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Electron binding energy for atoms : relativistic corrections

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Résumé. — L'énergie de liaison pour un atome de degré d'ionisation arbitraire est trouvée dans le cadre de la théorie statistique tenant compte de l'inhomogénéité de la densité électronique. La méthode de Schwinger permet d'obtenir la dépendance analytique de la correction relativiste en fonction du nombre d'électrons N et de la charge nucléaire Z . La seconde correction $\sim (\alpha Z)^4$ est estimée dans l'hypothèse d'électrons sans interaction. La comparaison avec les données précises montre que l'évaluation analytique trouvée reproduit l'énergie totale de la liaison pour les atomes ($10 \leq N \leq Z \leq 100$) avec une erreur de moins de 1 %.

Abstract. — Within the statistical theory a nonrelativistic binding energy for an atom with an arbitrary degree of ionization has been found with inhomogeneity of electron density taken into account. Based on Schwinger's method and using the improved estimate of the electron density at the nucleus, the analytical dependence of the leading relativistic correction on the nuclear charge Z and electron number N is obtained. The relativistic correction $\sim (\alpha Z)^4$ is estimated in the noninteracting electron approach. A comparison with accurate data has shown that the analytical estimates obtained give the total binding energy of an atom within 1 % for $10 \leq N \leq Z \leq 100$.

1. Introduction. — Derivation of analytical dependences for the physical properties of atoms on the nuclear charge and electron number has been for years attracting the attention of physicists. Studies on the nonrelativistic energy of an atom are most advanced. This has become possible due to the Z^{-1} perturbation theory for atoms with a small electron number and the statistical theory for many-electron systems. The analysis of the total electron energy including the relativistic corrections is now taking its first steps. For heavy many-electron systems no reliable analytical estimates are available at present.

Schwinger [1] has proposed a method to find the leading relativistic correction to the binding energy on the basis of the Thomas-Fermi (TF)-model and has analytically estimated this correction for a neutral atom.

The aim of our work is to study a dependence of the total binding energy for atoms on the nuclear charge Z and electron number N using accurate asymptotical expressions. First, we shall show that allowance for the inhomogeneity of the electron density and oscillation corrections results in a more accurate description of the energies of atoms in the nonrelativistic approximation. The relativistic contri-

bution to the energies for atoms with an arbitrary degree of ionization will be estimated analytically. The emphasis will be laid upon the leading relativistic correction.

2. Nonrelativistic approximation. — Consider a system of N electrons in nuclear field Z . For simplicity the nucleus will be considered to be a point and infinitely heavy. The total electron binding energy of an atom for moderate Z may be expressed as

$$E = E_{\text{NR}} + E_{\text{R}} . \quad (1)$$

Here E_{NR} is the nonrelativistic energy calculated from the Schrödinger equation, E_{R} is the relativistic correction to the energy (mass-velocity correction, spin-orbit and Breit-interaction and other relativistic effects).

The main part of E_{NR} is the energy E_{HF} calculated within the nonrelativistic Hartree-Fock method. A reliable estimate of E_{HF} was obtained within the statistical model of atoms.

Scott [2] expressed the binding energy as

$$E_{\text{HF}} \simeq E_{\text{TF}} + E_{q_0} + E_{\text{ex}} . \quad (2)$$

Here E_{TF} is the binding energy within the TF-model which, with allowance for the virial theorem, is equal

$$E_{TF} = - (3 \pi^2)^{2/3} \frac{3}{10} \int \rho^{5/3}(r) d^3r = - \frac{4}{5} \left(\frac{6}{\pi^2}\right)^{1/3} Z^{7/3} \int_0^{x_0} \Psi^{5/2}(x) x^{-1/2} dx \quad (3)$$

$\rho(r)$ is the electron density, $\Psi(x)$ is the screening function which is a solution of the TF-equation

$$\Psi''(x) = \Psi^{3/2}(x) \cdot x^{-1/2} \quad (4)$$

x is the dimensionless radius $x = \mu^{-1} r$,

$$\mu = (9 \pi^2)^{1/3} (128 Z)^{-1/3},$$

x_0 is the boundary of an ion, $\rho(r)$ is related with $\Psi(x)$ [3] by

$$\rho(r) = 32(9 \pi^3)^{-1} Z^2 \Psi^{3/2}(x) \cdot x^{-3/2} \quad (5)$$

$$E_{q0} = \frac{1}{2} Z^2$$

is the quantum-mechanical term introduced by Scott [2] as the boundary condition at the nucleus. Recently Schwinger [1] has shown that E_{q0} is a change of the binding energy due to correct treatment of the electrons with a large momentum.

