PERTURBATION THEORY FOR THE EXPANSION COEFFICIENTS OF A TWO-ELECTRON WAVE FUNCTION

PHYSICS

1967

SovietRxiv

Abstract

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UDC 539.182

PHYSICS

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PERTURBATION THEORY FOR THE EXPANSION COEFFICIENTS OF A TWO-ELECTRON WAVE FUNCTION

(Presented by Academician V. A. Fock, January 9, 1967)

1. Let us consider the Schrödinger equation for the S-state of a two-electron atom, assuming that the electrostatic interaction of the electrons contains a parameter ε, which determines its intensity:

$$(H_0 + \varepsilon V_{12})\Psi = E\Psi. \tag{1}$$

If we put $R = r_1^2 + r_2^2$, $\alpha = 2\,\mathrm{arctg}(r_1/r_2)$, and introduce the angle ϑ between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, which determine the positions of the electrons relative to an infinitely heavy nucleus ([1,2]), then for (1) we obtain $H_0 = -2R\Box + R^{-1/2}U_0$ and $V_{12} = R^{-1/2}v_{12}$; $\Box$ is the Laplace operator in four-dimensional space with spherical coordinates R, α, ϑ, and φ; $U_0 = -Z(1/\sin\frac{\alpha}{2} + 1/\cos\frac{\alpha}{2})$, where Z is the nuclear charge and $v_{12} = (1-\sin\alpha\cos\vartheta)^{-1/2}$. In the works ([1,2]), equation (1) was investigated by V. A. Fock in the neighborhood of the triple-collision point (of the two electrons and the nucleus) for the case of real interaction between the electrons ($\varepsilon = 1$). It was shown that the equation admits an expansion of Ψ in a series in the parameter R, small near the nucleus, the terms of the series having, in general, a weak logarithmic singularity at $R = 0$:

$$\Psi(R, \alpha, \vartheta) = \sum_{n=1,\,3/2,\ldots} R^{n-1} \sum_{k=0}^{[n-1]} (\ln R)^k \psi_{n,k}(\alpha, \vartheta). \tag{2}$$

The coefficients $\psi_{n,k}$ of the series are determined as a finite solution on the hypersphere $\Omega(\alpha, \vartheta, \varphi)$ of the system of equations (3.10) from ([2]), independent of the angle φ. The structure of the equations for $\psi_{n,k}$ and their general properties are connected, first of all, with the kinetic-energy operator $-2R\Box$. In deriving these equations, with respect to the potential energy of the atom essentially only the assumption of its homogeneity of degree $-1/2$ in R was made. Therefore, formally, expansion (2) can be written for an atomic potential depending arbitrarily on the angles α and ϑ.

2. In the present work we investigate in more detail the connection between the form of the series (2) and the atomic potential. For this purpose we shall apply to the expansion (2) the method of perturbation theory with respect to the parameter of the electron interaction ε. Writing Ψ and E in the form of series in ε: $\Psi = \Psi_0 + \varepsilon\Psi_1 + \varepsilon^2\Psi_2 + \ldots$, and $E = E_0 + \varepsilon E_1 + \varepsilon^2 E_2 + \ldots$, we obtain, as usual, a system of equations determining the functions Ψ_j and the energy coefficients E_j.

$$(H_0 - E_0)\Psi_0 = 0, \tag{3}$$

$$(H_0 - E_0)\Psi_j = -R^{-1/2}\omega^{-1}\Psi_{j-1} + \sum_{s=1}^{j} E_s \Psi_{j-s}, \qquad j = 1, 2, \ldots \tag{4}$$

The quantity $\omega = (1 - \sin\alpha\cos\vartheta)^{1/2}$, $0 \le \omega \le \sqrt{2}$, is reciprocal to the electrostatic interaction of the electrons on the hypersphere, v_{12}. The collision of electrons distant from the nucleus corresponds to the point $\alpha = \pi/2$, $\vartheta = 0$, at which $\omega = 0$.

