Second-order perturbation theory for a hydrogen atom in crossed electric and magnetic fields

E. A. Solov'ev

Leningrad State University

(Submitted 28 January 1983)
Zh. Eksp. Teor. Fiz. **85**, 109–114 (July 1983)

The equivalent second-order perturbation theory correction operators for the hydrogen atom in crossed electric and magnetic fields are computed with the aid of the Sturm basis. The corrections themselves are computed, and the question of the lifting the residual degeneracy in this order in the case of perpendicular fields is also investigated.

PACS numbers: 32.60. + i, 31.30.Jv

I. INTRODUCTION

The problem of the spectrum of the hydrogen atom in crossed fields is not only of general theoretical interest. It is important also in different areas of physics: in solid state physics (excitons in external fields), in astrophysics for the study of many-photon ionization processes in the field of a monochromatic wave, and in the physics of atomic collisions, where an effective magnetic field arises on going over into the rotating system of coordinates. Lately, because of new experimental techniques, much attention is being given to the direct investigation of the Rydberg states of the hydrogen atom in external fields.

The first-order perturbation theory for the hydrogen atom in crossed electric F and magnetic H fields was first considered in 1923 by Einstein within the framework of the old Bohr theory.[1] The first-order quantum perturbation theory was developed by Demkov *et al.*[2] In this problem, in spite of the strong degeneracy of the energy levels of the hydrogen atom, we can relatively simply find in the general case the correct wave functions of the zeroth-order approximation, and obtain the first order correction to the energy. The second order perturbation theory is also considered in Ref. 2, but the result for the correction due to the electric field turns out to be incorrect, since it is obtained under the erroneous assumption that the corresponding correction operator is diagonal in parabolic coordinates; this error has already been pointed in a number of papers (see, for example, Ref. 3). For the correction conneted with the magnetic field, an incorrect expression is given in Ref. 2 without derivation. All this impels us to return to the computation of the second-order corrections. In the present paper we obtain with the aid of the Sturm representation equivalent operators for the second-order corrections, compute the corrections themselves, and also investigate the question of the lifting in this order of the residual degeneracy in the important—for applications—case of perpendicular fields.

Following Ref. 2, we state the first-order perturbation theory results that will be needed below. The Hamiltonian $\mathscr{H}$ of the hydrogen atom in crossed fields has the form ($\hbar = m = e = 1$, c is the velocity of light)

$$\mathscr{H}=\mathscr{H}_0+V_1+V_2,$$

$$\mathscr{H}_0=-\frac{1}{2}\Delta-\frac{1}{r},\quad V_1=\mathbf{Fr}+\frac{1}{2c}\mathbf{HL},\quad V_2=\frac{1}{8c^2}[\mathbf{Hr}]^2.$$

In first order in the field intensities (the field intensities are assumed to be of the same order of smallness), the diamagnetic interaction potential V_2 does not make any contribution, and V_1 can be diagonalized because of the existence of an operator equality for the Runge-Lenz vector $\mathbf{A}$ normalized by the condition $A^2+L^2=n^2-1$, namely,

$$\mathbf{r}=-{}^3/{}_2n\mathbf{A}. \tag{1}$$

This equality is valid in the subspace of hydrogen wave functions with a fixed principal quantum n (i.e., on the n sheet). Using (1), we can write the interaction potential V_1 on the n sheet in terms of the generators $\mathbf{L}$ and $\mathbf{A}$ of the $O(4)$ group in the form[1)]

$$V_1=\boldsymbol{\omega}_1\mathbf{I}_1+\boldsymbol{\omega}_2\mathbf{I}_2, \tag{2}$$

where

$$\mathbf{I}_1={}^1/{}_2(\mathbf{L}+\mathbf{A}),\quad \mathbf{I}_2={}^1/{}_2(\mathbf{L}-\mathbf{A}),$$

$$\boldsymbol{\omega}_1=\frac{1}{2c}\mathbf{H}-\frac{3}{2}n\mathbf{F},\quad \boldsymbol{\omega}_2=\frac{1}{2c}\mathbf{H}+\frac{3}{2}n\mathbf{F}.$$