E_{ex} in (2) is the Dirac exchange energy of the electrons

$$E_{ex} = - \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(r) d^3r = - \frac{3}{(6 \pi^4)^{1/3}} Z^{5/3} \int_0^{x_0} \Psi^2(x) dx \quad (6)$$

Atomic units are used here and throughout the paper.

The improvement of E_{HF} estimate [4] allowing for the inhomogeneity of the electron density within the Kompaneets-Pavlovskii-equation gives in (2) an additional term $E_{q'}$, equal to

$$E_{q'} = - \frac{Z}{16 \mu^2} \int_0^{x_0} \Psi^2(x) dx = - \frac{2}{3} (6 \pi^4)^{-1/3} Z^{5/3} \int_0^{x_0} \Psi^2(x) dx \quad (7)$$

With (7) in mind, we have written E_{HF} including all the first-order terms with respect to the quantum parameter $\beta = \frac{3}{2}(6 \pi Z)^{-2/3}$ as

$$E_{HF} \simeq E_{TF} + E_{q0} + E_{q1} \quad (8)$$

Here $E_{q1} = 11/9 E_{ex}$.

For a neutral atom the expression (8) becomes

$$E_{HF} = -0.768 745 Z^{7/3} + 0.5 Z^2 - 0.269 899 Z^{5/3} \quad (9)$$

The analysis of the accuracy of expression (9) shows that the statistical model with allowance for the contribution of strongly bound electrons and other quantum corrections gives a reliable estimate of the nonrelativistic binding energy for atoms (for $Z \geq 5$ the error is within 1 % and for $Z \geq 56$, it is less than 0.1 %).

Recently, the coefficient of $Z^{5/3}$ equal to

$$- 0.275 \pm 0.005$$

was obtained from a numerical analysis of the Hartree-Fock nonrelativistic energies for atoms with large Z (up to $Z = 290$) [5]. This estimate fairly agrees with exact value from (9).

Equation (9) has a form of $Z^{-1/3}$ expansion. A question may arise about the nature of the deviation of E_{HF} from SCF data. Preliminary analysis [4] shows that the deviation δE is a periodic function of $Z^{1/3}$ with the amplitude of oscillation $\sim Z^a$

$$\delta E = E_{osc} \simeq Z^a F(CZ^{1/3})$$

where $F(x)$ is a periodic function $F(x + 1) = F(x)$.

Here we have continued studying E_{osc} for neutral atoms using harmonic analysis and found that : (1) the oscillation amplitude is $\sim Z^{4/3}$; (2) the oscillation period is $0.92 Z^{1/3}$ which is in good agreement with maximum azimuthal quantum number l (within the TF-model $l_{max} = 0.928 Z^{1/3}$); (3) the periodic function $F(0.92 Z^{1/3})$ may accurately be approximated by a trapezoid (Fig. 1).

The extrapolation of E_{osc} beyond $Z = 120$ (dotted line) has shown that inclusion of E_{osc} gives the Hartree-Fock energy of a neutral atom with an error below 0.001 %.

E_{osc} appears due to the difference between the discrete quantum state distribution of electrons and the continuous one given by the TF-model.

Summing up the main contributions gives the binding energy of an atom as

$$E_{HF} = E_{TF} + E_{q0} + E_{q1} + E_{osc} \quad (10)$$

Equations (8) and (10) are equally valid both for neutral atoms and for ions.

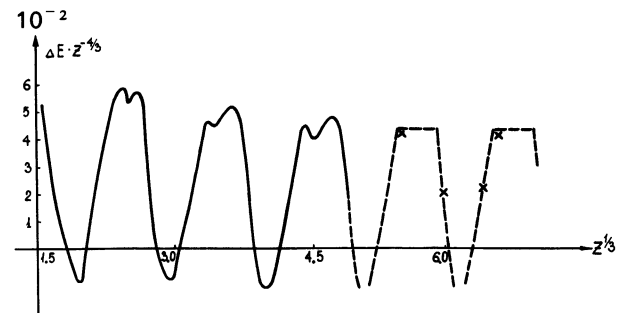


Fig. 1. — Deviation of the nonrelativistic energy for neutral atoms (Eq. (9)) from accurate data E_{ac} [20] as a function of $Z^{1/3}$. —, $(E_{HF} - E_{ac}) Z^{-4/3}$; - - -, the extrapolated curve; x, E_{HF} [5].

