calculated by means of a simple algebra (see below).

The Hamiltonian operator describing the spinless hydrogen atom in a constant magnetic field is well known,

$$H = -\nabla_r^2 - 2/r + \gamma \hat{l}_z + \tfrac{1}{4}\gamma^2 r^2 (1-\mu^2) \tag{11}$$

where r, θ, φ are the spherical coordinates, $\mu = \cos\theta$, $\hat{l}_z$ is the z-component of the

† An analogous statement for the ground state and a special form of the potential V_1 was given in Au and Aharonov (1980).

‡ It is assumed also that the coefficient of the lth harmonics contains powers of r, which are not less than l.

angular momentum operator, the z-axis is directed along the magnetic field $\mathscr{H}$, $\gamma = \mu_B \mathscr{H}/R$ is a dimensionless parameter characterising the field strength, μ_B is the Bohr magneton, and R is the Rydberg constant. Since the z-projection of the angular momentum is an integral of the motion, $\hat{l}_z\psi = m\psi$ and the term (γm) appears, describing the linear Zeeman effect, that may be at once added to the energy, and the remaining problem is that of the quadratic effect.

The perturbation potential is

$$V_1 = \tfrac{1}{4}\gamma^2 r^2(1-\mu^2). \tag{12}$$

The Coulomb wavefunction describing the unperturbed system, for the states in the families $(1a)$, $(1b)$, is

$$\psi_0 = r^l Y_{lm}(\theta, \varphi)\exp(-\alpha r) \tag{13}$$

where $Y_{lm}(\theta, \varphi)$ is the spherical harmonics in the standard normalisation (Erdelyi 1953), $\alpha = 1/N$, where N is the principal quantum number. Thus, we have in $(6a)$ and $(6b)$

$$\phi_0 = \alpha r, \qquad f_0 = r^l Y_{lm}(\theta, \varphi) \tag{13'}$$

while the Coulomb energy is

$$E_0 = -\alpha^2. \tag{13''}$$

The PT parameter is $\lambda = \gamma^2$.

It is easy to see that the nth term is the series for ϕ is a polynomial of degree n in $(1-\mu^2)$, so

$$\phi_n = \sum_{i=0}^{n} R_i^{(n)}(r)(1-\mu^2)^i. \tag{14}$$

Clearly, the pre-exponential factor is not affected by the perturbation, so that

$$f_n \equiv 0 \qquad \text{for } n \geqslant 1. \tag{15}$$

Now the equation (7) is

$$\Delta\phi_n + \left(\frac{2l}{r} - \frac{2}{N}\right)\frac{\partial\phi_n}{\partial r} + \frac{(k-l\mu^2)}{\mu r^2}\frac{\partial\phi_n}{\partial\mu} = E_n - \tilde{Q}_n \tag{16}$$

and $\tilde{Q}_n = Q_n$ of equation (8),

$$k = (1-|m|) = \begin{cases} 0 & m = \pm l \\ 1 & m = \pm(l-1). \end{cases}$$

Substituting ϕ_n in (16) by the polynomial (14) one gets equations for the coefficient functions

$$R_n^{(n)''} + \left(\frac{2l+2}{r} - \frac{2}{N}\right)R_n^{(n)'} - \frac{2n(2n+l+1)}{r^2}R_n^{(n)} = \mathrm{coef}_{(1-\mu^2)^n}\{E_n - \tilde{Q}_n\} \tag{17a}$$

$$R_i^{(n)''} + \left(\frac{2l+2}{r} - \frac{2}{N}\right)R_i^{(n)'} - \frac{2i(2i+l+1)}{r^2}R_i^{(n)}$$

$$= \mathrm{coef}_{(1-\mu^2)^i}\{E_n - \tilde{Q}_n\} - \frac{2i(2i+|m|)}{r^2}R_{i+1}^{(n)}. \tag{17b}$$

It is evident from the boundary conditions that $R_i(n)$ are polynomials of a degree no more than $(2n+1)$, and analysing the recursive relations resulting from (17) one gets the following expression

$$R_i^{(n)}(r) = \sum_{j=\max\{2,2i\}}^{2n+1} a_j r^j. \tag{18}$$

Thus the coefficient $R_n(n)$ at the highest degree $(1-\mu^2)^n$ contains only two terms, the coefficient at $(1-\mu^2)^{n-1}$ has four terms, etc. Note that the function $R_n(n)$ is independent of k.