The commuting operators $\mathbf{I}_1$ and $\mathbf{I}_2$ obey the normal commutation relations for the angular momentum operators in three–dimensional space, and on the n sheet

$$I_1^2=I_2^2=j(j+1),$$

where $j=(n-1)/2$ (see, for example, Ref. 4). The correct wave functions of the zeroth-order approximation are the eigenfunctions of the operators $I_{1\alpha}$ ($I_{1\alpha}$ is the projection of $\mathbf{I}_1$ onto $\boldsymbol{\omega}_1$) and $I_{2\alpha}$ ($I_{2\alpha}$ is the projection of $\mathbf{I}_2$ onto $\boldsymbol{\omega}_2$):

The explicit expression for the functions $\psi_{nn'n''}$ is given in terms of the hydrogen wave functions in parabolic coordinates in Ref. 2. In the basis of these functions the interaction V_1 is diagonal, and the first order correction to the energy is equal to $E^{(1)}=\omega_1n'+\omega_2n''$.

2. SECOND ORDER PERTURBATION THEORY FOR THE CASE OF ARBITRARY MUTUAL ORIENTATION OF THE FIELDS

The quadratic—in the field intensities—correction $E^{(2)}$ to the energy is the sum of the second order correction from V_1 and the first-order correction from V_2. In this case the magnetic field entering into V_1 does not make any contribution, since the operator $\mathbf{H}\cdot\mathbf{L}$ gives rise to only matrix elements that are off-diagonal in the principal quantum number, and are equal to zero. Choosing the direction of the z axis along the electric field, we can write the correction $E^{(2)}$ in the form

0038-5646/83/070063-04$04.00

$$E^{(2)}=\langle nn'n''|V_2-F^2zG_nz|nn'n''\rangle, \tag{3}$$

where

$$G_n=\sum_{\tilde{n}lm}{}' \frac{|\tilde{n}lm\rangle\langle\tilde{n}lm|}{E_{\tilde{n}}-E_n}+\int_0^\infty d\varepsilon\sum_{lm}\frac{|\varepsilon lm\rangle\langle\varepsilon lm|}{\varepsilon-E_n}$$

is that part of the Coulomb Green function which is regular at $E=E_n$ and the $|nlm\rangle$ are the eigenfunctions of the operator $\mathscr{H}_0$ in spherical coordinates.

To compute the contribution of the electric field, we transform in G_n from the hydrogen to the Sturm basis, in which only a finite number of the matrix elements of z are nonzero. The Sturm functions $|nlm)$, for which we shall use round brackets, are the eigenfunctions of the charge operator.

$$\mathscr{Z}=r(\mathscr{H}_0-E)+1$$

and differ by a normalization factor from the hydrogen wave functions for the same charge value Z and the same energy value E.[5] The Coulomb Green function $G(E,Z)$ in the Sturm basis has the form

$$G(E,Z)=\sum_{lm}\frac{|nlm)(nlm|}{Z_n-Z}+\sum_{\tilde{n}lm}{}'\frac{|\tilde{n}lm)(\tilde{n}lm|}{Z_{\tilde{n}}-Z}. \tag{4}$$

Here the part that is singular at $Z\to Z_n$ has already been separated out, but it differs from the singular part of the Green function for $E\to E_n$, since, on the one hand, the relation between the charge and the energy is nonlinear, i.e., $Z_n=n(-2E)^{1/2}$, and, on the other, the Sturm functions are taken at energy $E\neq E_n$. Expanding the Sturm functions and the denominator in the first sum up to first order in $\Delta E=E-E_n$, and then separating out the part that is regular for $\Delta E\to 0$, we obtain for G_n the expression

$$G_n=G_n^s+\frac{1}{2}\sum_{lm}\{[(n+l+1)(n-l)]^{1/2}[|nlm)(n+1lm| \\ +|n+1lm)(nlm|]-(n\to n-1)+|nlm)(nlm|\}, \tag{5}$$

where G_n^s is the second sum in (4) for $Z=Z_n=1$ and $E=E_n$ (i.e., the regular part of the Coulomb Green function in the Sturm representation).

Using for G_n the expression (5), we compute the matrix elements of the operator $W=zG_nz$ on the n sheet in the spherical basis. The matrix elements of z are computed in the Sturm basis with, as usual, the aid of the recursion formulas for the Sturm functions. It follows from the structure of the recursion formulas that, out of the infinite sum over $\tilde{n}$ in G_n^s, only the terms with $\tilde{n}=n\pm 1, n\pm 2$ makes nonzero contributions, and the matrix elements

$$W_{lml'm'}=(nlm|W|nl'm')$$

are nonzero only for $m=m'$; $l'=l, l\pm 2$. After simple, but tedious computations, we obtain for the $W_{lml'm'}$ the expressions

$$W_{lmlm} \\ =\frac{n^6}{8}\left\{\frac{(l^2-m^2)[(7-5l)n^2-3l^3+15l^2-19l+5]}{4l^2-1}+(l\to -l-1)\right\}, \\ W_{lml-2m} \\ =\frac{9n^6}{16}\left\{\frac{(l^2-m^2)(n^2-l^2)[(l-1)^2-m^2][n^2-(l-1)^2]}{(2l-3)(2l-1)^2(2l+1)}\right\}^{1/2} \tag{6}$$

