A hydrogen atom in weak electric and magnetic fields

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The behavior of the ground state of the hydrogen atom in weak electric $\mathscr{E}$ and magnetic $\mathscr{H}$ fields is investigated in the cases when the fields are parallel and perpendicular to each other. The coefficients of the perturbation theory series are computed right up to terms $\sim \mathscr{E}^2\mathscr{H}^4$ by a purely algebraic method based on a "nonlinearization" procedure. The problems of polarizability and magnetic susceptibility are discussed.

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The behavior of the hydrogen atom in constant electric and magnetic fields is one of the oldest problems in nonrelativistic quantum mechanics. But in contrast to other similar problems like the Stark and Zeeman effects, it has virtually not been investigated. Right up to the present time even the problem of the classification of the states of the atom in nonzero fields has not been solved, although it was posed in Ref. 1, where an attempt was made to investigate the situation for weak fields. For this reason, we shall limit ourselves in our analysis to the case of the ground state, since the application of the method employed by us requires knowledge of the explicit form of the unperturbed wave function. Not a single quantitative analysis has thus far been carried out for the problem in question, although the qualitative investigation performed in Ref. 2 indicates that the physics is interesting. Notice that this problem is of interest for different branches of physics: semiconductor physics (an exciton in fields), astrophysics, optics. In particular, it arises when an attempt is made to take into account the finiteness of the nuclear mass in the Zeeman-effect problem (see, for example, Ref. 3).

In the present paper we construct a perturbation theory in terms of the fields $\mathscr{E}$ and $\mathscr{H}$ for the lowest state of the spectrum in two important particular cases, of parallel and mutually perpendicular fields. The generalization to the case of arbitrary orientation of the fields $\mathscr{E}$ and $\mathscr{H}$ is obvious. To construct the perturbation theory, we shall use the "nonlinearization procedure,"[4] within the framework of which the computation of the coefficients of the perturbation theory series is a purely algebraic problem, boiling down to the solution of simple recursion relations.[5] In our previous paper[6] we successfully applied this procedure to the problem of the Zeeman effect, and for the first time determined the coefficients of the perturbation theory series in $\mathscr{H}$ right up to and including the $\mathscr{H}^6$ term for the states with zero radial quantum number and magnetic quantum numbers $m = \pm l$, $\pm(l-1)$, where l is the angular momentum.

Let us briefly recall the main points of the nonlinearization procedure as applied to the present problem. We write the wave function in the following form:

$$\psi = \exp\{-\Phi\}, \tag{1}$$

the function Φ having no singularities at real values of the arguments since we are considering the ground state. Substituting (1) into the Schrödinger equation $\hat{H}\psi = E\psi$, where $\hat{H} = -\nabla^2 + V$, we obtain the equation

$$\Delta\Phi - (\nabla\Phi)^2 = E - V. \tag{2}$$

Now let us set

$$V = V_0 + \lambda V_{10} + gV_{01}, \tag{3}$$

and begin to develop a perturbation theory for the quantities Φ and E in the following manner:

$$\Phi = \sum_{n,k=0}^{\infty} \lambda^n g^k \Phi_{nk}, \tag{4a}$$

$$E = \sum_{n,k=0}^{\infty} \lambda^n g^k E_{nk}. \tag{4b}$$

Substituting (3), (4a), and (4b) into Eq. (2), and collecting the terms of the order of $\lambda^n g^k$, we obtain the equation

$$\Delta\Phi_{nk} - 2\nabla\Phi_{00}\nabla\Phi_{nk} = E_{nk} - Q_{nk}, \tag{5}$$

where the quantity Q_{nk} plays the role of an effective perturbation potential, and is given by the following formulas:

$$\begin{aligned} &Q_{10} = V_{10},\ Q_{01} = V_{01}, \\ &Q_{nk} = -\Sigma\nabla\Phi_{mp}\nabla\Phi_{n-m,\,k-p}, \end{aligned} \tag{6}$$

where the summation is performed over all $m + p > 0$ and $m + p < n + k$. Equation (5) together with (6) gives us all that we need for the computation of the corrections.