Exploiting the recursive relations we start from $R_n(n)$, then calculate $R_{n-1}(n)$ etc. An explicit form is available for $R_n(n)$,

$$R_n^{(n)}(r) = \frac{(-)^{n+1}(2n+2)!}{n!(n-1)!3^n 2^{2n-1}} \frac{r^{2n+1}}{N^{-2n+1}} + \frac{(-)^{n+1}}{2n3^n}\left\{1+(l+1)\frac{(2n)!}{n!^2}2^{-2n}\right\}\frac{r^{2n}}{N^{-2n}}. \tag{19}$$

It follows from equations (17) that the coefficient at the higher term for an arbitrary correction, r^{2n+1}, is independent of the level quantum numbers†, and the coefficient at r^{2n} is independent of the angular momentum projection m. A dependence on m appears only in the coefficient at r^{2n-1}, and lower. For example, we present here the highest coefficient in $R_{n-1}(n)$,

$$R_{n-1}^{(n)}(r) = \frac{(-)^n(2n-2)!\,n(n-1)}{n!(n-1)!3^n 2^{2n-2}5} \frac{r^{2n+1}}{N^{-2n+1}} + \ldots. \tag{20}$$

Next coefficients in $R_{n-1}(n)$, as well as in the functions $R_{n-2}(n)$, $R_{n-3}(n), \ldots$, can be calculated subsequently, but the results become more and more cumbersome. Note that the procedure can not be completed in a reasonable manner; e.g. the coefficient at the term r^{2n+1} in the first coefficient $R_1(n)$ can not be written in a closed form. This fact is proven accurately. The coefficient at r^{2n+1} in $R_0(n)$ is zero exactly.

Now let us discuss a remarkable fact. It is known that the PT series in the field powers (6) are divergent, while the Borel summation leads to a correct result‡ (cf Avron *et al* 1977). Consider the series (6*a*) and sum up the terms with highest powers of r in every ϕ_n. It is easily seen that the series over the highest terms is converging (see in Turbiner 1979, 1980). For instance, the sum (6*a*) of the terms with the highest powers in r and $(1-\mu^2)$ is

$$\hat{\phi} = \sum_{n=0}^{\infty} \gamma^{2n} r^{2n+1}(1-\mu^2)^n \operatorname{coef}_{r^{2n+1}(1-\mu^2)^n}\{\phi_n\} = \alpha r\left(1+\frac{\gamma^2 r^2}{12N^{-2}}(1-\mu^2)\right)^{1/2}. \tag{21}$$

Note a resemblance between $\hat{\phi}$ and the exact function: at small r it is the same as in the pure Coulomb problem $\hat{\phi} \to \alpha r$, while for large r and small z it approaches the function for the two-dimensional harmonical oscillator, $\hat{\phi} \to \gamma(x^2+y^2)/2\sqrt{3}$.

It is not difficult to calculate also the sum (6*a*) over the next-to-highest terms, the series are also converging. The divergence of the PT series (6*a*) manifests itself only in the terms with the lowest powers in r, the corresponding coefficients are related to the cofficients E_n in the expansion of the energy. A similar situation is known in the quantum field theory in the leading-logarithm approximation: also in that case the sum over the main logarithms is converging, as well as several corrections, while the

† It may be shown that this is valid for any state, not only for those specified by (1*a*) and (1*b*).

‡ It is of importance here that no terms non-analytical in the field (like $\exp(-1/\gamma)$) are present in the series (6*b*), and the sum is just f_0.

series as a whole is usually diverging. In quantum field theory, as a rule, one needs a special and rather complicated investigation in order to decide what is the domain where the leading-logarithm approximation does work. As for the quantum mechanical problem, the Schrödinger equation is always at hand, so the situation is quite clear.

One can show that the sum

$$\hat{\phi}_0 = \sum_{n=0}^{\infty} \gamma^{2n} r^{2n+1} \operatorname{coef}_{r^{2n+1}}\{\phi_n\}$$

reproduces a number of properties of the true function. In particular

$$\hat{\phi}_0 \xrightarrow[r\to 0]{} \alpha r + O(1/r)$$

$$\hat{\phi}_0 \xrightarrow[r\to\infty]{} \tfrac{1}{4}\gamma(x^2+y^2) + O(x, y, z)$$

while the sum

$$\hat{\phi}_1 = \sum_{n=0}^{\infty} \gamma^{2n} r^{2n} \operatorname{coef}_{r^{2n}}\{\phi_n\}$$

is a small correction to $\hat{\phi}_0$ for any value of its arguments x, y, z. We discuss this aspect in more detail in § 5, where the case of arbitrary fields is considered.