Comparing (6) with the matrix elements of A_z^2, which are computed in Ref. 6, we obtain the following operation equation, which is valid on the n sheet[2)]:

$$W=\frac{n^4}{16}(5n^2+31+24L^2-21L_z^2+9A_z^2). \tag{7}$$

The equivalent operator for the diamagnetic interaction on the n sheet is derived in Ref. 6:

$$V_2=\frac{n^2H^2}{16c^2}(n^2+3+L_H^2+4A^2-5A_H^2), \tag{8}$$

where L_H and A_H are the components of the angular momentum and the Runge-Lenz vector along the direction of the magnetic field.

The correct zeroth-order functions $\psi_{nn'n''}$ are the eigenfunctions of the two independent momentum operators $\mathbf{I}_1$ and $\mathbf{I}_2$. Owing to the operator equations (7) and (8), the corrections $E^{(2)}$ can be computed with the aid of the standard techniques of the theory of angular momenta, if **L** and **A** are expressed in terms of $\mathbf{I}_1$ and $\mathbf{I}_2$. The final result for the correction $E^{(2)}$ has the form

$$E^{(2)}=-\frac{n^4F^2}{16}[17n^2+19-12(n'^2+n'n''\cos\gamma+n''^2)] \\ +\frac{n^2H^2}{48c^2}[7n^2+5+4n'n''\sin\gamma_1\sin\gamma_2+(n^2-1)(\cos^2\gamma_1+\cos^2\gamma_2) \\ -12(n'^2\cos^2\gamma_1-n'n''\cos\gamma_1\cos\gamma_2+n''^2\cos^2\gamma_2)], \tag{9}$$

where γ_1 and γ_2 are the angles between the vector **H** and the vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$ and $\gamma=\gamma_1+\gamma_2$. The correction $E^{(2)}$ is, in order of magnitude, proportional to the square of the field intensities, but it is not of the bilinear form in **F** and **H**; the dependence of $E^{(2)}$ on the field intensities has a more complex character, since the zeroth-order functions themselves depend on the mutual orientation of **F** and **H** and on the ratio of one field strength to the other.

3. THE CASE OF PERPENDICULAR FIELDS

The expression (9) obtained above for the second order correction is valid in those cases when the degeneracy is lifted completely in the first-order perturbation theory. If the degeneracy remains, we must further diagonalize the operator $A=V_2-F^2W$ in the subspace of the wave functions for which the energy levels are degenerate in the first-order perturbation theory. Such a situation arises in three particular, but important cases: the Stark effect ($\mathbf{H}=0$), the Zeeman effect ($\mathbf{F}=0$), and perpendicularly oriented fields. The quadratic Stark and Zeeman effects have already been investigated.[6,7] For perpendicularly oriented fields, the second-order perturbation theory has not been investigated. In this case $\omega_1 = \omega_2 = \omega$, and the first-order correction depends only on the sum $q = n' + n''$ of the quantum numbers n' and n''. The degree of degeneracy then turns out to be the same as for the linear Stark effect. The degeneracy of the levels with a given q is completely lifted in the second-order perturbation theory, and the correct zeroth-order functions in a subspace with fixed n and q are the eigenfunctions of the operator Λ. The nontrivial part of the operator Λ in this subspace has the form

$$\Lambda_q = bI_{1\alpha}I_{2\alpha} + 2aI_{1\beta}I_{2\beta}, \tag{10}$$

where

$$a = -\frac{n^2H^2}{2c^2}, \quad b = \frac{n^2H^2}{4c^2} - \frac{9n^4F^2}{4} + \frac{n^2H^4}{8c^4\omega^2},$$