The Hamiltonian corresponding to the hydrogen atom in constant electric and magnetic fields has the form

$$\hat{H}^{\parallel} = -\nabla^2 - 2/r - 2\mathscr{E}z - \mathscr{H}\hat{l}_z + {}^1/_4\mathscr{H}^2(x^2+y^2) \tag{7a}$$

in the case when the fields are parallel and

$$\hat{H}^{\perp} = -\nabla^2 - 2/r - 2\mathscr{E}x - \mathscr{H}\hat{l}_z + {}^1/_4\mathscr{H}^2(x^2+y^2), \tag{7b}$$

when the fields are perpendicular to each other. The field $\mathscr{H}$ is oriented in both cases along the z axis, while the electric field $\mathscr{E}$ is oriented in the second case along the x axis; $\hat{l}_z$ is the operator for the angular-momentum component along the z axis. The field $\mathscr{E}$ is given in ordinary atomic units; the field $\mathscr{H}$, in dimensionless units (one unit $= 2.3505 \times 10^9$ G). Since we are considering the ground state, we can discard the paramagnetic term $(\mathscr{H}\hat{l}_z)$ in the Hamiltonian (7a), and then

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$$V_{10}^{\parallel}=-2z=-2rY_1^0(\theta,\varphi),\quad V_{01}^{\parallel}=\frac{r^2}{6}(Y_2^0-Y_0^0),\quad (8a)$$

while in the case of mutually perpendicular fields

$$V_{10}^{\perp}=-2x=-2rY_1^1(\theta,\varphi),\quad V_{01}^{\perp}=1/6r^2(Y_2^0-Y_0^0).\quad (8b)$$

There is also a paramagnetic term ($i\mathscr{H}\partial/\partial\varphi$), since the angular momentum component along the z axis is no longer an integral of the motion[1]; r, θ, and φ are spherical coordinates and

$$Y_l^m=P_l^m(\cos\theta)\begin{cases}\cos m\varphi, & m\geqslant 0\\ \sin|m|\varphi, & m<0\end{cases}$$

are spherical harmonics.

Let us first consider the simpler case of parallel fields. Analyzing Eq. (5), we easily see that an arbitrary correction to the wave function $\Phi_{nk}^{\parallel}$ contains a finite number of harmonics, and has the following form:

$$\Phi_{nk}^{\parallel}=\sum_{i=0}^{[n+k/4]}R_{n,k,n+k-2i,0}^{\parallel}(r)\,Y_{n+k-2i}^0(\theta,\varphi),\quad (9)$$

where $[n+k/4]$ denotes the integer part of the number $(n+k/4)$. If k is an odd number, then

$$\Phi_{nk}^{\parallel}\equiv 0.\quad (9a)$$

The coefficient functions are polynomials in r, i.e.,

$$R_{n,k,n+k-2i,0}^{\parallel}(r)=\sum_{m=n+k-2i}^{n+k+1}a_m r^m,\quad (10)$$

and let us draw attention to the fact that the polynomial attached to the highest harmonic $Y_{n+k}^0(\theta,\varphi)$ contains only two terms; the polynomial attached to the next highest harmonic $Y_{n+k-2}^0(\theta,\varphi)$ four terms; etc. We shall not write out the recursion formulas; they are fairly simple, and can easily be derived by the reader. We need only note that some of them can be resolved explicitly in the case of an arbitrary correction. For example, the coefficient function of the highest harmonic is

$$R_{n,k,n+k,0}^{\parallel}(r)=\frac{(n+k)!^2(n+k/2-1)!}{(2n+2k)!n!(k/2)!}\left\{\frac{1}{2}+\frac{(2n+k)!(n+k/2)}{2^{2n+k}(n+k/2)!(n+k)}\right\}\times\frac{2^n}{3^{k/2}}r^{n+k}+\frac{(n+k)!^2(2n+k)!2^{-n-k}}{(2n+2k)!(n+k/2)!n!(k/2)!(2n+k-1)}r^{n+k+1}.\quad (11)$$

For $n=0$, i.e., for $\mathscr{E}=0$ (the Zeeman effect), the expression (11) coincides with the expression obtained in Ref. 6, while for $k=0$, i.e., for $\mathscr{H}=0$, the formula (11) goes over into the expression corresponding to the Stark effect. We can, in principle, find the coefficient function of next highest harmonic, etc., but the calculation becomes more and more complicated.

The determination of the first corrections offers no fundamental difficulties, but is rather tedious. Therefore, the computations were performed with the aid of the symbolic language REDUCE-2. The results for several first corrections to the wave function are given in the Appendix.