We expand $\psi_{n,k}$ from (2) in powers of the parameter ε:

$$\psi_{n,k} = \psi_{n,k}^{(0)} + \varepsilon\psi_{n,k}^{(1)} + \varepsilon^2\psi_{n,k}^{(2)} + \cdots \tag{5}$$

and assume, in accordance with (2), that

$$\Psi_j = \sum_{n=1,\,3/2,\ldots} R^{n-1} \sum_{k=0}^{[n-1]} (\ln R)^k \psi_{n,k}^{(j)}. \tag{6}$$

Then from (3)–(4) we obtain the desired perturbation-theory equations:

$$\Box^* \psi_{n,k}^{(j)} - \lambda_n \psi_{n,k}^{(j)} = F_{n,k}^{(j)} + Q_{n,k}^{(j)}, \tag{7}$$

where $\Box^*$ is the Laplace operator on the hypersphere, and the parameter $\lambda_n = -(n^2-1)$ for integer n is equal to an eigenvalue of this operator. The right-hand side of equations (7) has the following explicit form:

$$F_{n,k}^{(j)} = -(k+1)(k+2)\psi_{n,k+2}^{(j)} - 2n(k+1)\psi_{n,k+1}^{(j)} + \frac{1}{2}U_0\psi_{n-1/2,k}^{(j)} - \frac{1}{2}E_0\psi_{n-1,k}^{(j)}, \tag{8}$$

$$Q_{n,k}^{(j)} = \begin{cases} 0, & \text{if } j = 0, \\ \dfrac{1}{2}\omega^{-1}\psi_{n-1/2,k}^{(j-1)} - \dfrac{1}{2}\displaystyle\sum_{s=1}^{j} E_s \psi_{n-1,k}^{(j-s)}, & \text{if } j = 1, 2, \ldots . \end{cases} \tag{9}$$

Since the interaction ω^{-1} does not enter $F_{n,k}^{(j)}$, the perturbation in equations (7) is represented explicitly only by the term $Q_{n,k}^{(j)}$.

3. Consider the auxiliary system of equations on the hypersphere:

$$\Box^{*}\varphi_n - \lambda_n\varphi_n = \frac{1}{2}U_0\varphi_{n-1/2} - \frac{1}{2}E_0\varphi_{n-1}, \tag{10}$$

where $E_0 < 0$ is an arbitrary parameter, and n runs over a sequence of increasing integer and half-integer values. Suppose that $\varphi_n = 0$ if $n < p$, where p is an integer. Then equations (10) have as particular solutions the functions

$$\varphi_n^{(p,l)} = y_n^{(p,l)}(\alpha)\, P_l(\cos\vartheta),$$

which are finite if the degree l of the Legendre polynomial and the index p are related by the condition $0 \le l \le p-1$,

$$y_n^{(p,l)} = \sum_{r=l}^{2n-l-2} a_{n,r}(p,l)\left(\sin\frac{\alpha}{2}\right)^{2n-r-2}\left(\cos\frac{\alpha}{2}\right)^{r}. \tag{11}$$

The numerical coefficients $a_{n,r}$ are determined successively, beginning with $n = p$, then $n = p + \frac{1}{2}, \ldots$, each time from the recurrence formulas:

$$(2n-r-l-2)(2n-r+l-1)a_{n,r}+(r-l+2)(r+l+3)a_{n,r+2}+2Za_{n-1/2,r}+2Za_{n-1/2,r+1}+2E_0a_{n-1,r} = 0, \tag{12}$$

with the initial condition of the form

$$a_{n,l}(p,l) = \delta_{p,n}, \qquad n = p,\ p+\frac{1}{2}, \ldots .$$

For the functions $\varphi_n^{(p,l)}$ the orthogonality relations are satisfied:

$$\int_{(\Omega)} \left(U_0\varphi_{n-1/2}^{(p,l)} - E_0\varphi_{n-1}^{(p,l)}\right)\Phi_{n,l'}\, d\Omega = 0, \tag{13}$$

where n is an integer, $l' = 0, 1, \ldots, n-1$. Relations (13) include the nontrivial case, namely $l' = l$. Since the finite φ_n are determined up to a linear combination of four-dimensional spherical functions $\Phi_{n,l}$, the general solution finite on the hypersphere can be given–

written in the form

$$\Phi_n^{(p)} = \sum_{r=p}^{[n]} \sum_{l=0}^{r-1} c_{r,l}^{(p)} \varphi_n^{(r,l)}, \qquad n = p,\ p+\tfrac{1}{2}, \dots, \tag{14}$$

where $c_{r,l}^{(p)}$ are arbitrary constants.

