SOVIET PHYSICS JETP VOLUME 30, NUMBER 4 APRIL, 1970

ENERGY LEVELS OF A HYDROGEN ATOM IN CROSSED ELECTRIC AND MAGNETIC FIELDS

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Submitted May 15, 1969

Zh. Eksp. Teor. Fiz. 57, 1431—1434 (October, 1969)

The energy level splitting of a hydrogen atom in uniform electric and magnetic fields of arbitrary mutual orientation is obtained by first- and second-order perturbation theory. The symmetry of the four-dimensional Fock rotation group is used. Relativistic corrections and spin-orbit interaction are not considered. The first-order result coincides with that of the earlier Bohr theory. Cases are considered when degeneracy is not completely removed, particularly the case of mutually perpendicular electric and magnetic fields.

1. A hydrogen atom in crossed electric and magnetic fields **E** and **H** was already considered in 1923[1] in the earlier Bohr theory by first-order perturbation theory. It was shown that the slow variation of the electron elliptic orbit characterized by the energy $\mathscr{E}$ or by the principal quantum number $n = (-2\mathscr{E})^{-1/2}$, by the angular momentum **L**, and by the radius-vector $\bar{\mathbf{r}}$ (perpendicular to **L**) averaged over the orbit, can be described as a uniform and independent precession of the vectors $(3/2)n\mathbf{L} - \bar{\mathbf{r}}$ and $(3/2)n\mathbf{L} + \bar{\mathbf{r}}$ with angular velocities

$$\omega_1 = \frac{1}{2c}\mathbf{H} - \frac{3}{2}n\mathbf{E}, \quad \omega_2 = \frac{1}{2c}\mathbf{H} + \frac{3}{2}n\mathbf{E}$$

respectively. The energy level splitting was hence easily obtained.

It is surprising that, as far as we know, this important problem was not considered after the establishment of quantum mechanics, apparently because it was not apparent that its solution is difficult in principle, and at the same time the problem of diagonalizing matrices of order n^2 is quite cumbersome already when $n > 2$.

We show that, using the hydrogen atom symmetry group discovered by Fock[2], one can solve this problem comparatively simply and obtain a simple and clear result, coinciding to first-order approximation with that obtained in the earlier quantum theory. Moreover, by using the group property of the zeroth-order transformed functions, we obtain a second-order perturbation theory correction, and also a diamagnetic correction of the same order of magnitude in the first-order approximation.

In the calculation we neglect relativistic corrections and the spin-orbit interaction, assuming that the splitting induced by the external fields is large compared with the fine structure, i.e.,

$$E \gg 10^5/n^4 \text{V/cm}, \quad H \gg 10^5/n^3 \text{Oe}.$$

2. We construct a representation in which the perturbation operator

$$\mathscr{H}_1 = \mathbf{Er} + \frac{1}{2c}\mathbf{HL} \tag{1}$$

is diagonal in the function subspace of a given energy level n. For this we use the symmetry of the unperturbed energy operator

$$\mathscr{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r}, \tag{2}$$

which for the discrete spectrum is invariant under the four-dimensional rotational group O(4). The infinitesimal operators of this group are[3,4] the components of the vector **L** and of the Runge-Lenz vector

$$\mathbf{A} = (-2\mathscr{H}_0)^{-1/2}\left\{\frac{1}{2}([\mathbf{pL}] - [\mathbf{Lp}]) - \frac{\mathbf{r}}{r}\right\}, \tag{3}^*$$

where **p** is the electron momentum. In parabolic coordinates having the axis in the z direction, the operators $\mathscr{H}_0$, L_z, and A_z are diagonal, with

$$\langle n_1 n_2 m | A_z | n_1 n_2 m \rangle = n_2 - n_1,$$

where n_1 and n_2 are parabolic quantum numbers and $n = n_1 + n_2 + |m|$[3]. In the eigenfunction subspace with a given n the operator z is also diagonal[5] in this basis, and

$$\langle n_1 n_2 m | z | n_1 n_2 m \rangle = {}^3\!/_2 n (n_1 - n_2).$$

Consequently, in this subspace the operator identity

$$\mathbf{r} = -{}^3\!/_2 n\mathbf{A}, \tag{4}$$

is satisfied and the perturbation operator $\mathscr{H}_1$ can be replaced by the operator $\tilde{\mathscr{H}}_1$

$$\tilde{\mathscr{H}}_1 = -\frac{3}{2}n\mathbf{EA} + \frac{1}{2c}\mathbf{HL} \tag{5}$$

in the subspace n.