Let us represent the expansion for the energy in the form

$$E=E_{SZ}+E^{\parallel(\perp)},\quad (12)$$

where the term E_{SZ} is the sum of the energy expansions in the case of the Stark- and Zeeman-effect problems:

$$E_{SZ}=-1-\frac{9}{2}\mathscr{E}^2+\frac{\mathscr{H}^2}{2}-\frac{3555}{32}\mathscr{E}^4-\frac{53}{96}\mathscr{H}^4+\ldots,\quad (13)$$

while $E^{\parallel}$ contains the cross–in the fields–terms:

$$E^{\parallel}=\frac{159}{16}\mathscr{E}^2\mathscr{H}^2-\frac{1742009}{26880}\mathscr{E}^2\mathscr{H}^4+\ldots.\quad (14)$$

Notice that the cross terms in (14) were not known before.[2]

Let us now proceed to consider the case of mutually perpendicular fields. If we neglect the term $(\mathscr{H}\hat{l}_z)$ in the Hamiltonian (7b), then the perturbation theory can be constructed in a manner entirely similar to the case of parallel fields. Let us give only the final results for the cross terms:

$$E^{\perp}=\frac{93}{4}\mathscr{E}^2\mathscr{H}^2-\frac{22770991}{107520}\mathscr{E}^2\mathscr{H}^4+\ldots\quad (15)$$

and note that the structure of the arbitrary correction $\tilde{\Phi}_{nk}^{\perp}$ resembles that of $\Phi_{nk}^{\parallel}$:

$$\tilde{\Phi}_{nk}^{\perp}=\sum_{i=0}^{[n+k/4]}\sum_{m=0}^{[n/2]}\tilde{R}_{n,k,n+k-2i,n-2m}^{\perp}Y_{n+k-2i}^{n-2m}(\theta,\varphi),\quad (16)$$

where $\tilde{\Phi}_{nk}^{\perp}\equiv 0$ when k is odd. The coefficient functions are polynomials, and resemble the $\Phi_{nk}^{\parallel}$ in structure: there are two terms in each of those attached to the highest harmonics $Y_{n+k}^{n-2m}(\theta,\varphi)$; four in each of those attached to the next highest harmonics, etc. The degrees of the polynomials are the same as in $\Phi_{nk}^{\parallel}$.

The situation is somewhat different in the case when the paramagnetic term $(\mathscr{H}\hat{l}_z)$ is taken into consideration. First, Eq. (5) gets modified, and it assumes the following form:

$$\Delta\Phi_{nk}^{\perp}+i\frac{\partial\Phi_{n,k-1}^{\perp}}{\partial\varphi}-2(\nabla\Phi_{00}^{\perp}\nabla\Phi_{nk}^{\perp})=E_{nk}-Q_{nk},\quad (17)$$

the Q_{nk} being given as before by the formula (6). Second, the structure of the correction $\Phi_{nk}^{\perp}$ to the wave function is significantly more complicated: they have the same fundamental form and are given by the formula (16) in the case of even k, but do not vanish and are pure imaginary in the case of odd k;

$$\Phi_{nk}^{\perp}=i\sum_{j=0}^{[n+k/4-1]}\sum_{m=0}^{[(n-1)/2]}R_{n,k,n+k-1-2j,-n+2m}^{\perp}Y_{n+k-1-2j}^{-n+2m}(\theta,\varphi),\quad (18)$$

where k is an odd number. The coefficient functions are polynomials having the same structure as the $R^{\parallel}$ (see (10)) in the case of even k, and

$$R_{n,k,n+k-1-2j,-n+2m}^{\perp}(r)=\sum_{p=n+k-1-2i}^{n+k+1}a_p r^p\quad (19)$$

in the case of odd k. Notice that, in the case of odd k, the polynomial attached to the highest harmonics $Y_{n+k-1}^{-n+2m}(\theta,\varphi)$ contains three terms; that attached to the next highest harmonics $Y_{n+k-3}^{-n+2m}(\theta,\varphi)$ five terms, etc. As in the case of parallel fields, the coefficient functions attached to the highest harmonics can be found explicitly, but we shall not give their explicit form: the formulas are similar to (11).

As in the case of parallel fields, to find the first corrections, we used the symbolic language REDUCE-2. The expressions for the corrections $\Phi_{nk}^{\perp}$ are given in the Appendix.