Let us calculate the first terms of the PT series (6*a*) and (6*c*). The problem is to apply the recursive relations resulting from (17); it is a pure algebra and we were able to exploit a computer program† REDUCE-2. The final expression for the energy of states (1*a*, *b*) is

$$\begin{aligned} E = {} & -N^{-2} + \gamma m + \tfrac{1}{4}\gamma^2 N^2(N+1)(N-k) - \tfrac{1}{16}\gamma^4 N^6(N+1) \\ & \times [\tfrac{46}{45}N^3 + \tfrac{137}{60}N^2 + \tfrac{17}{15}N - \tfrac{1}{45} - (\tfrac{185}{108}N^2 + \tfrac{359}{108}N + \tfrac{61}{54})k + (\tfrac{3}{4}N + \tfrac{7}{6})k^2] \\ & + \tfrac{1}{64}\gamma^6 N^{10}(N+1)[\tfrac{407}{135}N^5 + \tfrac{16373}{1080}N^4 + \tfrac{3071}{108}N^3 + \tfrac{3182}{135}N^2 + \tfrac{22}{3}N \\ & - (\tfrac{513433}{68040}N^4 + \tfrac{8626423}{249480}N^3 + \tfrac{2785715}{49896}N^2 + \tfrac{26985163}{748440}N + \tfrac{183107}{24948})k \\ & + (\tfrac{1055}{168}N^3 + \tfrac{2759}{108}N^2 + \tfrac{24851}{756}N + \tfrac{673}{54})k^2 - (\tfrac{7}{4}N^2 + \tfrac{221}{36}N + \tfrac{11}{2})k^3] + \ldots \end{aligned} \tag{22}$$

where $N = l+1$ is the principal quantum number, and k is given in (16).

Let us discuss the expression (22). In the case $N = 1$ (the ground state) it coincides with the standard results (e.g. Avron *et al* 1979). However, for $N = 2$, $l = 1$, we have found a slight numerical discrepancy with Galindo and Pascual (1976). The coefficient at the term γ^2 for any N coincides with the known expression (see e.g. Garstang 1977). We are not aware of PT coefficients for other states of the type (1*a*, *b*), calculated elsewhere.

A few comments on the general structure of arbitrary correction E_n. The functional form of any term in the sum (6*c*) is

$$E_n = (-1)^{n+1} N^{4n-2}(N+1) P_{2n-1}(N) \tag{23}$$

where $P_{2n-1}(N)$ is a polynomial of order $(2n-1)$, and its coefficient at N^{2n-1} is independent of the angular momentum projection, i.e. of k, and is positive. Note that the contribution from the quadratic Zeeman effect to the energy vanishes at the non-physical points $N = 0, -1$. The vanishing at $N = 0$ takes place also for any state,

† The computations were performed by means of ES-1060.

not only for those in (1*a*, *b*). All corrections to the wavefunction also vanish at this point. Remarkably, a similar situation was found for the anharmonical oscillator, $V(r) = r^2 + gr^4$, in d-dimensional configuration space; there are corrections vanish at $d = -2$ (see Dolgov and Popov 1978). In that case, an exact solution of the Schrödinger equation was found for the ground state at $d = -2$, and PT in the space dimensionality, i.e. in the number $(d+2)$, was attempted. Unfortunately, in the case considered no solution of the Schrödinger equation was found for $N = 0$.

Consider a highly excited hydrogen atom, $N \gg 1$. Then the series (22) is written as

$$E = -N \pm \gamma N + \tfrac{1}{4}\gamma^2 N^4 - \tfrac{23}{360}\gamma^4 N^{10} + \tfrac{407}{8640}\gamma^6 N^{16} + \ldots + (-)^{n+1} c_n \gamma^{2n} N^{6n-2} + \ldots \qquad (24)$$

where c_n are some positive numbers, unknown at present. Analysis of asymptotics of the series (6*c*), carried out by Avron (1981), is of no use here, since the limits $n \to \infty$ and $N \to \infty$ are not commutative. This is clear because the asymptotics of E_n is a polynomial in N of order $(6n-3)$, cf equation (23). What information can we extract from (22) and (24)? It is known that the coefficients of the series (22) increase as a factorial, so it has zero convergence radius (see Avron 1981, Avron *et al* 1977, 1979, Kaschiev *et al* 1980). Besides, in the case of highly excited states the coefficients of the PT series increase as a power of the principal quantum number. Therefore, the domain of the applicability of PT is shrinking rapidly with N. A simple estimate shows that for $N \gg 1$, the domain of the perturbation theory is

$$(\gamma^2)_{\mathrm{PT}} \leqslant \frac{4}{N^2}. \qquad (25)$$

Thus for states with $N \geqslant 30$–40 even the standard laboratory fields of 2–4 T are strong, PT is not applicable and the level energies are not known, because no numerical calculations were performed for $N \geqslant 4$. It is noteworthy that states with principal quantum numbers $N \leqslant 60$ are observed in laboratories by means of laser techniques; moreover, excitations with $N \leqslant 400$ were observed for hydrogen in outer space.