In order to obtain the analytical function $E_{\text{HF}}(N, Z)$, an explicit expression of the screening function $\Psi(x)$ for ions is necessary. It has been earlier shown [6] that the solution of the TF-equation (6) may be expressed as

$$\Psi(x) = \sum_{k=0}^{\infty} \varphi_k \left(\frac{x}{x_0} \right) \left(\frac{N}{Z} \right)^k. \quad (11)$$

Using (11), it is possible to express the expectation values E_{TF} and E_{q1} for ions as the N/Z series

$$E_{\text{TF}}(N, Z) = -Z^2 N^{1/3} \sum_{k=0}^{\infty} a_{1k} \left(\frac{N}{Z} \right)^k \quad (12)$$

$$E_{q1}(N, Z) = -ZN^{2/3} \sum_{k=0}^{\infty} a_{3k} \left(\frac{N}{Z} \right)^k. \quad (13)$$

The representation of $E_{\text{TF}}(N, Z)$ in form (12) was postulated in [7]. We have shown the validity of series (12) and found the exact values of the first coefficients a_{1k} [8]

$$a_{10} = \sqrt[3]{\frac{3}{2}}; \quad a_{11} = -\sqrt[3]{\frac{3}{2}} \left(1 - \frac{256}{45 \pi^2} \right);$$

$$a_{12} = \sqrt[3]{\frac{3}{2}} \left(\frac{2}{3} + \frac{223}{30 \pi^2} - \frac{262 \ 144}{2 \ 025 \ \pi^4} \right);$$

$$a_{13} = 0.002 \ 789 \ 6.$$

Here, using (6), (7) and (11), we give the exact values of a_{3k}

$$a_{30} = \frac{44}{9 \pi^2} \sqrt{\frac{2}{3}}; \quad a_{31} = -\sqrt[3]{\frac{2}{3}} \left(\frac{45 \ 056}{405 \ \pi^4} - \frac{341}{36 \ \pi^2} \right)$$

$$a_{32} = \frac{4}{\pi^2} \sqrt[3]{\frac{2}{3}} \left(\frac{77}{27} - \frac{1 \ 159 \ 631}{5 \ 670 \ \pi^2} + \frac{31 \ 719 \ 424}{18 \ 225 \ \pi^4} \right)$$

which allows complete estimation of the smooth part of $E_{\text{HF}}(N, Z)$ within β^2 .

Equations (12) and (13) have the form of the well known Z^{-1} expansion series

$$E_{\text{HF}}(N, Z) = \sum_{k=0}^{\infty} \varepsilon_k(N) Z^{2-k}. \quad (14)$$

Combining (8), (12) and (13), we find the analytical expression for coefficients $\varepsilon_k(N)$

$$\begin{aligned} \varepsilon_0(N) &= -a_{10} N^{1/3} + 1/2 \\ \varepsilon_k(N) &= -a_{1k} N^{k+1/3} - a_{3k-1} N^{k-1/3}; \quad k > 0. \end{aligned} \quad (15)$$

Equations (15) give the asymptotically exact (at $N \gg 1$) value of $\varepsilon_0(N)$ and asymptotically exact smooth terms in $\varepsilon_k(N)$ at $k > 0$. Examination of $\varepsilon_k(N)$ shows that the frequently used geometrical approximation of series (14)

$$E(N, Z) = \varepsilon_0 Z^2 + \varepsilon_1 Z + \varepsilon_2 \left(1 - \frac{\varepsilon_3}{\varepsilon_2 Z} \right)^{-1}$$

is slightly effective for atoms with large N . Indeed, it follows from physical considerations that the singularity of $E(N, Z)$ is localized at $Z \gtrsim 0.5 N$ whereas