As was established by Pauli[6], the operators $\mathbf{I}_1 = \frac{1}{2}(\mathbf{L} + \mathbf{A})$ and $\mathbf{I}_2 = \frac{1}{2}(\mathbf{L} - \mathbf{A})$ obey the ordinary commutation relations for angular momentum operators, $\mathbf{I}_1^2 = \mathbf{I}_2^2 = j(j + 1)$, where $j = (n - 1)/2$. This results from the fact that the algebras of the groups O(4) and O(3) × O(3) are isomorphic. Expressing the perturbation operator in terms of $\mathbf{I}_1$ and $\mathbf{I}_2$

$$\tilde{\mathscr{H}}_1 = \omega_1\mathbf{I}_1 + \omega_2\mathbf{I}_2, \tag{6}$$

we see that for its diagonalization it is necessary to choose a representation in which the projection of $\mathbf{I}_1$ on $\boldsymbol{\omega}_1$ and the projection of $\mathbf{I}_2$ on $\boldsymbol{\omega}_2$ have definite values. Denoting these projections by n' and n'', we obtain for the first-order corrections to the energy

$$\mathscr{E}^{(1)}_{nn'n''} = \omega_1 n' + \omega_2 n'', \tag{7}$$

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*$[\mathbf{pL}] \equiv \mathbf{p} \times \mathbf{L}$.

where $n', n'' = -j, -j+1, \ldots, j$. Equation (7) coincides with the result obtained in[1] and, thus, the quantum-mechanical calculation and the earlier Bohr theory provide here the same result (as for many other properties connected with the hydrogen atom).

If account is taken of the electron spin, one must add $\pm H/2c$ to (7), depending on whether the spin orientation is parallel or antiparallel to the field.

3. It is convenient to describe the correct zeroth-order functions $\Psi_{nn'n''}$ in terms of the wave functions obtained by separating the variables in parabolic coordinates with the axis in the **E** direction. These functions can be characterized by quantum numbers i_1 and i_2, which are the eigenvalues of the projections of $\mathbf{I}_1$ and $\mathbf{I}_2$ on the **E** axis and are connected as follows with the ordinary parabolic quantum numbers

$$i_1 = {}^1/_2(m + n_2 - n_1), \quad i_2 = {}^1/_2(m - n_2 + n_1).$$

The function $\Psi_{nn'n''}$ is a linear combination of the functions $\psi_{ni_1i_2}$, where the coefficients are expressed in terms of the Wigner function $D^j_{mm'}(\vartheta, \varphi, \psi)$, which realize the irreducible representation of the group O(3)

$$\Psi_{nn'n''} = \sum_{i_1, i_2=-j}^{j} D^j_{n'i_1}(0, \alpha_1, 0)\, D^j_{n''i_2}(0, \alpha_2, 0)\, \psi_{ni_1i_2}, \tag{8}$$

where α_1 and α_2 are the angles between the vector **E** and the vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$.

Passing to the calculation of the second-order correction to the energy, we note that the interaction with the magnetic field does not contribute to the second and higher order corrections. This is directly connected with the fact that the term $\mathbf{H}\cdot\mathbf{L}/2c$ in the operator $\mathscr{H}_1$ is a rigorous integral of motion for the unperturbed problem (it commutes with $\mathscr{H}_0$). We obtain

$$\mathscr{E}^{(2)}_{nn'n''} = \langle nn'n'' | V_n | nn'n'' \rangle, \tag{9}$$

where

$$V_n = \sum_{\tilde{n} \neq n} \sum_{i_1, i_2} \frac{\mathbf{Er} | \tilde{n} i_1 i_2 \rangle \langle \tilde{n} i_1 i_2 | \mathbf{Er}'}{\mathscr{E}_n - \mathscr{E}_{\tilde{n}}}. \tag{10}$$