The analysis of PT series, as it was shown in this section, is reduced to a simple algebra; the corrections up to γ^6 were found.

The obtained results indicate that in the case of highly excited states the domain of strong fields is relevant to the laboratory conditions and must therefore be investigated.

5. Hydrogen atom in constant magnetic field (the case of arbitrary field)

In § 4 we have considered the case of small magnetic fields and shown that the domain of applicability of the conventional perturbation theory describing the behaviour of the hydrogen atom in the weak field depends substantially on the level of the atom excitation. The purpose of the present section is a non-standard approach to the spectral problem; we are going to deal with fields of arbitrary intensities. We restrict oursevles to the states (1*a*, *b*). Actually, we shall carry out a correct variational calculation with an appropriate trial function and estimate the accuracy.

Our approach to the problem is based upon three main arguments. (i) It is reasonable to apply a variant of the perturbation theory that does not require the knowledge of the whole spectrum of the unperturbed problem. (ii) In order to get a converging PT one should take the wavefunction of the zeroth approximation in such a way that the corresponding potential V_0 would reproduce all the singularities of the

investigated potential V and its asymptotics. Then 'Dyson's argument' would not lead to divergencies in the method. (iii) The result of any variational calculation may be considered as the first two terms of some perturbation theory.

We will explain first the latter point. The result of a variational calculation with a normalised trial function is written as follows

$$E_{\text{var}} = \int \psi_0 H \psi_0 = \int \psi_0 H_0 \psi_0 + \int \psi_0 (H - H_0)\psi_0 = E_0 + E_1 \tag{26}$$

where H is the Hamiltonian of the problem in view, and H_0 is a Hamiltonian corresponding to the trial function, $H_0 = p^2 + V_0$, where $V_0 - E_0 = \Delta\psi_0/\psi_0$, and E_1 is the first perturbational correction with the perturbation potential $V_1 = V - V_0$. Thus the variational energy corresponds to the first and second terms of PT series in the deviation from the original potential. Calculating $E_2, E_3, \ldots$ (cf (6c)), one gets, on one hand, an estimate for the accuracy of the variation calculation, and, on the other hand, one has an *iterative* procedure for making the variational results more exact, provided that the PT series has a non-zero convergence radius.

Now we turn to the second point and discuss the principle for a reasonable choice of the wavefunction for the zeroth approximation. Thus one gets a criterion for selection of trial functions for the variational calculations.

Clearly, the wavefunction is characterised suitably by the corresponding potential. 'Dyson's argument' (Dyson 1952) (see also a discussion in Turbiner (1979, 1980, 1981a, 1982) provides one with a criterion of convergence of PT series. In essence, one should deal with a perturbation potential which is less singular than the potential of the problem considered. So one should construct such a trial function ψ_0 that the corresponding potential V_0 have as many properties of the original potential V as it is possible, in particular, its singularities and the asymptotics. The closer V_0 is to V, the more exact will be the result.

With all this in view we shall construct the wavefunction of the zeroth approximation. The corresponding potential must have the Coulomb behaviour at the origin and the asymptotics of the two-dimensional harmonical oscillator at large distances (see (11)). The simplest wavefunction satisfying these requirements and corresponding to the states (1*a*, *b*) is

$$\psi_0 = r^l Y_{lm}(\theta, \varphi) \exp[-\alpha r/N - \tfrac{1}{4}\gamma(x^2 + y^2)]. \tag{27}$$

The potential related to this function is

$$V_0 = -2\alpha/r + \tfrac{1}{4}\gamma^2(x^2 + y^2) + (\alpha\gamma/N)(x^2 + y^2)/r \tag{28}$$

and the energy is

$$E_0 = -\alpha^2/N^2 + \gamma(|m| + m + 1) \tag{29}$$

where $\alpha = 1$. The choice of the wavefunction is rather successful, as the deviation of V_0 from the original potential is small not only in the asymptotical regions but also in the intermediate space, and the deviation decreases with the number of the state investigated. Moreover, the energy (29) has the Coulomb limit at small fields, and approaches the Landau formula, describing the spectrum of electrons in constant magnetic field, in the region of large field strengths.

The PT expansion will be developed in the deviation of the potential (27) from the true potential of the problem. The perturbation potential is

$$V_1 = V - V_0 = -(\gamma/N) r \sin^2 \theta. \tag{30}$$

Table 1. Energies of 1s and 2p levels as functions of the magnetic field strength γ. The results of the present work are compared with those by Brandi (1975), Kaschiev *et al* (1980), Galindo and Pascual (1976), Praddaude (1972). Results by Larsen (1968) are marked by an asterisk. The energies are given in Rydberg units.

