GROUND STATE ENERGY OF TWO-ELECTRON ATOMS WITH AN ARBITRARY NUCLEAR CHARGE $Z \leq 137$

G. L. KLIMCHITSKAYA and L. M. LABZOVSKIĬ

The A. A. Zhdanov Leningrad State University

Submitted December 17, 1970

Zh. Eksp. Teor. Fiz. 60, 2019–2025 (June, 1971)

The ground-state energy of a two-electron atom with an arbitrary nuclear charge Z is calculated on the basis of quantum-electrodynamics perturbation theory. The zeroth approximation is envisaged as two noninteracting Dirac electrons in the Coulomb field of the nucleus. Corrections of the first and second order with respect to Coulomb interaction between the electrons are calculated. A variational principle is proposed for the second-order corrections. All corrections are calculated as functions of Z in the interval $1 \leq Z \leq 137$.

1. The problem of refining the calculations of the energy levels of all the electrons in a multi-electron atom reduces mainly to allowance for corrections of two types: correlation and relativistic. Calculations of correlation and relativistic corrections in the lowest order in α^2 (α is the fine-structure constant) have been the subject of many works. However, as a rule, these calculations were made under the assumption that $Z_{eff}\alpha \ll 1$, where Z_{eff} is the effective charge of the nucleus. For electrons of the K layer, these calculations thus become meaningless already at $Z > 10$. The main scheme of the calculation of the correlation and relativistic corrections to the energy levels of an electron in an atom with an arbitrary charge Z was described earlier[1]. Following this scheme, we present here a calculation of different corrections to the energy of the ground state of a two-electron atom. The corrections will be calculated as functions of Z, making it possible to determine the relative importance of different corrections for different values of the nuclear charge. Our results will be valid not only for multiply charged two-electron ions, but also for electrons of the K layer of multi-electron atoms, in view of the insignificant screening of the K electrons by the electrons of the outer shells of the atom.

2. We first attempt to visualize, from general considerations, the role of different corrections as the nuclear charge Z changes from 1 to 137. To this end, it is most convenient to use the diagram shown in Fig. 1. We start from the approximation of non-interacting electrons. The abscissas of Fig. 1 represent the charge Z, and the ordinates the quantity $\log|\Delta E_i/\Delta E_0|$, where ΔE_0 is the summary binding energy of the two

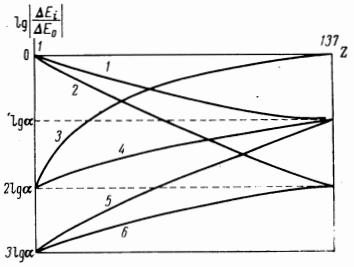

FIG. 1

non-interacting electrons in the atom, and ΔE_i represents different corrections to the energy. We use units $\hbar = c = 1$, and also $m = 1$, where m is the electron mass. All the curves of Fig. 1 are drawn to arbitrary scale. Curve 1 pertains to the correction of first order in the Coulomb interaction of the electrons ΔE_1^C. At small Z we have $\Delta E_0 \sim \alpha^2 Z^2$. The ratio $\Delta E_1^C/\Delta E_0$ at small Z proportional to Z^{-1}[2], i.e., is of the order of unity. At $Z \sim 137$ we obtain $\Delta E_0 \sim 1$, and ΔE_1^C is of the order of α. Curve 2 pertains to the correction of second order in the Coulomb interaction ΔE_2^C. The ratio $\Delta E_2^C/\Delta E_0$ at small Z is proportional to Z^{-2}, and at $Z \sim 137$ we have $\Delta E_2^C \sim \alpha^2$, which explains the form of the curve 2. Curve 3 shows the relativistic Pauli corrections ΔE_p—the dependence of the mass on the velocity and the spin-orbit interaction. The ratio $\Delta E_p/\Delta E_0$ at small Z is of the order of $\alpha^2 Z^2$[2], and at large Z it is of the order of unity. Curve 4 represents the relativistic Breit corrections ΔE_B to the electron interaction. At small Z we obtain $\Delta E_B/\Delta E_0 \sim \alpha^2 Z$; at $Z \sim 137$ the value of ΔE_B is of the same order as ΔE_1^C, i.e., $\sim\alpha$. Curve 5 represents the radiative corrections of lowest order ΔE_R, due to the self-energy of the electron, the polarization at vacuum, and the anomalous magnetic moment. For $Z \sim 1$ we have $\Delta E_R/\Delta E_0 \sim \alpha^3 Z^2$ (Lamb shift[2]) and for $Z \sim 137$ we obtain $\Delta E_R \sim \alpha$. Finally, curve 6 represents the relativistic corrections to the interaction $\Delta E_B'$ of the next order beyond the Breit corrections[3]. The remaining corrections are not indicated in Fig. 1.