4. Let us return to equations (7), restricting ourselves to the particular case of the ground state of the atom. Then $E_0 = -Z^2$, $E_1 = \frac{5}{8}Z$. We also have the relation $\psi_{n,k}^{(j)}(\alpha, \vartheta) = \psi_{n,k}^{(j)}(\pi - \alpha, \vartheta)$, which expresses the symmetry of Ψ with respect to permutation of the coordinates of the atomic electrons. We shall consider equations (7) in increasing order of j, the order of approximation in perturbation theory, and for a given j in the sequence $k = [n-1], \dots, 1, 0$ and $n = 1, \frac{3}{2}, \dots$

In the zeroth approximation $j = 0$, the term $Q_{n,k}^{(0)}$ on the right-hand side of (7) is equal to zero. The general solution, finite on the hypersphere, has the form

$$\psi_{n,0}^{(0)} = \Phi_n^{(1)}, \qquad \psi_{n,k}^{(0)} = 0, \quad \text{if } k \geqslant 1. \tag{15}$$

Indeed, the equations for $\psi_{1,0}^{(0)}$ and $\psi_{3/2,0}^{(0)}$ have the form (10) for $n = 1$ and, respectively, for $n = \frac{3}{2}$, if one sets $p = 1$. At the same time, if all the functions $\psi_{n',k'}^{(0)}$, for $n' \leqslant n$, are determined by formula (15), then from equations (10) and the orthogonality relations (13) it follows that formulas (15) are also valid for $\psi_{n+1/2,k}^{(0)}$ and $\psi_{n+1,k}^{(0)}$ for all admissible k. Thus, in the zeroth approximation of perturbation theory the logarithmic terms of expansion (2) prove to be forbidden, if the coefficients of this series are subject to the condition of finiteness. The particular solution of the form

$$\psi_{n,0}^{(0)} = \frac{(-Z)^{2(n-1)}}{(2n-2)!} \left(\sin\frac{\alpha}{2} + \cos\frac{\alpha}{2}\right)^{2(n-1)}, \qquad \psi_{n,k}^{(0)} = 0, \quad \text{if } k \geqslant 1, \tag{16}$$

corresponds to the expansion (2), which for any finite R converges to the hydrogen-like function $\Psi(R, \alpha)$ of the 1^1S-state of an atom with two electrons.

5. We first consider the inclusion of the interaction between the electrons in the first approximation of perturbation theory. For $j = 1$ the perturbation $Q_{n,k}^{(1)}$ formally enters into all equations (7). However, from (15) it follows that in fact the only nonzero terms are $Q_{n,0}^{(1)} = \frac{1}{2}\omega^{-1}\psi_{n-1/2,0}^{(0)} - \frac{5}{16}Z\psi_{n,1}^{(0)}$. Thus, the equations for the functions $\psi_{n,k}^{(1)}$ for $k \geqslant 2$ have the same structure as the equations for the functions $\psi_{n,k}^{(0)}$ for $k \geqslant 1$. Consequently, the condition $\psi_{n,k}^{(1)} = 0$ for $k \geqslant 2$ is necessary for finiteness of the functions $\psi_{n,1}^{(1)}$.

The functions $\psi^{(1)}_{n,1}$ satisfy equations (10) with $p = 2$, so that $\psi^{(1)}_{n,1} = \Phi^{(2)}_n$. The coefficients $c^{(2)}_{n,l}$, entering, according to (14), into the functions $\Phi^{(2)}_n$ for integer n, must be determined from the condition

$$\int_{(\Omega)} \left(F^{(1)}_{n,0} + Q^{(1)}_{n,0}\right) \Phi_{n,l}\, d\Omega = 0, \qquad l = 0, 1, \ldots, n-1, \tag{17}$$

which ensures finiteness of the functions $\psi^{(1)}_{n,0}$. The perturbation $Q^{(1)}_{n,0}$, containing the interaction ω^{-1}, is certainly nonorthogonal to the four-dimensional spherical functions $\Phi_{n,l}$, so that the coefficients $c^{(2)}_{n,l}$ and, consequently, the functions $\psi^{(1)}_{n,1}$ are different from zero.*