	1s				$2p_0$			$2p_{+1}$		
γ	Brandi	Kaschiev	Galindo	This work	Praddaude	Galindo	This work	Praddaude	Galindo	This work
0				−1			−0.25			−0.25
0.1	−1	−0.999 957	−0.995 05	−0.9916	−0.224 82	−0.224 46	−0.2179	−0.101 69	−0.100 39	−0.089 71
0.2			−0.980 76	−0.9706		−0.165 17	−0.1574		0.115 15	0.119 45
0.3			−0.958 38	−0.9409		−0.088 13			0.366 95	0.348 30
0.4			−0.929 23	−0.9047		−0.002 08	−0.0085		0.637 48	0.588 59
0.5			−0.894 47	−0.8634		0.088 75	0.0731		0.918 04	0.836 57
0.6			−0.855 05	−0.8179		0.182 33	0.1576		1.204 41	1.0901
0.7			−0.811 70	−0.7689		0.277 62	0.2443		1.494 37	1.3480
0.8			−0.765 00	−0.7169		0.374 01	0.3326		1.786 70	1.6094
0.9			−0.715 42	−0.6224		0.471 17	0.4223		2.080 65	1.8736
1	−1	−0.662 28	−0.663 31	−0.6056	0.479 99	0.568 88	0.5130	2.086 82	2.375 76	2.1402
2	−0.002 94	−0.044 43	−0.050 53	0.0452	1.404 61	1.558 38	1.4527	4.800 83	5.353 37	4.8861
3		0.671 19	0.658 17	0.7845	2.359 96	2.554 84	2.4197	7.592 97	8.345 80	7.7086
4		1.438 72	1.419 07	1.572		3.553 06	3.3979		11.3420	10.569
5		2.2396	2.213 82	2.392		4.551 99	4.3821	13.28*	14.3397	13.453
10			6.457 37	6.741			9.3901			28.050
20	15.683 83	15.5927		15.95			19.3087			57.586
25			20.1511	20.67		24.5486	24.3007	71.81*	74.332 4	72.422
100	92.74	92.5223	92.4045	93.65		99.5479	99.2694	294.7*	299.33	296.20

Table 2. Energies of higher excited states calculated by means of equations (29) and (31), in Rydberg units. At $\gamma = 1$ the relative accuracy is 10^{-N}, where N is the principal quantum number.

γ	$3d_{+2}$	$3d_{+1}$	$4f_{+3}$	$4f_{+2}$	$5g_{+4}$	$5g_{+3}$	$6h_{+5}$	$6h_{+4}$	$7i_{+6}$	$7i_{+5}$	$8k_{+7}$	$8k_{+6}$
0	−0.111 11	−0.111 11	−0.0625	−0.0625	−0.04	−0.04	−0.0278	−0.0278	−0.020 41	−0.020 41	−0.015 65	−0.0156 25
0.1	0.2370	0.0951	0.4875	0.3374	0.7162	0.5611	0.9356	0.7771	1.1500	0.9890	1.3612	1.1983
0.2	0.6559	0.3532	1.1166	1.8001	1.5533	1.2284	1.9790	1.6484	2.3984	2.0635	2.8173	2.4760
0.3	1.0954	0.6254	1.7647	1.2762	2.4078	1.9081	3.0383	2.5308	3.6693	3.1486	4.2884	3.7576
0.4	1.5459	0.9046	2.4227	1.7588	3.2712	2.5934	4.1052	3.4183	4.9417	4.2371	5.7615	5.0986
0.5	2.0035	1.1882	3.0869	2.2452	4.1402	3.2821	5.1795	4.3087	6.2148	5.3253	7.2348	6.3430
0.6	2.4660	1.4747	3.7556	2.7342	5.0131	3.9730	6.2660	5.2012	7.4885	6.4208	8.7089	7.6391
0.7	2.9324	1.7632	4.4275	3.2249	5.8888	4.6654	7.3404	6.0938	8.7630	7.5170	10.1842	8.9360
0.8	3.4018	2.0533	5.1020	3.7169	6.7669	5.3589	8.4101	6.9873	10.0389	8.6139	11.6613	10.2334
0.9	3.8736	2.3446	5.7786	4.4100	7.6457	6.0532	9.4860	7.8857	11.3161	9.7113	13.1402	11.5311
1	4.3473	2.6368	6.4569	4.7309	8.5281	6.7483	10.5631	8.7829	12.5949	10.8089	14.6208	12.8291
2	9.1514	5.5885	13.2963	9.6663	17.3328	13.7262	21.3984	17.7635	25.4521	21.7912	29.4978	25.8239
3	14.0173	8.5631	20.1890	14.6470	26.2200	20.7116	32.3088	26.7505	38.3804	32.7814	44.4706	38.8992
4	18.9132	11.5468	26.9940	19.6346	35.1482	27.7008	43.2546	35.7413	51.3389	43.7734	59.9843	51.9982
5	23.8274	14.5352	33.9186	24.6301	44.0991	34.6927	54.2186	44.7348	64.3158	54.7777	74.9843	64.9843
10	48.5368	29.5050	68.7695	49.6069	88.9852	69.6714	109.1385	89.7195	129.9759	109.9795		
25	123.178	74.4791	173.642	124.583	223.905	174.656	274.286	224.870				
100	498.083	299.453	698.571	499.568	899.101	699.837						