In the sections that follow we calculate the corrections ΔE_1^C, ΔE_2^C, ΔE_p, and plot the curves 1–3.

3. We consider the ground state of an atom with configuration $(1s)^2$, or, in relativistic notation[4] $(1s_{1/2})^2$. In this case[2]

$$\Delta E_0 = 2(\sqrt{1-(\alpha Z)^2} - 1). \tag{1}$$

For ΔE_1^C we have, in accordance with the formulas given in[1],

$$\Delta E_1^c = \alpha \left(\frac{1}{r_{12}}\right)_{AB;AB}, \tag{2}$$

where

$$(F)_{A'B';AB} \equiv (F)_{A'B'AB} - (F)_{A'B'BA}, \tag{3}$$

$$(F)_{A'B'AB} \equiv \int \psi_{A'}^*(\mathbf{r}_1)\psi_{B'}^*(\mathbf{r}_2)F(\mathbf{r}_1,\mathbf{r}_2)\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 \tag{4}$$

and $r_{12} \equiv |r_1 - r_2|$. Each of the symbols A and B is decoded in accordance with[4] as the aggregate of four symbols $nljm$, where n is the principal quantum number, l the orbital angular momentum of the upper component of the Dirac bispinor, j is the total angular momentum of the electron, and m its projection. In our case $A \equiv 10\,{}^1/_2\,{}^1/_2$ and $B \equiv 10\,{}^1/_2 - {}^1/_2$. The wave functions are given by[2]

$$\psi_A = \begin{pmatrix} g(r)\,Y_{00}(\Omega) \\ 0 \\ -i\frac{1}{\sqrt{3}} f(r)\,Y_{10}(\Omega) \\ i\frac{2}{\sqrt{3}} f(r)\,Y_{11}(\Omega) \end{pmatrix}; \psi_B = \begin{pmatrix} 0 \\ g(r)\,Y_{00}(\Omega) \\ -i\sqrt{\frac{2}{3}} f(r)\,Y_{1,-1}(\Omega) \\ i\frac{1}{\sqrt{3}} f(r) Y_{10}(\Omega), \end{pmatrix}; \tag{5}$$

$$g(r) = (2Z)^{3/2}\sqrt{\frac{1+\gamma}{2\Gamma(2\gamma+1)}}\, e^{-\alpha Z r}(2Z\alpha r)^{\gamma-1}, \tag{6}$$

$$f(r) = -\sqrt{\frac{1-\gamma}{1+\gamma}}\, g(r), \tag{7}$$

where $\gamma = \sqrt{1-(\alpha Z)^2}$ and $\Gamma(x)$ is the gamma function. Substituting expressions (5)—(7) in (2) and integrating, we get

$$\left(\frac{1}{r_{12}}\right)_{ABAB} = \frac{Z\alpha\Gamma(4\gamma+1)}{2^{4\gamma-1}(2\gamma+1)[\Gamma(2\gamma+1)]^2} F\left(1,4\gamma+1,2\gamma+2;\frac{1}{2}\right), \tag{8}$$

$$\left(\frac{1}{r_{12}}\right)_{ABAB} = \frac{Z\alpha(1-\gamma)^2\Gamma(4\gamma+1)}{75\cdot 2^{4\gamma-2}(2\gamma+3)[\Gamma(2\gamma+1)]^2} F\left(1,4\gamma+1,2\gamma+4;\frac{1}{2}\right), \tag{9}$$

where F is the hypergeometric function. In the nonrelativistic limit when $\alpha Z \ll 1$, the exchange integral (9) vanishes, and the integral (8) goes over into the well known expression $(5/8)\alpha^2 Z$[2].

4. We proceed to calculate the correction ΔE_2^c. According to[1]

$$\Delta E_2^c = \frac{1}{2}\alpha^2 \sum_{\substack{n_1 n_2 \\ (n_1 n_2 \neq AB)}} \frac{1}{E_A + E_B - E_{n_1} - E_{n_2}} \left\{ \left| \left(\frac{\Lambda_1^{(+)}\Lambda_2^{(+)}}{r_{12}} \right)_{AB;n_1 n_2} \right|^2 - \left| \left(\frac{\Lambda_1^{(-)}\Lambda_2^{(-)}}{r_{12}} \right)_{AB;n_1 n_2} \right|^2 \right\}, \tag{10}$$