$$\varepsilon_3/(\varepsilon_2 Z) \simeq 0.027 N/Z.$$

The terms proportional to $N^{k-1/3}$ in (15) must include the oscillating contribution. To do this, it is necessary to find an explicit analytical expression for $E_{\text{osc}}(N, Z)$. We have failed to obtain the expression from the first principles within the TF-model. The only explicit form $E_{\text{osc}}(N, Z)$ may be obtained using the quantum noninteracting electrons model [8]. Eliminating E_{q0} from the quantum contribution of noninteracting electrons (Eq. (8) from [8]) gives $E_{\text{osc}}(N, Z)$ in the algebraic form

$$\begin{aligned} E_{\text{osc}}(N, Z) &= -Z^2 \left\{ N^{-1/3} \left(\frac{2}{3} \right)^{1/3} \left[y(y-1) + \frac{1}{12} \right] + \right. \\ &\quad \left. + \frac{1}{3} \left(\frac{2}{3} \right)^{2/3} N^{-2/3} y(2y-1) \cdot (1-y) + \dots \right\}. \end{aligned} \quad (16)$$

Here $0 \leq y \leq 1$ is the fractional occupancy of the outermost shell, $y = M/2n^2$, M is the electron number in the outermost shell, n is the principal quantum number of this shell.

The leading oscillating term for highly ionized atom is proportional to $Z^2 N^{-1/3}$. The oscillation amplitude for a neutral atoms is $\sim Z^{4/3}$ as was shown in this paper. Thus, the oscillating contribution of $\sim Z^2 N^{-1/3}$ vanishes for a neutral atom. With this in mind, we propose a simple approximation of $E_{\text{osc}}(N, Z)$ in the form

$$E_{\text{osc}}(N, Z) = -N^{-1/3} \left(\frac{2}{3} \right)^{1/3} \left[y(y-1) + \frac{1}{12} \right] Z(Z-N) \quad (17)$$

which correctly describes both limiting cases : the neutral atom and the atom with no electron interaction.

The inclusion of $E_{\text{osc}}(N, Z)$ improves the estimates of $\varepsilon_0(N)$ and $\varepsilon_1(N)$ in (15) for small N . Comparison of $\varepsilon_k(N)$ with exact results [9, 10] shows that equations (15) and (17) reproduce well the quantum data beginning from $N = 10$ (Table I). Our analysis of the accuracy of equation (10) with (15) and (17) has shown that inclusion of E_{osc} allows $E_{\text{HF}}(N, Z)$ [11]

Table I. — Coefficients of Z^{-1} expansion of E_{HF} .

N	$-\varepsilon_{11}(N)$	$\varepsilon_2(N)$	$-\varepsilon_3(N)$
6	3.377 (3.262)	3.647 (3.061)	0.967 (0.841)
8	5.666 (5.662)	8.214 (7.672)	2.581 (2.490)
10	8.776 (8.771)	15.01 (15.48)	5.510 (5.572)
28	37.91 (37.97)	206.5 (204.4)	178.2

In brackets are data [9, 10].

to be estimated with an error $< 1\%$ for the isoelectronic series from $N = 6$ up to $N = 20$. Taking into account that expressions (15) and (17) have correct asymptotic behaviour, it is clear that all nonrelativistic series for large N would be described by (15) and (17) within 1% .

3. Relativistic corrections. — Estimation of the total binding energy of an atom is extremely complicated since at present there is no complete relativistic theory. Bethe and Salpeter [12] have shown that, for moderate Z , the relativistic effects may be considered within the perturbation theory and have given the expressions for the main corrections of relative order (αZ^2) , α being the fine structure constant, $\alpha = 137.037^{-1}$.

In this paper we give an approximate expression for the first order correction E_R^1 .

The leading relativistic correction may be written as

$$E_R^1 = E_{e1} + E_B, \quad (18)$$

where E_B is the Breit-interaction and E_{e1} is determined as [12]

$$E_{e1}^1 = -\frac{\alpha^2}{8} \sum_i \langle p_i^4 \rangle + \frac{\alpha^2}{8} \sum_i \langle \text{div}_i \epsilon_i \rangle + \frac{\alpha^2}{8} \sum_i \mathbf{l}_i \mathbf{s}_i \left\langle \frac{1}{r_i} \frac{dv}{dr_i} \right\rangle. \quad (19)$$

Here \mathbf{p}_i , \mathbf{r}_i , \mathbf{l}_i and \mathbf{s}_i are the operators of momentum, position, azimuthal momentum and spin of the i -th electron, $\epsilon_i = -\nabla_i V$ is the field intensity due to the nucleus and electrons of atom. The second term in (19) with the Poisson equation yields

$$\sum_i \langle \text{div}_i \epsilon_i \rangle \simeq 4\pi Z\rho(0) - 4\pi \int \rho^2(r) d^3r. \quad (20)$$

The term due to the electron spin-orbit interaction in (19) may be neglected; it is essential for the description of the level splitting and has no effect on the relativistic shift.