Dyson's argument suggests that the expansion is converging because the perturbation potential is small as compared with the original potential in the regions $r \to \infty$ and $r \to 0$, and the convergence is improved with rise of the principal quantum number. The first correction to the energy E_1 has the standard form of the averaged perturbation potential (see e.g. Landau and Lifshitz 1974) and it is reduced to

$$E_1 = -\frac{\gamma}{N} \frac{\int_0^\infty dr\, r^{2N+1} \int_{-1}^1 d\mu (1-\mu^2) P_{lm}^2 \exp[-2r/N - \frac{1}{2}\gamma r^2(1-\mu^2)]}{\int_0^\infty dr\, r^{2N} \int_{-1}^1 d\mu\, P_{lm}^2 \exp[-2r/N - \frac{1}{2}\gamma r^2(1-\mu^2)]} \tag{31}$$

where P_{lm} is the associated Legendre polynomial or, equivalently, in terms of the single integrals,

$$E_1 = -\gamma(k+1)(N-k) \frac{\int_0^\infty d\eta [\eta^N e^{-\eta}/(1+\frac{1}{2}\gamma N^2 \eta)^{N+1}](\frac{1}{2}\gamma N^2 k\eta^2 + k\eta - N)}{\int_0^\infty d\eta [\eta^N e^{-\eta}/(1+\frac{1}{2}\gamma N^2 \eta)^{N}](\frac{1}{2}\gamma N^2 k\eta^2 + k\eta - N + k)}. \tag{31'}$$

The sum $E_0 + E_1$ has some properties of the true level energy: at small γ it describes correctly the linear Zeeman effect, though the coefficient at γ^2 is wrong by a factor of two; for $\gamma \to \infty$ when the Coulomb term in the potential is inessential, the correct spectrum of electron in the constant magnetic field is reconstructed with corrections logarithmic in the field strength. The term E_1 contains a singularity at $\gamma^2 = 0$, and this is the reason why the PT series is diverging. As in the case of the anharmonic oscillator, there is a cut in the complex plane of γ^2, from $\gamma^2 = 0$ to $-\infty$. Avron (1981) has calculated the discontinuity at the cut in the limit $\gamma^2 \to -0$, that was found to be exponentially small. The expression in (31) has also a cut along the negative semi-axis, and the discontinuity is exponentially small at $\gamma^2 \to -0$, but the pre-exponential factor differs from that obtained by Avron.

Unfortunately, the expression for the energy $E_0 + E_1$ also has some defects. Odd powers of γ, that must be absent *a priori*, do appear in the power series for (31). We can prove that the odd powers are removed with account for next corrections E_2, E_3 etc. The expression contains no term $\sim \ln^2 \gamma$, which is next to the leading term in the asymptotics, and the expansion starts from a term $\sim \ln \gamma$ for (1*a*), and a constant for (1*b*). This defect is also eliminated with account for higher corrections. Nevertheless, equations (29) and (31) provide with a rather accurate description of the spectrum for all γ. Results of the calculations by means of these formulae are given in tables 1 and 2 for the states with $N = 1, 2, \ldots, 8$ and non-negative projection of the angular momentum . It is seen that the field dependence of the energy becomes almost linear at strong fields, but none of the considered states does move to the continuous spectrum, i.e. their energy remains less than the energy of an unbound electron in the constant magnetic field. Table 1 contains also a comparison of our results with the calculations by other authors, and the agreement is satisfactory. The accuracy of the present results will be discussed in the following, here they are considered just as the variational results with the trial function (27).

Equations (29) and (31) show the correspondence between the Coulomb states (small fields) and the states of the two-dimensinal harmonical oscillator (large fields, the Landau levels). There is a complete agreement with the correspondence scheme, presented in the review by Garstang (1977) for the first excited levels. The present approach enables one to obtain more general results. An evident result is that all lower components of the multiplets with $m = -l, -l+1$ go to the Landau zero zone, while the upper components leave for different Landau zones. Therefore various level crossovers take place. In particular, all the levels with $m = -l, -(l-1)$ with $l \geq 2$ (i.e.