$I_{i\alpha}$ is the component of $\mathbf{I}_i$ along the vector $\boldsymbol{\omega}_i$, while $I_{i\beta}$ is the component of $\mathbf{I}_i$ in the direction lying in the $(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ plane and orthogonal to the vector $\boldsymbol{\omega}_i$. The operator Λ differs from the operator Λ_q by terms that are constant in the (n, q) subspace and are given by the right-hand side of (11). The components of the vectors $\mathbf{I}_1$ and $\mathbf{I}_2$ in (10) are taken in different coordinate systems, but because $\mathbf{I}_1$ and $\mathbf{I}_2$ commute with each other, the operator Λ_q has the same eigenvalues λ ($\Lambda_q \psi_{nq\lambda} = \lambda \psi_{nq\lambda}$) as it would if these components pertained to the same coordinate system. In the last case the spectral problem is solved through the separation of the variables in ellipsoidal cylindrical coordinates on a sphere in four-dimensional momentum space.[8] The ellipsoidal cylindrical coordinates α, β, φ are specified by the parameter $k = [(b + a)/(b - a)]^{1/2}$, and are connected with the Cartesian coordinates in the following manner:

$$x_1 = \sin\alpha\,[1 - k'^2 \sin^2\beta]^{1/2} \cos\varphi,$$

$$x_2 = \sin\alpha\,[1 - k'^2 \sin^2\beta]^{1/2} \sin\varphi,$$

$$x_3 = [1 - k^2 \sin^2\alpha)^{1/2} \sin\beta, \quad x_4 = \cos\alpha\cos\beta,$$

$$0 \leqslant \varphi < 2\pi, \quad 0 \leqslant \alpha \leqslant \pi, \quad -\pi/2 \leqslant \beta \leqslant \pi/2,$$

where $k'^2 = 1 - k^2$. The correction $E^{(2)}$ to the energy is connected with the eigenvalue λ by the relation

$$E^{(2)} = -\frac{n^4F^2}{16}\left[17n^2 + 19 - 12q^2 + \frac{3H^2}{2c^2\omega^2}(n^2 - 1 - 6q^2)\right] + \frac{n^2H^2}{16c^2}(3n^2 + 1 - 4q^2) + \lambda. \tag{11}$$

The separation of the variables in ellipsoidal cylindrical coordinates leads to the generalized Lamé equations, for which the eignevalues λ cannot be computed analytically. The solution to these equations is analyzed in detail in Ref. 8. The correct zeroth-order functions $\psi_{nq\lambda}$ can be expressed in terms of the functions $\psi_{nn'n''}$ with a fixed value of the sum $q = n' + n''$:

$$\psi_{nq\lambda} = \sum_{n'n''} C^{\lambda}_{n'n''}(k)\,\psi_{nn'n''},$$

where the expansion coefficients $C^{\lambda}_{n'n''}(k)$ are the same as in the expansion of the hydrogen wave functions in ellipsoidal cylindrical coordinates in terms of the wave functions obtained through the separation of the variables in cylindrical coordinates on a four-dimensional sphere. These coefficients can be regarded as generalized Clebsch-Gordan coefficients, since they relate two types of unitarily equivalent bases of one and the same representation of the $O(4)$ group.

There exists another version of the problem of the hydrogen atom in perpendicular fields, that arises in the theory of collisions. In certain cases the effect of the incoming particle on the hydrogen atom amounts to the action of a uniform electric field directed along the internuclear axis. According to the Larmor theorem, there appears, on going over to the coordinate system rotating with the internuclear axis, an effective magnetic field directed perpendicularly to the collision plane, but the diamagnetic interaction V_2 does not occur. Because of the absence of the diamagnetic interaction, the correction $E^{(2)}$ and the parameter k each has a different value:

$$E^{(2)} = -\frac{n^4F^2}{16}\left[17n^2 + 19 - 12q^2 - \frac{3H^2}{4c^2\omega^2}(n^2 - 1 - 6q^2)\right] + \lambda,$$