Then :

$$E_{e1}^1 = -\frac{\alpha^2}{8} [\langle p^4 \rangle - 4\pi Z\rho(0) + 4\pi \langle \rho \rangle]. \quad (21)$$

Here $\rho(0)$ is the electron density at the nucleus, $\langle A \rangle$ is the expectation value of the operator A for an atom.

In order to include the Breit-interaction, we use the local-density approximation [13]. Taking the leading term in the transverse exchange energy expansion on α^2 yields

$$E_R^1 = -\frac{\alpha^2}{8} [\langle p^4 \rangle - 4\pi Z\rho(0) - 6\pi \langle \rho \rangle]. \quad (22)$$

Equation (22) allows rapid numerical estimation of E_R^1 using the nonrelativistic HF-wavefunctions.

The first analytical estimates of E_R^1 for the systems with a large electron number were made by Schwinger [1] who obtained the exact asymptotic dependence of the leading relativistic correction on Z for neutral atoms within the TF-model with correct treatment of strongly bound electrons

$$E_R^1 \simeq -\alpha^2 Z^4 (b_1 + b_2 Z^{-1/3}) \quad (23)$$

where $b_1 = 5\pi^2/24 - \zeta(3) \simeq 0.854$; $\zeta(3)$ is the Riemann ζ -function,

$$b_2 = 16(6\pi^4)^{-1/3} \int_0^{x_0} \Psi^{5/2}(x) \Psi'(x) x^{-1/2} dx. \quad (24)$$

In (23), the first contribution due to the electrons of large momentum is calculated by summation of the relativistic corrections $\sim \alpha^2 Z^4$ from Sommerfeld formula and does not depend on the degree of ionization. The second contribution depends on the degree of ionization and includes the part of $\langle p^4 \rangle$ given by the TF-model.

Having calculated the integral in (24), Schwinger has obtained for a neutral atom

$$E_R^1 \simeq -\alpha^2 Z^4 (0.854 - 2.075 Z^{-1/3}). \quad (25)$$

Equations (23) and (25) include asymptotic estimates of $\langle p^4 \rangle$ up to relative order $Z^{-2/3}$ and the leading term in $\rho(0)$, proportional to Z^3 . We will improve the estimate of $\rho(0)$, using the Kompaneets-Pavlovskii-model [14]. Following this model there exists an inner boundary of an atom at $x_1 \simeq 0.1 Z^{-2/3}$ [4]. The electron density at x_1 is

$$\rho(x_1) \simeq \frac{32 Z^2}{9 \pi^3} \left\{ \left(\frac{\Psi}{x} \right)^{3/2} - \frac{\beta}{12} \left(\frac{x}{\Psi} \right)^{3/2} \left[\frac{d}{dx} \left(\frac{\Psi}{x} \right) \right]^2 \right\}_{x=x_1}. \quad (26)$$

Bearing in mind that $x_1 \ll 1$ and that the real electron density changes but slightly over the length between $x = 0$ and x_1 it is possible to assume that at $x \leq x_1$ $\rho(x) \simeq \text{const.} = \rho(x_1)$. Expanding (26) with respect to $Z^{-2/3}$ and taking the first term of the expansion give the approximation

$$\rho(0) = C_1 Z^3 + C_2 \Psi'(0) Z^{7/3} \quad (27)$$

where $\Psi'(0)$ is a function of N/Z and C_1 and C_2 are coefficients.