Table 3. Crossovers for various levels.

	$3d_{-2}$	$3d_{-1}$	$4f_{-3}$	$4f_{-2}$	$5g_{-4}$	$5g_{-3}$	$6h_{-5}$	$6h_{-4}$	$7i_{-6}$	$7i_{-5}$	$8k_{-7}$
$2p_{+1}$	0.062	0.090	0.087	0.119	0.105	0.137	0.115	0.149	0.125	0.159	0.132
$3d_{+1}$			0.015	0.021	0.023	0.030	0.028	0.036	0.032	0.041	0.035
$3d_{+2}$			0.011	0.013	0.016	0.019	0.019	0.022	0.021	0.025	0.023
$4f_{+2}$					0.0042	0.005	0.0065	0.0075	0.0078	0.0092	0.0088
$4f_{+3}$					0.0035	0.0040	0.0052	0.0058	0.0063	0.0071	0.0070

$N \geq 3$) cross the level $2p_{+1}$, the levels with $l \geq 3$ (i.e. $N \geq 4$) cross the levels $3d_{+2}$, $3d_{+1}$, the levels with $l \geq 4$ (i.e. $N \geq 5$) cross the levels $4f_{+3}$, $4f_{+2}$ etc. The crossovers occur indeed, because the levels have different symmetry as the magnetic quantum number is conserved. Positions of the first crossovers are given in table 3. Note that the crossover of the levels $2p_{+1}$ and $3d_{-2}$ takes place at a field strength about 10^8 G.

Because the angular momentum projection is a conserved quantum number, there is an evident relation between the upper and lower components in the multiplets,

$$\Delta E_{l,m} \equiv E_{l,m} - E_{l,-m} = 2\gamma m \tag{32}$$

that is valid for any field. This relation leads to another one,

$$\hat{\Delta} E_{l,m} = \Delta E_{l,m} - \Delta E_{l,m-1} = \delta^+ E_l + \delta^- E_l = 2\gamma \tag{33}$$

where $\delta^+ E_l = E_{l,m} - E_{l,m-1}$ is the distance between the upper components, $\delta^- E_l = E_{l,-m+1} - E_{l,-m}$ is the distance between the lower components for the states (1*a*, *b*). Note that the RHS of (33) is independent of the principal quantum number N. These quantities are useful, probably, for identification of the spectral lines. It is seen at once from equations (29) and (31) what is the field dependence of the quantities $\delta^+ E_l$, $\delta^- E_l$: at small fields they are approximately equal, $\delta^+ E_l = \delta^- E_l$, since the splitting is proportional to the field strength, while with rising γ one gets the inequality $\delta^+ E_l > \delta^- E_l$, and $\delta^+ E_l = 2\gamma - O(\ln \gamma)$. This effect has been observed in an experiment (Gershenzon *et al* 1977), it is especially clear for the states with $N = 2$. A scheme of the level behaviour is shown in figure 1.

The level behaviour at large magnitudes of the principal quantum number is also rather interesting. By means of equations (29), (31), one gets the asymptotics for $\gamma \gg 1$, for instance, for the extreme components $m = \pm l$,

$$E_N = \gamma(|m| + m + 1) - (2^{5/4}/e)\gamma^{-3/4} N^{-7/4} + \ldots \tag{34}$$

where $e = 2.718\ldots$. Thus in the region of large N the level approaches rapidly the Landau behaviour, and it never does reach the continuous spectrum, as the correction to the Landau formula is negative. Note that the distance to the boundary of the continuous spectrum falls as a power of the quantum number, and the speed of approaching is higher for larger fields. One should have in mind also that the limits of strong fields and high excitations are not commutative.

Let us discuss the accuracy of the results obtained. The first and second terms of the PT series have been used until now; the procedure is equivalent to the variational approach. We have supposed that the PT is converging, having in mind 'Dyson's argument'. So a calculation of E_2 would provide us not only with another correction

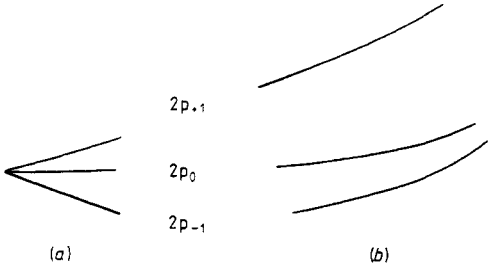

Figure 1. Distance between upper and lower components of the multiplet as a function of the field strength for (*a*) small fields, and (*b*) large fields.

to the perturbational expansion, but also enables to estimate the accuracy of the variational calculation with the trial function (27). Recall the expression for the second correction to the energy,

$$E_2 = -\int (\nabla\phi_1)^2\psi_0^2 \, \mathrm{d}^3x \Big/ \int \psi_0^2 \, \mathrm{d}^3x$$

where ϕ_1 is the first correction to the exponential function (see (6*a*)). It is important that the second correction to the energy is always negative, so with two terms for the energy, $E_0 + E_1$, we have an upper bound.