where $\Lambda^{(\pm)}$ are the projectors on states with positive (negative) energies. Expression (10) differs somewhat from formula (32) in[1], although the method of derivation is exactly the same. The differences lie, first, in the fact that the region of summation over $n_1 n_2$ in (10) is somewhat different. This is connected with the use of the approximation of non-interacting electrons as the initial approximation, whereas in[1] we used the Hartree-Fock approximation. Further, formula (32) in[1] takes into account the contribution of two diagrams shown in Fig. 2 (for a system of two electrons), and in (10) account is taken of only the contribution of diagram a. The point is that the contribution of the diagram b at small Z is of the order of α^3[3], and according to our classification it pertains to the correction $\Delta E_B'$. Generally speaking, the second term of formula (10), which contains summation over states with negative energy, is of the same order. It is more convenient, however, to include this term in ΔE_2^c, so as to extend the summation over the entire spectrum

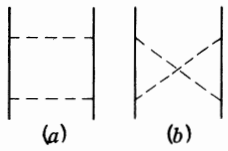

FIG. 2

of the Dirac equation for the electron in the field of the nucleus.

We shall attempt to construct a variational principle for the calculation of the correction ΔE_2^c. Expression (10) is not convenient for this purpose, owing to the presence of the projectors. This expression is obtained from the Gell-Mann and Low formula for the energy level shift after going over to the limit in accord with the adiabatic parameter ϵ[1] (in[1] this parameter is denoted by α). Let us retrace our steps somewhat in the derivation of (10) and consider the intermediate expression, which still contains the limit with respect to ϵ[1]:

$$\Delta E_2^c = \frac{32i\alpha^2}{(2\pi)^2}\lim_{\varepsilon\to 0}\varepsilon^3 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\omega_1\, d\omega_2 [(\omega_1+\omega_2+E_A+E_B)^2+(2\varepsilon)^2]^{-2} \times \left\{ J(\omega_1\omega_2) - \frac{|(1/r_{12})_{AB;AB}|^2}{[E_A(1-i0)+\omega_1][E_B(1-i0)+\omega_2]} \right\}, \tag{11}$$

$$J(\omega_1\omega_2) = \sum_{n_1 n_2} \left| \left(\frac{1}{r_{12}}\right)_{n_1 n_2; AB} \right|^2 [E_{n_1}(1-i0)+\omega_1]^{-1}[E_{n_2}(1-i0)+\omega_2]^{-1}. \tag{12}$$

The second term in the curly brackets in (11) compensates for the divergence with respect to ϵ at $n_1 n_2 = AB$. In spite of its apparent complexity, expression (11) is more convenient than the final formula (10), in that the summation over $n_1 n_2$ in (12) does not contain any projectors. We now write out the variational principle for the quantity $J(\omega_1\omega_2)$. Using the rules of matrix multiplication, it is easy to verify that this quantity contracts into the matrix element

$$J(\omega_1\omega_2) = \left(\frac{1}{r_{12}}\frac{1}{H_1(1-i0)+\omega_1}\frac{1}{H_2(1-i0)+\omega_2}\frac{1}{r_{12}}\right)_{AB;AB}, \tag{13}$$

where H is the Dirac Hamiltonian for the electron in the field of the nucleus. Let us consider the functional

$$I[\psi_1\psi_2] = \left\langle \psi_1^+(12\omega_1\omega_2) \left| \frac{1}{r_{12}} \right| \psi_A(1)\psi_B(2) \right\rangle - \left\langle \psi_1^+(12\omega_1\omega_2) \left| \frac{1}{r_{12}} \right| \psi_B(1)\psi_A(2) \right\rangle + \left\langle \psi_A^+(1)\psi_B^+(2) \left| \frac{1}{r_{12}} \right| \psi_2(12\omega_1\omega_2) \right\rangle - \langle \psi_1^+(12\omega_1\omega_2)|[H_1(1-i0)+\omega_1] \times [H_2(1-i0)+\omega_2]|\psi_2(12\omega_1\omega_2)\rangle. \tag{14}$$

By varying this functional with respect to ψ_1 and ψ_2, we verify that its stationary value coincides with $J(\omega_1\omega_2)$. The equations for the extremals are

$$[H_1(1+i0)+\omega_1][H_2(1+i0)+\omega_2]\psi_1(12\omega_1\omega_2) = \frac{1}{r_{12}}\psi_A(1)\psi_B(2), \tag{15}$$

$$[H_1(1-i0)+\omega_1][H_2(1-i0)+\omega_2]\psi_2(12\omega_1\omega_2) = \frac{1}{r_{12}}[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]. \tag{16}$$