We calculate C_1 and C_2 within the nonrelativistic electron approach. The exact value of $\rho(0)$ for this approach is given by the expression

$$\rho(0) = \frac{2}{\pi} \sum_{n=1}^{n_m} Z^3 n^{-3} \simeq \frac{Z^3}{\pi} [2\zeta(3) - n_m^{-2}] \simeq \frac{Z^3}{\pi} \left[2\zeta(3) - \left(\frac{2}{3N} \right)^{2/3} \right]. \quad (28)$$

Comparison of (27) and (28) gives

$$C_1 = \frac{2}{\pi} \zeta(3); \quad C_2 = \frac{1}{\pi} \left(\frac{32}{3\pi} \right)^{2/3}. \quad (29)$$

Here it is taken into account that $\Psi'(0)$ in the non-interacting electrons model within the TF-theory is equal to

$$\Psi'(0) = - \left(\frac{\pi}{16} \right)^{2/3} Z^{2/3} N^{-2/3}.$$

With (29) in mind, we get from (27) and (22) an expression for the leading relativistic correction

$$E_R^1 \simeq -\alpha^2 Z^4 \left[b_1 + N^{-1/3} b_2 \left(\frac{N}{Z} \right) + N^{-2/3} b_3 \left(\frac{N}{Z} \right) \right]. \quad (30)$$

Here $b_3(N/Z) = -2^{7/3} (3\pi)^{-2/3} Z^{-2/3} N^{2/3} \Psi'(N/Z)$.

For a neutral atom, expression (30) is quite simple [15]

$$E_R^1 = -\alpha^2 Z^4 (0.854\ 11 - 2.075 Z^{-1/3} + 1.793\ 7 Z^{-2/3}). \quad (31)$$

The analytical functions $b_2(N/Z)$ and $b_3(N/Z)$ for an atom with an arbitrary degree of ionization may easily be found by substituting series (11) into (30) and (24)

$$\begin{aligned} b_2 \left(\frac{N}{Z} \right) &= \sum_{k=0}^{\infty} b_{2k} \left(\frac{N}{Z} \right)^k \\ b_3 \left(\frac{N}{Z} \right) &= \sum_{k=0}^{\infty} b_{3k} \left(\frac{N}{Z} \right)^k \end{aligned} \quad (32)$$

where the first two coefficients are exact

$$\begin{aligned} b_{20} &= -\frac{5}{4} \left(\frac{2}{3} \right)^{1/3}; \quad b_{21} = \left(\frac{2}{3} \right)^{1/3} \left(\frac{5}{2} - \frac{1\ 792}{45\ \pi^2} \right) \\ b_{30} &= 18^{-1/3}; \quad b_{31} = 18^{-1/3} \left(2 + \frac{1\ 024}{45\ \pi^2} \right) \end{aligned}$$

and the coefficients b_{22} and b_{32} are estimated numerically as $b_{22} = 0.426$ and $b_{32} = -0.242$.

Equations (30) and (32) give E_R^1 as a relativistic Z^{-1} expansion [16]

$$E_R^1 = -\alpha^2 Z^4 \sum_{k=0}^{\infty} \varepsilon_{1k}(N) Z^{-k}, \quad (33)$$

the coefficients $\varepsilon_{1k}(N)$ being expressed by

$$\begin{aligned} \varepsilon_{10} &= b_1 + N^{-1/3} b_{20} + N^{-2/3} b_{30} = \\ &= 0.854\ 11 - 1.092\ 0 N^{-1/3} + 0.381\ 57 N^{-2/3} \\ \varepsilon_{11} &= N^{2/3} b_{21} + N^{1/3} b_{31} = \\ &= -1.340\ 8 N^{2/3} + 1.642\ 9 N^{1/3} \\ \varepsilon_{12} &= N^{5/3} b_{22} + N^{4/3} b_{32} = 0.426 N^{5/3} - 0.242 N^{4/3}. \end{aligned} \quad (34)$$

Expression (34) gives asymptotically the exact values of the first two coefficients in $\varepsilon_{10}(N)$ and asymptotically the exact coefficient at $N^{k-1/3}$ in $\varepsilon_{1k}(N)$ at $k > 0$.

Note that the coefficient $\varepsilon_{10}(N)$ has a form different from ε_{1k} at large N ; whereas $\varepsilon_{1k}(k > 0)$ increases as $N^{k-1/3}$, there is no dependence on N in the main part of ε_{10} .