Let us represent the expansion for the energy in a form similar to (12), and give the final result for the cross terms:

$$E^{\perp}=\frac{731}{48}\mathscr{E}^2\mathscr{H}^2-\frac{15308863}{120960}\mathscr{E}^2\mathscr{H}^4+\ldots. \tag{20}$$

It can be seen from a comparison of (20) with (15) that allowance for the term $(\mathscr{H}\hat{l}_z)$ in the Hamiltonian decreases the coefficients of $\mathscr{E}^2\mathscr{H}^2$ (by 34%) and of $\mathscr{E}^2\mathscr{H}^4$ (by 40%). Notice also the quite large values of the coefficients of the cross terms in (14) and (20), which is important for various investigations within the framework of perturbation theory, since the region of applicability of the theory shrinks sharply. Also worthy of note is the fact that the coefficients attached to the cross terms in the case of mutually perpendicular fields are consistently much greater than in the case of parallel fields.

CONCLUSION

Thus, we have succeeded in computing, for the first time ever, the coefficients attached to the cross terms in the problem of the hydrogen atom in constant electric and magnetic fields. This became possible as a result of the application of the "nonlinearization" method, since it is difficult to conceive such calculations within the framework of the standard approach with the use of sums over intermediate states or Green functions. Within the framework of the method used, all the calculations reduce to the solution of simple recursion relations.

Let us discuss the physical meaning of the results obtained. To begin with, let us note that, since we are working within the framework of perturbation theory, the region of applicability of the results obtained is limited to the case of fairly low $\mathscr{E}$ and $\mathscr{H}$ fields. This is due to the fact that the series in powers of $\mathscr{H}$ for fixed $\mathscr{E}$ has a zero convergence radius, and its coefficients increase in a factorial fashion. The series in powers of $\mathscr{E}$ for fixed $\mathscr{H}$ has a convergence zero radius with factorial growth of the coefficients in the case of parallel fields and a finite radius of convergence in the case of perpendicular fields.[3)] This circumstance is easy to understand when expressed in terms of Dyson's argument,[4)] and we shall not discuss it in detail here. We only note that the atom is unstable in the case of parallel fields, although the probability for tunneling is exponentially small (in fairly weak fields). Let us now fix the electric-field strenght $\mathscr{E}$, and write down the expression for the magnetic susceptibility of the atom:

$$\begin{aligned}\chi^{\parallel}&=-1-\frac{159}{8}\mathscr{E}^2+\frac{53}{24}\mathscr{H}^2+\frac{1742009}{6720}\mathscr{E}^2\mathscr{H}^2+\ldots,\\ \chi^{\perp}&=-1-\frac{731}{24}\mathscr{E}^2+\frac{53}{24}\mathscr{H}^2+\frac{15308863}{30240}\mathscr{E}^2\mathscr{H}^2+\ldots.\end{aligned} \tag{21}$$

It can be seen that the standard term $\sim\mathscr{H}^2$ tries to decrease the magnitude of the susceptibility and make the atom less "diamagnetic," whereas the term $\sim\mathscr{E}^2$ (which originates from a cross term in the energy) increases the susceptibility, thus stabilizing the situation. This effect is more strongly pronounced in the case of perpendicular fields.

Let us now consider a different aspect of the problem: let us fix the magnitude of $\mathscr{H}$, and write down the expression for the polarizability of the atom:

$$\begin{aligned}\alpha^{\parallel}&=9+\frac{3555}{8}\mathscr{E}^2-\frac{159}{8}\mathscr{H}^2+\frac{1742009}{13440}\mathscr{H}^4+\ldots,\\ \alpha^{\perp}&=9+\frac{3555}{8}\mathscr{E}^2-\frac{731}{24}\mathscr{H}^2+\frac{15308863}{60480}\mathscr{H}^4+\ldots.\end{aligned} \tag{22}$$

If now we take a sufficiently weak field $\mathscr{E}$, so that we can neglect the term $\sim\mathscr{E}^2$, then it is evident that the term $\sim\mathscr{H}^2$ decreases effectively the polarizability of the hydrogen atom. Notice that, as in the preceding case, the effect manifests itself more strongly in the case of perpendicular fields. It is also worth while to emphasize that in fields of sufficiently high intensities $\mathscr{E}$ and $\mathscr{H}$ ($\mathscr{E}\ll\mathscr{H}$), in the case when they are related in a certain fashion, there occurs an effect, first observed by Burkova *et al.*,[2] whereby it is advantageous for the electron to be localized in some region of space away from the proton. From the physical point of view this is due to the appearance of a second well that under certain conditions can become effectively deeper than the Coulomb well. Thus, the atom acquires a large "stable" dipole moment.