In choosing the trial functions ψ_1 and ψ_2, it is necessary to see to it that the divergence in ϵ, which appears when the approximate expression for $J(\omega_1\omega_2)$ is

substituted in (11), is the same as for the exact expression. We take the trial functions in the form

$$\psi_1 = c_1\psi_A(1)\psi_B(2) + c_2\frac{1}{r_{12}}\psi_A(1)\psi_B(2), \tag{17}$$

$$\psi_2 = c_3[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)] + c_4[\psi_n(1)\psi_m(2) - \psi_m(1)\psi_n(2)], \tag{18}$$

where ψ_n and ψ_m are arbitrary eigenfunctions of the operator H and c_i are the varied parameters. Such functions satisfy the condition imposed above. In addition, the function ψ_2 is antisymmetrical with respect to permutation of the arguments, as follows from (16). Variation leads to a system of equations for the parameters c_i, which can be easily solved. Leaving out the rather cumbersome manipulations, we present immediately the final expression for ΔE_2^c:

$$\Delta E_2^c = \frac{\alpha^2}{2}\left[\left(\frac{1}{r_{12}^2}\right)_{AB;AB} - \left(\frac{1}{r_{12}}\right)^2_{AB;AB}\right]\frac{1}{E_A + E_B - E_n - E_m}. \tag{19}$$

Calculation of the integrals with the functions (5) yields

$$\left(\frac{1}{r_{12}^2}\right)_{ABAB} = \frac{(2Z\alpha)^2\Gamma(4\gamma)}{2^{4\gamma-1}[\Gamma(2\gamma+1)]^2} \times \sum_{k=1}^{\infty}\frac{1}{(2k-1)(2\gamma+2k-1)}F\left(1.4\gamma, 2\gamma+2k; \frac{1}{2}\right), \tag{20}$$

$$\left(\frac{1}{r_{12}^2}\right)_{ABBA} = \frac{(2Z\alpha)^2(1-\gamma)^2}{15[\Gamma(2\gamma+1)]^2}\left\{\frac{\Gamma(4\gamma)}{2^{4\gamma+1}}\sum_{k=1}^{\infty}\frac{1}{2k-1} \times \left[\frac{6}{2\gamma+2k}F\left(1,4\gamma, 2\gamma+2k+1; \frac{1}{2}\right) - \frac{1}{2\gamma+2k-1}F\left(1.4\gamma, 2\gamma+2k; \frac{1}{2}\right) + \frac{6}{2\gamma+2k-2}F\left(1.4\gamma, 2\gamma+2k-1; \frac{1}{2}\right)\right] - \frac{3}{2}\Gamma(2\gamma+1)\Gamma(2\gamma-1)\right\}. \tag{21}$$

We choose for the states n and m the two $2s_{1/2}$ states, i.e., we put $n \equiv 20\,{}^1/_2\,{}^1/_2$ and $m \equiv 20\,{}^1/_2 - {}^1/_2$. Then we obtain in the nonrelativistic limit $\Delta E_2^c = -0.1720\alpha^2$, which is close to the exact nonrelativistic value calculated with a large number of parameters[2]: $\Delta E_2^c = -0.1577\alpha^2$. This confirms the correctness of our choice of the trial function.

5. We consider now the relativistic corrections. To calculate the correction ΔE_p, it obviously suffices to expand the Sommerfeld formula (1) for the energy ΔE_0:

$$\Delta E_p = \Delta E_0 - \Delta E_0^{nr} = 2\left[\sqrt{1-(\alpha Z)^2} - 1 + \frac{1}{2}(\alpha Z)^2\right], \tag{22}$$

where ΔE_0^{nr} is the total nonrelativistic binding energy of the two electrons in the atom. For our configuration there is no spin-orbit interaction and the entire correction reduces to a dependence of the mass on the velocity. At small Z we obtain from (22) $\Delta E_p = -(\alpha Z)^4/4$, and at Z = 137 we have $\Delta E_p = -1$.

Let us consider the correction ΔE_B. We borrow the expression for ΔE_B from[5]:

$$\Delta E_B = -\alpha\left[\left\langle AB\left|\frac{\alpha_1\alpha_2}{r_{12}} + \frac{1}{2}(\nabla_1\alpha_1)(\nabla_2\alpha_2)r_{12}\right|AB\right\rangle - \left\langle BA\left|\frac{\alpha_1\alpha_2}{r_{12}}\cos[(E_A - E_B)r_{12}]\right.\right. - (\nabla_1\alpha_1)(\nabla_2\alpha_2)\frac{1}{r_{12}}\frac{\cos[(E_A-E_B)r_{12}]-1}{(E_A-E_B)^2}\left.\left|AB\right\rangle\right], \tag{23}$$

where α are Dirac matrices.

