THE GROUND STATE OF TWO-ELECTRON ATOMS AND IONS

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Abstract

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PHYSICS

1. Variational calculations of the nonrelativistic S-states of helium and helium-like ions, carried out by many authors in connection with the experimental study of the radiation shift in two-electron atoms, undoubtedly show that solving this problem with the required accuracy is an exceptionally difficult task, unless the properties of the wave equation at singular points are taken into account. A rigorous investigation of the equation for S-states in the neighborhood of the point of triple collision $r_1 = r_2 = 0$ was carried out by V. A. Fock [1]. Using the example of the 1^1S-state of He and of some ions, we shall consider a method, based on Fock' s work, for taking singularities into account in the wave equation with the interaction potential of the particles of the system

$$V(r_1, r_2, r_{12}) = -Z(r_1^{-1} + r_2^{-1}) + r_{12}^{-1}.$$

2. First we shall establish the analytic form of a function which, up to certain coefficients, coincides with the function Ψ satisfying the wave equation at $R = r_1^2 + r_2^2 = 0$ and $R \to \infty$. Consider, in the variables R, α, and ϑ ($\alpha = 2 \operatorname{arcctg} r_1/r_2$, ϑ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, $0 \leq \vartheta \leq \pi$), the expression

$$\Psi_N(R, \alpha, \vartheta) = \exp\left[-\frac{k}{2}\sigma(\alpha)\sqrt{R}\right] \sum_{n=1,\,3/2,\,2,\ldots} R^{n-1} \sum_{p=0}^{[n-1]} g_{np}(\alpha, \vartheta) \ln^p R, \tag{1}$$

in which $\sigma(\alpha) = \sin\alpha/2 + \cos\alpha/2$, k is a scale parameter. Ψ_N has the proper asymptotic behavior as $R \to \infty$, if $k = 2\sqrt{-E}$ (E is the total energy of the atom). This function also satisfies the equation near $R = 0$ up to accuracy R^N, if the coefficients g_{np} entering (1) are defined by the formulas $g_{np} = (j!)^{-1}\sigma^j \psi_{n-j/2,p}$ (with j summed from 0 to $2(n-p-1)$) through the coefficients $\psi_{n'p}$ of the expansion of Ψ in Fock' s series.

As was shown in (1), the functions ψ_{np} must be determined successively, beginning with $n = 1$, then $n = 3/2, 2, \ldots$, and, for a given n, in the order of decreasing second index p, beginning with its maximum value $p = [n-1]$ down to $p = 0$, from the differential equations

$$L[\psi_{np}] = \Box^* \psi_{np} + (n^2 - 1)\psi_{np} = F_{np}, \tag{2}$$

$$F_{np} = -(p+1)(p+2)\psi_{n,p+2} - 2n(p+1)\psi_{n,p+1} + \tfrac{1}{2}U\psi_{n-1/2,p} - \tfrac{1}{2}E\psi_{n-1,p}.$$

Here $\Box^*$ is the Laplace operator on the four-dimensional sphere with angles $\alpha, \vartheta, \varphi$ (the solution does not depend on φ, since the potential energy $U(\alpha, \vartheta)$ on this sphere does not depend on φ). The eigenvalues of the operator $-\Box^*$ are $\lambda_n = n^2 - 1$ for $n = 1, 2, 3, ...$, and its eigenfunctions are the generalized spherical functions $\Phi_{nl}(\alpha, \vartheta)$. Finite solutions of these equations exist, and all functions ψ_{np} (under the additional condition $\psi_{np}(\alpha, \vartheta) = \psi_{np}(\pi - \alpha, \vartheta)$ for singlet states) are determined uniquely, with the exception of ψ_{n0} with integer n. Arbitrary combinations of Φ_{nl} of the corresponding order n enter into ψ_{n0} [1]. The functions $\psi_{n,[n-1]}$ can be written in finite form. In the case of integer n, the equations for $\psi_{n,n-1}$ are homogeneous, so that $\psi_{n,n-1} \sim \Phi_{nl}$, and the sum of the indices $n + l$ must be odd. For half-integer n, when $[n-1] = n - 3/2$, the functions $\psi_{n,n-3/2}$ satisfy equations with singu

regular right-hand side, ${}^1/_2$ and $\psi_{n-{}^1/_2,\, n-{}^3/_2}$. These equations have solutions in the form of polynomials of degree $2(n-1)$ in σ and in $\omega = \sqrt{1 - \sin\alpha\cos\vartheta}$. For example,

$$\psi_{{}^3/_2,0} = -Z\sigma + {}^1/_2\omega; \quad \psi_{{}^5/_2,1} = \frac{Z(\pi-2)}{6\pi}\left[\frac{Z}{2}\sigma(1-\omega^2) - \frac{1}{2}\omega - \frac{5}{12}\omega^3\right] \tag{2}$$