* More precisely, what is meant is the nonorthogonality of $Q^{(1)}_{n,0}$ to the spherical functions $\Phi_{n,l}$ with an odd value of the sum of indices $n + l$, since in the ground state of the atom $Q^{(1)}_{n,0}(\alpha, \vartheta) = Q^{(1)}_{n,0}(\pi - \alpha, \vartheta)$, while the four-dimensional spherical functions possess the property: $\Phi_{n,l}(\alpha, \vartheta) = (-1)^{n+l+1}\Phi_{n,l}(\pi - \alpha, \vartheta)$.

The functions $\psi^{(1)}_{n-1/2,0}$ and $\psi^{(1)}_{n-1,0}$, which enter into $F^{(1)}_{n,0}$, formula (17), are determined by equations (7), whose right-hand sides contain the term $Q^{(1)}$. The method of solution considered above is not applicable to these equations. However, one may assert that, as functions with zero second subscript, they include arbitrary constants; moreover, by virtue of (13), these constants do not enter the coefficients $c^{(2)}_{n,l}$. Thus, expansion (2), to accuracy through first order of perturbation theory, has the form

$$\Psi = \sum_{n=1,\,3/2,\ldots} R^{n-1}\left(\psi^{(0)}_{n,0} + \varepsilon\psi^{(1)}_{n,0}\right) + \varepsilon \ln R \sum_{n=2,\,5/2,\ldots} R^{n-1}\psi^{(1)}_{n,1}, \tag{18}$$

where $\psi^{(0)}_{n,0}$ and $\psi^{(1)}_{n,1}$ are determined uniquely. Arbitrary constants enter only the functions $\psi^{(1)}_{n,0}$. To determine them, the condition to which the function Ψ is subject as $R \to \infty$ must be used.

6. The established connection between the form of expansion (2) and the order of perturbation theory in ε is strictly generalized to any order of this theory. Introduce the notation $\Psi^{(k)}_j = \sum_{(n)} R^{n-1}\psi$, where $n = k + 1,\ k + 3/2, \ldots$. Then expansion (2), written to accuracy through terms of q-th order in ε, takes the form:

$$\Psi(R, \alpha, \vartheta) = \sum_{q'=0}^{q} \varepsilon^{q'} \sum_{k=0}^{q'} (\ln R)^k \Psi^{(k)}_{q'}. \tag{19}$$

This result is based on the fact that in the q-th approximation of perturbation theory the coefficients $\psi^{(q)}_{n,k}$ for $k \geq q + 1$ are strictly equal to zero.

7. The formulas given establish a connection between two types of expansions of the solution of equation (1): between the expansion of Ψ in the parameter R, small in a neighborhood of the triple-collision point, and the expansion of Ψ in the parameter of the electron interaction ε. Logarithmic terms in (2) are absent only for $j = 0$, i.e., when there is no interaction between the electrons. Inclusion of the electrostatic interaction leads to the appearance, at the point $R = 0$, of a weak logarithmic singularity. In the case of a symmetric state, the leading term of this singularity has the form

$$-\frac{Z(\pi-2)}{6\pi} R \ln R \sin\alpha \cos\vartheta.$$

In the case of an antisymmetric state, for which the general results established above remain valid, the corresponding term has the expression

$$\frac{2Z}{15\pi}\left(\frac{7}{4}\pi - \frac{19}{3}\right) R^2 \ln R \sin 2\alpha \cos\vartheta.$$

In this case expansion (2) begins with the term $R\cos\alpha$, linear in R. In both cases the leading terms presented appear already in the first approximation of perturbation theory in the electron-interaction parameter, i.e., for $j = 1$.

The author expresses gratitude to Academician V. A. Fock for discussion of the work.

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Received
21 XII 1966

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Note: Figure translations are in progress. See original paper for figures.