Separation of the variables in the parabolic coordinates along the **E** axis leads to

$$\langle n i_1 i_2 | V_n | n i_1' i_2' \rangle = \langle n i_1 i_2 | V_n | n i_1 i_2 \rangle \delta_{i_1 i_1'} \delta_{i_2 i_2'}, \tag{11}$$

where, as is well known from the theory of the quadratic Stark effect for hydrogen,

$$\langle n i_1 i_2 | V_n | n i_1 i_2 \rangle = -\frac{n^4 E^2}{16} [17n^2 - 12(i_1^2 + i_1 i_2 + i_2^2) + 19]. \tag{12}$$

Consequently, in the function subspace with a given n the operator V_h can be replaced by

$$V_n = -\frac{n^4}{16} \{17n^2E^2 - 12[(\mathbf{I}_1\mathbf{E})^2 + (\mathbf{I}_1\mathbf{E})(\mathbf{I}_2\mathbf{E}) + (\mathbf{I}_2\mathbf{E})^2] + 19E^2\}, \tag{13}$$

which gives immediately

$$\mathscr{E}^{(2)}_{nn'n''} = -\frac{n^4E^2}{16} \Big\{ 17n^2 - 12[n'^2 \cos^2\alpha_1 + n'n'' \cos\alpha_1 \cos\alpha_2 + n''^2 \cos^2\alpha_2] - 6\Big[\frac{n^2-1}{4} - n'^2\Big] \sin^2\alpha_1 - 6\Big[\frac{n^2-1}{4} - n''^2\Big] \sin^2\alpha_2 + 19 \Big\}. \tag{14}$$

Taking account of the diamagnetic term $[\mathbf{H}\times\mathbf{r}]^2/8c^2$ in first-order perturbation theory also gives a correction to the energy quadratic in the field, for which we obtain

$$\Big\langle nn'n'' \Big| \frac{1}{8c^2} [\mathbf{Hr}]^2 \Big| nn'n'' \Big\rangle = \frac{n^2}{16c^2} H^2 \Big\{ 3n^2 - 4[n'^2 \cos^2\beta_1 - n'n'' \cos\beta_1 \cos\beta_2 + n''^2 \cos^2\beta_2] - 2\Big[\frac{n^2-1}{4} - n'^2\Big] \sin^2\beta_1 - 2\Big[\frac{n^2-1}{4} - n''^2\Big] \sin^2\beta_2 + 1 \Big\}, \tag{15}$$

where β_1 and β_2 are the angles between the vector **H** and the vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$. Thus, the level shift is given by the sum of expressions (7), (14), (15) and the spin term, accurate to terms cubic in the fields.

4. We consider several special cases, limiting the discussion to first-order perturbation theory. If the frequencies ω_1 and ω_2 are commensurate, the degeneracy is not completely removed. In particular, $\omega_1 = \omega_2$ if and only if $\mathbf{E}\cdot\mathbf{H} = 0$, i.e., if the fields are perpendicular or if one of them vanishes. The splitting then depends only on the sum $n' + n''$ and there occurs an additional degeneracy for all energy levels, quite similar to that of the linear Stark effect or the simple Zeeman effect. If the fields **E** and **H** are parallel, both parts of the perturbation operator $\mathscr{H}_1$ commute and the energy level splitting is calculated in an elementary way. In this case one can select for each n a ratio $E/H = (3nc)^{-1}$ such that one of the frequencies ω_1 or ω_2 vanishes. Each of the split energy levels remains then n-fold degenerate.

When there is degeneracy an additional study is needed in second-order perturbation theory; it is necessary to solve a secular equation and to select the correct linear combination of wave functions. Several of the intersecting levels can disappear and be replaced by pseudointersecting ones.

Just these points of intersection or pseudointersection are interesting from the experimental point of view, since they can be detected by the polarization effect.

In conclusion we note that the given calculation is, perhaps, the most direct and clearest application of the properties of the four-dimensional Fock rotational group. Its symmetry enables one to construct two commuting operators $\mathbf{I}_1$ and $\mathbf{I}_2$ similar to the ordinary three-dimensional angular momentum. We can then select as integrals of motion the projections of $\mathbf{I}_1$ and $\mathbf{I}_2$ in an arbitrarily chosen direction. Moreover, for given fields **E** and **H** we can select this direction such as to diagonalize the matrix perturbation for a given n and thus solve the problem.

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Translated by N. Jacobi
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