Some terms in the derivation of (32) were omitted. Now, we estimate the order of magnitude of these terms. There exists an oscillating contribution due to the shell effects in the expectation value $\langle p^4 \rangle$, with amplitude $\sim \alpha^2 Z^4 N^{-2/3}$. The account of oscillation must change the coefficients at $N^{k-2/3}$ in (34). Other effects which were not included into the derivation of (30) are proportional to $\langle \rho \rangle$. Having estimated $\langle \rho \rangle$ within the quasi-classical consideration we obtain

$$\alpha^2 \langle \rho \rangle \sim \alpha^2 Z^3 \ln N \quad (35)$$

that makes up a small part of the relativistic corrections for an atom with an arbitrary degree of ionization.

Thus, equations (30) to (34) determine the main part of the leading relativistic correction to the binding energy of an atom. These expressions give a clear understanding of the change of E_R^1 along the isoelectronic series and allow a rapid estimation of E_R^1 for atom with an arbitrary degree of ionization.

For large Z , higher order contributions with respect to $(\alpha Z)^2$ become essential. Estimation of these terms is difficult and can be carried out for the non-interacting electrons approximation only.

Let us estimate the second-order contribution E_R^2 . Expanding the Sommerfeld formula up to the terms $\sim \alpha^4 Z^6$ we find ($j = l \pm 1/2$)

$$E_R^2 = -\alpha^4 Z^6 \sum_k n_k^{-4} \left\{ \frac{n_k}{(2j_k + 1)^3} + \frac{3}{2(2j_k + 1)^2} - \frac{3}{2n_k(2j_k + 1)} + \frac{5}{16n_k^2} \right\}.$$

Summation over j yields

$$E_R^2 = -\alpha^4 Z^6 \varepsilon_{20} \quad (36)$$

$$\varepsilon_{20} = \sum_{n=1}^{n_m} n^{-4} \left\{ \frac{1}{2n} + \frac{19}{8} + \frac{1}{2} \sum_{l=0}^{n-1} \left[\frac{n}{(l+1)^2} + \frac{3}{l+1} \right] \right\} \quad (37)$$

which results in the first two terms of the ε_{20} expansion in $(n_m + 1/2)^{-1}$ for closed shells

$$\varepsilon_{20} \simeq 0.281\ 03 - \frac{\pi^2}{24} \left(n_m + \frac{1}{2} \right)^{-2} \simeq 0.281\ 03 - \frac{\pi^2}{24} \left(\frac{2}{3} \right)^{2/3} N^{-2/3}. \quad (38)$$

Table II. — Coefficients of Z^{-1} expansion of the relativistic corrections (34) and (38).

N	$\varepsilon_{10}(N)$	$-\varepsilon_{11}(N)$	$\varepsilon_{12}(N)$	$\varepsilon_{20}(N)$
10	0.429 5 (0.437 5)	2.684 (2.571)	14.55 (10.74)	0.213 4 (0.210 9)
28	0.535 9 (0.535 9)	7.375 (7.287)	89.35 (84.55)	0.247 0 (0.242 8)

In brackets are data [10, 18, 19] and $\varepsilon_{20}(N)$ from (37).

The comparison shows that the asymptotical form (38) agrees well with the exact values from (37) even for $N = 10$ (Table II).

The first term in (38) is exact and independent of the electron-electron interaction. The allowance for the latter only leads to a somewhat higher absolute value of the second term. With this in view, equations (36) and (38) can be used for the approximate estimation of the relativistic correction E_R^2 .

The analysis of the Sommerfeld formula shows that the higher order terms have the same form ⁽¹⁾

$$E_R^n = -(\alpha Z)^{2n} Z^2 (\gamma_1 - \gamma_2 N^{-2/3}).$$

We shall show that equations (30) to (34) can be used not only for qualitative but also for quantitative estimates of the relativistic contribution to the energy of an atom with an arbitrary degree of ionization. First, we examine the accuracy of (34). Though the coefficients $\varepsilon_{1k}(N)$ are obtained with the assumption that $N \gg 1$, expression (34) reproduces well accurate ε_{10} and ε_{11} [18, 19] at $N \geq 10$ (Table II). As far as N rises, the accuracy of $\varepsilon_{1k}(N)$ obtained from (34) rapidly increases.