In order to find ϕ_1 one has to solve the differential equation

$$\nabla(\psi_0^2\nabla\phi_1) = (E_1 - V_1)\psi_0^2 \tag{35}$$

which is like the equation of electrostatics with a variable dielectric permeability ψ_0^2. The boundary condition for the equation is

$$|\psi_0^2\nabla\phi_1| \to 0 \qquad \text{at } |x| \to \infty.$$

Unfortunately, we have not succeeded in finding an analytical solution for this equation, so an approximation will be used. The asymptotics of the function ϕ_1 is easily found,

$$\begin{aligned} &\phi_1 \xrightarrow[r\to 0]{} E_1 r^2/2(2N+1) \\ &\phi_1 \xrightarrow[r\to\infty]{} Nr(1-|\mu|). \end{aligned} \tag{36}$$

for intermediate values of r we take an interpolation function, having the correct asymptotics,

$$\phi_1 = [E_1 r^2/2(2N+1)][1 + E_1 r/2(2N+1)N(1-|\mu|)]^{-1}. \tag{37}$$

Putting this function into equation (35), one sees that corrections to this approximate expression are small. Substituting (37) in E_2, we estimate the second correction to the level energy. The calculation was performed for $\gamma = 1$; it was found that the relative error of the results presented is about 10^{-N} (see tables 1 and 2), by the order of magnitude.

6. Conclusion

We have investigated the behaviour of the energy levels and corrections to the wavefunctions for two sets of states of the hydrogen atom in a constant magnetic field in the case when the Coulomb classification of states remains applicable. The boundary of the weak field region was specified, and the domain of applicability of the perturbation theory was found. Corrections to the energy and to the wavefunctions of orders γ^4 and γ^6 are found for the first time. Since the procedure expoited was purely algebraical, one can use special computer programs to calculate higher corrections analytically. One should have in mind, however, that it is hardly reasonable to calculate the corrections, as the PT series is asymptotical.

An alternative method enables us to describe the region of arbitrary magnetic fields, provided that the non-relativistic approach is valid. Even with a simple trial function (27) we were able to get rather accurate results, and moreover, to study the problem analytically. Seemingly, it is clear in what manner one can modify the trial

function (27) in order to get higher precisions. First, the calculation may be treated as a standard variational method, as it was done in fact in Rau and Spruch (1976), variating the parameter α in (27).

One would not meet with trouble, since the above reasoning suggests that the PT series remains convergent, as a Coulomb term with a coefficient, less than that in the unperturbed potential, is added to the perturbation (30). Thus one can improve the accuracy appreciably (see table 4). Second, the exponential in (27) may be modified in such a way that, besides the correct asymptotics, the structure of the series in the powers of the field would be also correct (only even powers of the field would be present in the expansion, the functional correction at the term γ^2 would be correct etc). For example, here is one of the simplest modifications,

$$\psi_0 = r^l Y_{lm}(\theta, \varphi) \exp\{-[\alpha^2 r^2/N^2 + \tfrac{1}{16}\gamma^2(x^2+y^2)^2]^{1/2}\}. \tag{38}$$

Odd powers of the field are eliminated in this function. In turn, this function may be treated as a trial function in the variational method, looking for minimum in the parameter α (see table 4).

Table 4. Energy of 1s level at $\gamma = 1$ calculated by means of equations (27) and (38) without and with minimisation over parameter α.

Equation (27)		Equation (38)		Kaschiev *et al*
$\alpha = 1$	$\alpha = \alpha_{min} = 0.879$	$\alpha = 1$	$\alpha = \alpha_{min} = 1.1359$	
−0.6056	−0.6201	−0.6352	−0.6543	−0.6623

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Note added in proof. After submitting the manuscript some new papers have appeared. In particular, (i) the ground state has been investigated in detail by Le Guillou and Zin-Justin (1983); (ii) the family of excited states other than (1*a*, *b*) has been studied by Friedrich (1982) and (iii) the state $^1\Sigma$ of the molecule H_2 in a magnetic field of arbitrary strength was firstly considered by means of obvious modification of the wavefunction of zeroth approximation (27) and it was shown that two atoms repel at large distances in the presence of a magnetic field (Turbiner 1983).

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