In our case $E_A = E_B$ and (23) goes over into

$$\Delta E_B = -\alpha\left(\frac{\alpha_1\alpha_2}{r_{12}} + \frac{1}{2}(\nabla_1\alpha_1)(\nabla_2\alpha_2)r_{12}\right)_{AB;AB}. \tag{24}$$

Further, using the relation

$$((\nabla_1\alpha_1)(\nabla_2\alpha_2)f(r_{12}))_{AB;AB} = -([H_1[H_2 f(r_{12})]])_{AB;AB} = (E_A - E_B)^2(f(r_{12}))_{AB;AB}, \tag{25}$$

we verify that the contribution of the second term in the direct and exchange matrix element (24) is equal to zero, i.e.,

$$\Delta E_B = -\alpha\left(\frac{\alpha_1\alpha_2}{r_{12}}\right)_{AB;AB}. \tag{26}$$

A direct calculation of (26) with the functions (5) for a configuration of the type $(ns_{1/2})^2$ results in $\Delta E_B = 0$.

The calculation of the correction ΔE_R as a function of Z is much more complicated. So far, only the values of ΔE_R for small Z have been calculated[6-8], and also for Z = 80[9]. There is also a calculation for Z = 137[10]. The corrections $\Delta E_B'$ were likewise calculated only for small Z[6,8].

6. Figure 3 shows curves 1–3 (corresponding to the notation of Fig. 1), plotted from formulas (2), (19), and (22). As seen from the figure, the contributions of the corrections ΔE_2^c and ΔE_p become comparable already at Z = 10 in accordance with the previous estimates[11]. At Z > 35, the value of ΔE_p exceeds also ΔE_1^c in order of magnitude. Curves 1 and 2 reveal a tendency towards a sharp increase as Z → 137, with $\Delta E_2^c \to \infty$. This is due to the singularity of the Coulomb Dirac functions in the region near the nucleus. As Z → 137, this singularity becomes appreciable (of the type r^{-1}), so that the matrix elements in (2) increase sharply, and in (19) they diverge. In the region of such large Z it is already necessary to take into account the finite dimensions of the nucleus[12].

Finally, Fig. 4 shows the corrections $\Delta E_1^c/Z\alpha^2$ and $\Delta E_2^c/\alpha^2$ as functions of Z. It is seen from the figure that the deviations from the corresponding nonrelativ-

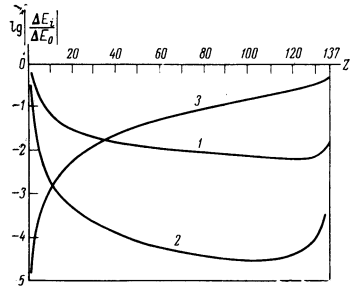

FIG. 3

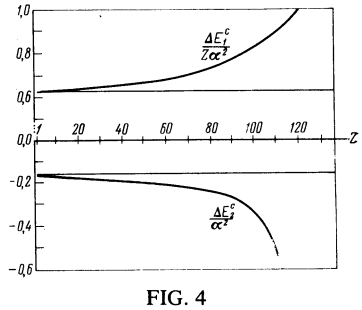

FIG. 4

istic expressions (represented in the figure by straight lines) become noticeable at $Z = 20 - 30$. At $Z = 40$, the relative error for ΔE_2^C reaches 20%.

[1]L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. 59, 168 (1970) [Sov. Phys.-JETP 32, 94 (1971)].
[2]H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Atoms, Springer, 1957.
[3]M. A. Braun and L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. 53, 1776 (1967) [Sov. Phys.-JETP 26, 1017 (1968)].
[4]I. P. Grant, Proc. Roy. Soc. 262, 555 (1961).
[5]M. A. Braun, Yu. Yu. Dmitriev, and L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. 57, 2189 (1969) [Sov. Phys.-JETP 30, 1188 (1970)].
[6]J. Sucher, Phys. Rev., 109, 1019 (1958).
[7]C. Schwartz, Phys. Rev., 123, 1700 (1961).
[8]E. E. Salpeter and M. H. Zaidi, Phys. Rev., 125, 248 (1962).
[9]G. E. Brown and D. F. Mayers, Proc. Roy. Soc. A251, 92 (1959).
[10]L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. 59, 2165 (1970) [Sov. Phys.-JETP 32, 1171 (1971)].
[11]A. Fröman, Rev. Mod. Phys., 32, 317 (1960).
[12]V. S. Popov, ZhETF Pis. Red. 11, 254 (1970) [JETP Lett. 11, 162 (1970)].

Translated by J. G. Adashko
219