We fail to compare (30) with the accurate values of the leading relativistic correction for ions because no data are available even for ions with moderate Z and N . For neutral atoms alone it was possible to perform a comprehensive comparison of E_R^1 with the relativistic contribution E_R calculated within the Dirac-Fock method [20]. Equation (31) gives a greater part of E_R up to $Z = 120$. Inclusion of approximate E_R^2 from (36), (38) decreases the error in E_R to 2% at $25 \leq Z \leq 80$ (Fig. 2).

With such an encouraging result in hand, we calculate through the total binding energies for

⁽¹⁾ It should be noted that the asymptotic behaviour of E_R^n at large N given on the basis of the Vallarta-Rosen equation [17] is erroneous; the exact asymptotic behaviour may only be obtained with the correct treatment of strongly bound electrons.

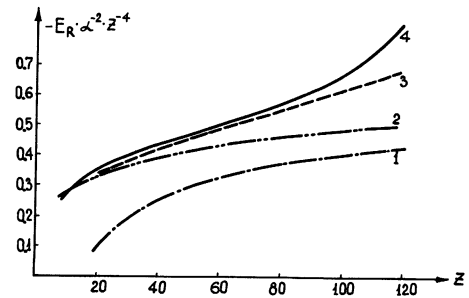


Fig. 2. — Relativistic corrections as a function of the atomic number. 1) $-E_R^1$ (Eq. (25)); 2) $-E_R^1$ (Eq. (31)); 3) $-E_R^1 + E_R^2$ (Eqs. (31) and (36, 38)); 4) E_R , the data by Desclaux [20].

neutral atoms in the Dirac-Fock approximation E_{DF} (Table III). It is seen that equations (9), (31) and (38) perfectly reproduce E_{DF} up to $Z \sim 100$. Estimating E_{DF} for Cu isoelectronic series, we obtain the same result (Table IV). The estimate of E_{DF} is made using equations (10), (12), (13), (17), (30) and (38). The Padé-approximants are used at $N/Z \sim 1$, giving the exact neutral atom values.

The analysis performed shows that within the statistical theory with quantum and relativistic corrections it is possible to obtain not only qualitative estimates but also reliable values of the binding energy for atoms with an arbitrary degree of ionization, which for the moment are not available. The use of the leading relativistic correction (30) to (34) and of the approximate second order correction from (36, 38) allows a description of the total binding energy for atoms in the wide range of N and Z ($10 \leq N \leq Z \leq 100$) with an error less than 1%.

To conclude, let us enumerate the main results of this paper :

- 1) the analytical estimates of the nonrelativistic binding energy including the inhomogeneity correction are obtained;
- 2) the coefficients of Z^{-1} expansion of the non-

Table III. — Total binding energy for neutral atoms ($-E_{DF} \times 10^{-3}$).

Z	20	30	40	50	60	70	80	90	100	110
(*)	0.677	1.795	3.590	6.166	9.622	14.07	19.62	26.42	34.63	44.43
(**)	0.679	1.794	3.595	6.171	9.616	14.05	19.62	26.47	34.81	44.95

(*) Our results, equations (9), (31) and (36, 38).

(**) Data by Desclaux [20].

Table IV. — *Binding energy for isoelectronic series of Cu.*

Z	$-E_R^1$	$-E_{DF}$ (our results)	$-E_{DF}$ [21]
29	14.3	1 654.4	1 652.7
32	25.0	2 096.3	2 094.5
35	32.3	2 595.9	2 594.4
38	46.1	3 153.9	3 152.5
42	71.0	3 989.6	3 988.4
46	105	4 932	4 931
50	151	5 983	5 982
54	211	7 145	7 144
58	268	8 422	8 421
62	386	9 816	9 815
66	507	11 331	11 331
70	656	12 971	12 979
74	838	14 740	14 746
78	1 068	16 665	16 657
82	21	18 689	18 712

relativistic energy are improved by including the inhomogeneity and oscillation correction ;

3) an approximate expression for the leading relativistic correction to the binding energy is obtained with allowance for the Breit-interaction ;

4) the analytical estimates of the leading relativistic correction are given for atoms with an arbitrary degree of ionization ;

5) the asymptotical expression of the coefficients of relativistic Z^{-1} expansion series is found to be in good agreement with accurate quantum-mechanical data.

After the work has been completed, we became aware of the Schwinger's paper [22] in which the consistent treatment of the $Z^{-2/3}$ -order correction to the binding energy in TF-model is done.

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