$$k = (8c^2\omega^2 - H^2)^{1/2}/(8c^2\omega^2 + H^2)^{1/2}.$$

4. CONCLUSION

The problem considered in the present paper is unique in the sense that we have been able to obtain here, apparently for the first time, the second-order correction in the problem with unseparable variables in the elementary form. Until now, such results have been obtained only for systems that admit of complete separation of the variables (the hydrogen atom in an electric field, the problem of two Coulomb centers, etc.), for which the asymptotic methods of the theory of ordinary differential equations can be used. The computation of the second-order corrections for the hydrogen atom in crossed fields was made possible by the introduction for the operators W and V_2 of equivalent—on the n sheet—operators, i.e., operators having the same matrix elements on the n sheet and expressible in terms of the integrals of motion $\mathbf{L}$ and $\mathbf{A}$ of the unperturbed problem (or in terms of $\mathbf{I}_1$ and $\mathbf{I}_2$). There is, generally speaking, no universal recipe for the determination of the equivalent operators, but we can indicate a procedure that will help greatly in those cases when the original operator is a function of the coordinates and of the momenta, $F(\mathbf{x}, \mathbf{p})$. This method consists in the preliminary solution of the classical problem, and is used in Ref. 6 to find an additional integral of motion for the hydrogen atom in a weak magnetic field. The equivalent operator obtained there for the diamagnetic interaction has been used in the present paper to determine the second order correction. The analog in classical mechanics of the equivalent operator on the n sheet is the value of the functions $F(\mathbf{x}, \mathbf{p})$, averaged over the unperturbed classical trajectory. The averaged function $\bar{F}(\mathbf{x}, \mathbf{p})$ can be expressed only in terms of the integrals of the motion for the unperturbed problem i.e., $\bar{F}(\mathbf{x}, \mathbf{p}) = F_0(\mathbf{L}, \mathbf{A})$, and allows us to purposefully choose the equivalent operator in quantum mechanics. When this procedure does not lead to an exact expression for the equivalent operator, it is natural to use the operator $F_0(\mathbf{L}, \mathbf{A})$ as its approximate value. The procedure proposed here is not always applicable. For example, the operator W cannot be represented in the form of a function of the coordinates and the momenta, and therefore there is no simple analog for it in classical mechanics. In this case we are obliged to choose the equivalent operator blindly, which makes the solution of the problem considerably difficult.

The use of the Sturm basis for the hydrogen atom is natural when the perturbation is a polyomial in the coordinates and the momenta. In this case only a finite number of the Sturm states become involved in each order of the perturbation theory. The problem can be reduced with the aid of the recursion formulas for the Sturm functions to an algebraic problem, and its subsequent solution can be carried out on a computer, using standard analytic languages such as REDUCE-2. This approach can be used to investigate the hydrogen atom in crossed fields in the higher orders of the perturbation theory.

The author is grateful to T. P. Grozdanov, Yu. N. Demkov, and V. N. Ostrovskiĭ for useful discussions.

---

1) The expression (2) for the interaction V_1 was first obtained by Einstein in the old Bohr theory.[1] Einstein also showed that the problem is reducible in first order with the aid of this expression to the quantization of the two independent angular momenta $\mathbf{I}_1$ and $\mathbf{I}_2$.

2) In Ref. 2 it is assumed in the derivation of the second-order correction due to V_1 that the operator $zG_n z$ is diagonal in the parabolic system of coordinates, as a result of which an incorrect expression is obtained for the equivalent operator on the n sheet. It can be seen from the relation (7) that the diagonal character is destroyed because of the presence of the operator L^2.

[1] M. Born, Vorlesungen über Atommechanik, Springer, Berlin, 1925 (Russ. Transl., ONTI, 1934); W. Pauli, Trudy po kvantovoĭ teorii (Collected Papers on Quantum Theory), Nauka, Moscow, 1975.

[2] Yu. N. Demkov, B. S. Monozon, and V. N. Ostrovskiĭ, Zh. Eksp. Teor. Fiz. **57**, 1431 (1969) [Sov. Phys. JETP **30**, 775 (1970)].

[3] N. L. Manakov, V. D. Ovsyannikov, and L. P. Rapoport, Zh. Eksp. Teor. Fiz. **70**, 1697 (1976) [Sov. Phys. JETP **43**, 885 (1976)].

[4] A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, Rasseyanie, reaktsii i raspady v nerelyativistskoĭ kvantovoĭ mekhanike (Scatering, Reactions, and Decay in Nonrelativistic Quantum Mechanics), Nauka, Moscow, 1971, p. 40 (Eng. Trans., Wiley, New York, 1969).

[5] V. A. Fock, Nachala kvantovoĭ mekhaniki (Fundamentals of Quantum Mechanics), Nauka, Moscow, 1976.

[6] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **82**, 1762 (1982) [Sov. Phys. JETP **55**, 1017 (1982)].

[7] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, Moscow, 1974 (Eng. Transl., Pergamon Press, Oxford, 1977).

[8] E. G. Kalnins, W. Miller, and P. Winternitz, Siam. J. Appl. Math. **30**, 630 (1976).

Translated by A. K. Agyei