In all other cases, including the most important one, when $p = 0$ (for $n \geqslant 2$), the solution of the singular equations (2) is not representable in finite form. However, even in this general case one can separate out from ψ_{np} the principal part χ_{np}, which also has the form of a polynomial in σ and in ω. Its coefficients are determined by the requirement that the function $\overset{0}{F}_{np}$ and its derivatives be finite at all points of the four-dimensional sphere, including the regions corresponding to double collisions. $\overset{0}{F}_{np}$ is the free term of the equation $L[\overset{0}{\psi}_{np}] = \overset{0}{F}_{np}$, where $\overset{0}{\psi}_{np} = \psi_{np} - \chi_{np}$. After the function χ_{np}, and together with it also $\overset{0}{F}_{np}$, have been determined, the difference $\overset{0}{\psi}_{np}$ can be represented by a rapidly convergent series in generalized spherical functions Φ_{sl}. The functions g_{np}, which determine Ψ_N, differ only by power factors σ^j from the sum of the functions $\psi_{n-i/2,p}$. In this connection $g_{n,[n-1]}$, just as $\psi_{n,[n-1]}$, can be written in finite form, while for the remaining g_{np}, just as for ψ_{np} in the general case, a convenient representation of the form

$$g_{np}(\alpha, \vartheta) = \chi_{np}(\sigma, \omega) + \sum_{s=1}^{\infty}\sum_{l=0}^{s-1} a_{sl}^{np}\Phi_{sl}, \qquad s + l \text{ odd}. \tag{3}$$

can be obtained.

The polynomial functions χ_{np} take into account the strongest of the singularities of g_{np}, caused by double collisions.

3. The method of numerical calculation was as follows. The series entering into Ψ_N were truncated. In the expression obtained, $\widetilde{\Psi}_N$, some of the coefficients in χ_{np} and the coefficients of the generalized functions Φ_{sl} were regarded as arbitrary ($\widetilde{\Psi}_N$ is a linear function with respect to these coefficients), and their values, which below we shall denote by c_i, were determined from the variational principle for the total energy of the atom. The condition to which the function Ψ_N is subject near $R = 0$, in this method, is generally speaking violated, since it makes arbitrary only ${}^1/{}_2N(N+1)$ coefficients entering into g_{n0} with the functions ψ_{n0}. At the same time, the possibility arises of improving the approximation of the wave function at large R. In this case the degree of agreement between the variational and theoretical values of the coefficients entering into the initial terms of the expansions of $\widetilde{\Psi}_N$ and Ψ at $R = 0$ may serve as a criterion of the quality of the variational function $\widetilde{\Psi}_N$ near the nucleus—in the region where the approximation usually proves to be very poor.

We investigated the ground state of H$^-$, He, Li$^+$, Be^{+2}, Be^{+3}, O^{+6}, and Ne^{+8}. The first part of the calculations was carried out with a function A containing 30 linear parameters c_i and a nonlinear scale parameter k. The explicit form of this function is determined by formula (1) for $N = 2$, if the following expressions are taken for g_{np}:

$$\begin{gathered}
g_{10} = 1; \qquad g_{{}^3/{}_2,0} = c_1\sigma + c_2\omega; \qquad g_{21} = c_3\Phi_{21}; \\
g_{20} = c_4\sigma + c_5\omega + c_6\sigma\omega + c_7\sigma^2 + c_8\omega^3 + c_9\Phi_{10} + c_{10}\Phi_{21}; \\
g_{{}^5/{}_2,1} = c_{11}\sigma(1-\omega^2) + c_{12}\omega\left(1 - \frac{5}{6}\omega^2\right); \\
g_{{}^5/{}_2,0} = c_{13}\sigma + c_{14}\omega + c_{15}\sigma^2\omega + c_{16}\sigma^3 + c_{17}\omega^3 + c_{18}\Phi_{10} + c_{19}\Phi_{21}; \\
g_{32} = c_{20}\Phi_{30} + c_{21}\Phi_{32}; \qquad g_{31} = c_{22}\omega; \\
g_{30} = c_{23}\sigma + c_{24}\omega + c_{25}\sigma^2\omega^2 + c_{26}\sigma^4 + c_{27}\Phi_{10} + c_{28}\Phi_{21} + c_{29}\Phi_{30} + c_{30}\Phi_{32}.
\end{gathered} \tag{4}$$