In conclusion, let us briefly discuss the case in which the angle between the directions of the electric and magnetic fields is equal to α. Let us assume as before that the field $\vec{\mathscr{H}}$ is oriented along the z axis, and let us choose the x axis such that the field $\vec{\mathscr{E}}$ lies in the x–z plane. Then the components of the vector $\vec{\mathscr{E}}$ are equal to $\mathscr{E}_z=\mathscr{E}_{\parallel}=\mathscr{E}\cos\alpha$, $\mathscr{E}_x\equiv\mathscr{E}_{\perp}=\mathscr{E}\sin\alpha$, and $\mathscr{E}_y=0$. It is easy to show that the energy E will be a function of only $\mathscr{E}_{\parallel}^2$ and $\mathscr{E}_{\perp}^2$, as well as of $\mathscr{H}^2$. Hence it is clear that nontrivial dependences on the angle α occur in the perturbation-theory-series terms that are of higher order than those considered above, e.g., in the terms $\mathscr{E}_{\parallel}^2\mathscr{E}_{\perp}^2\mathscr{H}^2$, etc., with the possible exception of the term $\mathscr{E}_{\parallel}^2\mathscr{E}_{\perp}^2$, whose coefficient is clearly equal to $-3555/16$.

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APPENDIX

Here we give a few first corrections to the wave function in the cases when the fields are parallel or perpendicular to each other. Their explicit form may turn out to be useful in different investigations performed within the framework of perturbation theory for the case of weak fields, as well as in

the construction of variational trial functions that are reasonable from the point of view of the "Dyson argument" (see the discussion in Ref. 4).

Thus, the expansion of the ground-state wave function is taken in the form

$$\psi(x)=\exp\left\{-\Phi_{00}-\mathscr{E}\Phi_{10}-\mathscr{E}^2\Phi_{20}-\frac{\mathscr{H}^2}{4}\Phi_{02}-\mathscr{E}\mathscr{H}\Phi_{11}-\ldots\right\}, \tag{A.1}$$

and the corrections are given by the following expressions

$$\Phi_{00}=r, \tag{A.2}$$

$$\Phi_{10}^{\parallel}=-\left(r+\frac{r^2}{2}\right)Y_1^0, \quad \Phi_{10}^{\perp}=-\left(r+\frac{r^2}{2}\right)Y_1^1, \tag{A.3}$$

$$\Phi_{20}^{\parallel}=-\left(\frac{7}{12}r^2+\frac{r^3}{12}\right)Y_0^0-\left(\frac{7}{24}r^2+\frac{r^3}{12}\right)Y_2^0, \tag{A.4}$$

$$\Phi_{20}^{\perp}=-\left(\frac{7}{12}r^2+\frac{r^3}{12}\right)Y_0^0+\left(\frac{7}{48}r^2+\frac{r^3}{24}\right)Y_2^0 -\left(\frac{7}{96}r^2+\frac{r^3}{48}\right)Y_2^2,$$

$$\Phi_{02}^{\parallel(\perp)}=\left(\frac{r^2}{3}+\frac{r^3}{9}\right)Y_0^0-\left(\frac{r^2}{6}+\frac{r^3}{9}\right)Y_2^0, \tag{A.5}$$

$$\Phi_{11}^{\parallel}\equiv 0, \quad \Phi_{11}^{\perp}=i\left(\frac{11}{12}r+\frac{11}{24}r^2+\frac{r^3}{12}\right)Y_1^{-1}. \tag{A.6}$$

With the aid of the expressions (A.2)–(A.6) we can find the corrections to the wave function in the Rayleigh–Schrödinger perturbation theory series. To do this, we must expand the exponential function in the formula (A.1) in a series, taking the groundstate Coulomb wave function $\psi_0=\exp\{-r\}$ to be a common factor. As a result, it turns out that each correction to the wave function in the standard perturbation theory is a sum of a finite number of harmonics with coefficient functions that are finite polynomials in r and have the Coulomb wave function as a common factor. If now we recall the standard-perturbation-theory formulas for the corrections to the wave function, expressed in terms of a sum over intermediate states, we obtain sum rules for the Coulomb matrix elements for the transitions from the ground into the excited states. These sum rules may turn out to be useful in applications and, in particular, in the investigation of the problem of the classification of the states in the present problem.

[1)]The presence of this term leads to some modification of the procedure for constructing the perturbation theory described above (see below).
[2)]In Ref. 5 the coefficient of $\mathscr{E}^2\mathscr{H}^2$ is computed within the framework of the present approach, but there is an error in the final result.
[3)]With the exception of the case $\mathscr{H}=0$, for which the radius of convergence is zero.
[4)]The Dyson argument is applied to the case of quantum mechanics is discussed in the papers cited in Ref. 4.

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