The values of the nonrelativistic energy $E_2^A(Z)$ (the motion of the nucleus was not taken into account), calculated with function A, turned out to be as follows: $E_2^A(1) = -0.5277318$, $E_2^A(2) = -2.9037233$, $E_2^A(3) = -7.2799118$, $E_2^A(4) = -13.655564$, $E_2^A(5) = -22.030469$, $E_2^A(8) = -59.156592$, $E_2^A(10) = -93.906803$, a.u.* These values are in good agreement with the results of Perkins' s 203-parameter calculations: $\varepsilon(1) = 19.2$, $\varepsilon(2) = 1.0$, $\varepsilon(3) = 1.4$, $\varepsilon(4) = 2.0$, $\varepsilon(5) = \varepsilon(8) = \varepsilon(10) = 3.0$ (3).

The deviation near the nucleus of the variational function Ψ_N from the exact solution is conveniently estimated from the values of the quantities $\Delta_1 = (Z + \alpha_1) \cdot 10^3$ and $\Delta_2 = (1/2 - \alpha_2) \cdot 10^3$, where α_1 and α_2 are the coefficients of $\sigma\sqrt{R}$ and $\omega\sqrt{R}$ in the expansion of the variational function. For the exact function Ψ the quantities Δ are zero. The largest values, $\Delta_1 = 27.2$ and $\Delta_2 = 38.4$, as was to be expected, were obtained by us for the negative hydrogen ion. It is remarkable, however, that the order of this deviation is the same as for the 252-parameter helium function, for which it follows from (4): $\Delta_1 = 27.2$ and $\Delta_2 = 43.6$. The values of Δ in our calculations for $Z \geq 2$ are practically independent of Z and have the values $\Delta_1 \sim 7$ and $\Delta_2 \sim 15$ (for comparison, we note that the 1078-parameter helium function (4) gives $\Delta_1 = 15.6$ and $\Delta_2 = 26.1$). The discrepancy in the ratios for the theoretical coefficients and for the coefficients of function A increases in the subsequent terms of the expansion to 10–30%. We note that in methods that do not take into account the properties of the solution near $R = 0$, even the initial coefficients of the functions may fail to have stable values.**

Table 1

1^1S-state of He, Li$^+$, and O^{+6}

Z	Function	Δ_1	Δ_2	$\varepsilon(Z)$
2	F	64.0	91.8	−4.4
2	C	6.2	14.4	+0.2
2	B	5.0	8.4	+0.1
2	D	0.0	0.0	0.0
2	G	4.2	6.2	+0.5
3	B	6.3	12.4	+0.3
3	G	5.6	8.5	+0.7
8	G	4.5	6.9	+1.0

4. To estimate the influence of refining the initial g_{np} on the convergence of the method, functions B and D were considered with a number of parameters m equal to 31, and G ($m = 37$), defined by (1) for $N = 2$. If the g_{np} from (4) are taken as the initial ones, then B is obtained by supplementing g_{20} with the terms Φ_{30} and Φ_{32}, $g_{5/2\,0}$ with the term Φ_{32}, and by excluding g_{31} and g_{32}. In function D the coefficients in $g_{3/2\,0}$ were taken to be theoretical, and the terms Φ_{30} and Φ_{32} were introduced into g_{20}. In function G, Φ_{30}, Φ_{32}, and Φ_{41} were included in g_{20}, Φ_{30} and Φ_{32} in $g_{5/2\,0}$, and a term with s in g_{31}. To assess the prospects of the subsequent steps in N, function C ($m = 31$) was considered, containing four terms proportional to $R^{5/2}$ and R^3. Finally, function F was taken as a characteristic example of a function containing no logarithmic terms. The values of $\varepsilon(Z)$ and Δ, calculated with these functions for He, Li$^+$, and O^{+6}, are given in Table 1.

Table 2

$\varepsilon_N(Z)$

N	Number of variational-method parameters m	$\varepsilon_N(Z) = [E_2^A(Z) - E_N(Z)] \cdot 10^6$, $Z = 2$	$\varepsilon_N(Z) = [E_2^A(Z) - E_N(Z)] \cdot 10^6$, $Z = 3$	$\varepsilon_N(Z) = [E_2^A(Z) - E_N(Z)] \cdot 10^6$, $Z = 8$
1/2	3	−12 500	−13 100	−11 400
1	14	−61.6	−115.2	−39.0
3/2	25	−6.1	−8.3	−6.0
2	37	+0.5	+0.7	+1.0

The data of Table 2 show that rapid convergence of $\varepsilon_N(Z)$ with increasing N (and with the corresponding increase in m) occurs for all the ions considered. In contrast to this, for methods in which the features of the wave equation are not taken into account, a quite–

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* The values $E(Z)$ obtained by us in additional calculations, as well as by other authors, will subsequently be given for convenience in the form $\varepsilon(Z) = [E_2^A(Z) - E(Z)] \cdot 10^6$.

** The 70-parameter helium function of first-order variational perturbation theory has, near the nucleus, deviations $\Delta_1 = 81.4$ and $\Delta_2 = -543.3$ (5).

there is weak convergence of $\varepsilon(Z)$ with increasing m, and not only for helium, but also for ions with $Z > 2$. Thus, the calculations (^{6}), ($m = 20$), give $\varepsilon(2) = -5.4$, $\varepsilon(3) = -6.4$, and $\varepsilon(8) = -10$, whereas in (^{7}), with m equal to 31, for the same atoms the values −1.1, −6.3, and −11 were obtained. To refine the terms corresponding to the transition from $N = 3/2$ to $N = 2$ in Table 2 (where the deviation of the terms from the exact values is reduced to $2 \cdot 10^{-7}$–$3 \cdot 10^{-8}$), in these methods it is necessary to introduce into the functions about a hundred additional variational parameters.

5. The mean value of the operator $\mathbf{p}_1\mathbf{p}_2$, calculated with the functions A, B, D, and G, which gives the correction to the level due to nuclear motion, as well as the mean values of powers of r_1 and r_{12}, agree to an accuracy of 10^{-6} and better with the known values for He and Li$^+$ from (^{4,8}). At the same time, the quantities $\langle \delta_3^1(r_1) \rangle$ and $\langle \delta^{(3)}(r_{12}) \rangle$, which enter into the expression for the relativistic correction and also into the radiation shift and depend strongly on the properties of the variational functions at special points*, show a deviation from the values obtained by Pekeris. Function A gives, for all ions, values corresponding to $m = 95$; function B, values corresponding to $m = 161$–203. Functions G and D lead to quantities which, for He and Li$^+$, lie beyond the interpolation values obtained

in calculations with $m = 1078$. For helium the latter values are 1.810427 and 0.106345, whereas the values obtained with G and D are 1.810462 and 0.106299 and, respectively, 1.810646 and 0.106238. The interpolation values $\langle\delta\rangle$ from (^{4,8}), apparently, are reliable only to an accuracy of 10^{-5} -10^{-4}. This circumstance must be kept in mind in studying the radiation shift, if it proves possible to increase the accuracy of the experimental determination of ionization potentials. An example of another problem in which it would also be important to estimate the influence of allowance for singularities is the study of the hyperfine structure in 2^3S He^3. The discrepancy between the measured value of the splitting and its theoretical value, which also depends on $\langle\delta^{(3)}(r_1)\rangle$, turns out to be 5—10 times greater than the experimental error (^{9,4}), amounting to 10^{-5}.

6. The expansion found by V. A. Fock, on which the present method is based, admits generalization to states with nonzero angular momentum and to systems of particles whose number is greater than 3 (^{10}). However, the S-state of a two-electron atom is probably at present an exceptional example of such a problem in which allowance for singularities can actually be carried out.
7. The numerical calculations were performed on the BESM-2 at the Computing Center of the Leningrad Division of the V. A. Steklov Mathematical Institute of the Academy of Sciences of the USSR.

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[*] The value $\langle p_1^4 \rangle$ also depends strongly on these properties. For the relativistic correction to the ionization potential as a whole, this dependence proves stronger than for the quantities $\langle p_4^1 \rangle$ and $\langle \delta_3^1(r_1) \rangle$ entering into it separately.

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