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Estimation of two-electron expectation values for atoms

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Abstract. — The TF model is used to obtain the analytical expressions of $\langle r_{12}^4 \rangle$ and $\langle \delta^3(r_{12}) \rangle$ within $-3 < k < 3$ for a neutral and within $-3 < k < \infty$ for an ionized atom. At $-3 < k < 1$, the expressions for the exchange contribution are derived in a closed form. They are used to find the analytical dependences of $\langle r_{12}^4 \rangle$ and $\langle \delta^3(r_{12}) \rangle$ on the nuclear charge $Z$ and the electron number $N$. The amplitude and the period of quantum oscillations are shown to be of the order of $Z^{5/3}$ and $Z^{1/3}$. The relationships between one- and two-electron expectation values of electron positions are obtained. With allowance for the strongly bound electron contribution and the exchange interaction, the relationship between the expectation values of $\langle \delta^3(r_{12}) \rangle$ and one-particle density $\rho(r)$

$$\langle \delta^3(r_{12}) \rangle = \frac{1}{4} \langle \rho \rangle,$$

cette relation étant approximativement valide dans le cadre de la méthode de Hartree-Fock. Grâce à cette relation, on obtient une valeur approchée de $\langle \delta^3(r_{12}) \rangle$ pour un atome dans un degré d'ionisation arbitraire.

1. Introduction.

A knowledge of the expectation values of two-electron operators is necessary to study atomic properties such as incoherent scattering cross-section and total scattered X-ray intensity at small momentum transfer, when the X-ray frequency is greater than the atomic K-shell absorption frequency, the total cross-section for inelastic scattering of fast charged particles [1], relativistic and radiative corrections for binding energy, etc. The calculation of the simplest two-electron expectation values such as:

$$\langle r_{12}^4 \rangle = \sum_{i<j} \int \psi^*(r_1, ..., r_n) |r_i - r_j|^4 \psi(r_1, ..., r_n) \, d^3r_1 ... d^3r_n, \quad -3 < k < \infty$$

$$\langle \delta^3(r_{12}) \rangle = \sum_{i<j} \int \psi^*(r_1, ..., r_n) \delta(r_i - r_j) \psi(r_1, ..., r_n) \, d^3r_1 ... d^3r_n$$

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for heavy atoms and ions requires to know the wave function of a system and to make tedious calculations of multi-dimensional integrals. This hampers not only the analysis of $\langle r_{12}^k \rangle$ and $\langle \delta^3(r_{12}) \rangle$ as a function of the nucleus charge $Z$ and the electron number $N$ but accounts also for the absence of even numerical expectation values for ions with $N > 2$, except for $\langle r_{12}^{-1} \rangle$ which is calculated along with the binding energy.

The $Z^{-1}$ perturbation theory [2, 3] may be used to estimate $\langle r_{12}^k \rangle$ for isoelectronic series with small $N$ and sufficiently large $Z$. The Thomas-Fermi (TF) model [4] is at present the only tool allowing to derive analytical dependences of some two-electron averages on $N$ and $Z$ for many-electron atoms. The study of one-particle operators within the TF model [5, 6] has shown that this model gives reliable qualitative estimates and, in some cases, semiquantitative ones. The aim of the present paper is to obtain analytical estimates of the expectation values $\langle r_{12}^k \rangle$ and $\langle \delta^3(r_{12}) \rangle$ using the TF model with allowance for the exchange interaction. With this model, we shall also establish the relationship between the expectation values of one- and two-electron operators which approximately hold for real atomic systems.

2. Operators $r_{12}^k$.

To calculate the two-electron expectation values, it is sufficient to know the diagonal element $\rho_2(r_1, r_2) = \rho(r_1, r_2)$ of the two-particle density matrix. For sake of simplicity, $\rho_2(r_1, r_2)$ will be called as a two-particle density.

The expectation value of $r_{12}^k = \sum_{i<j} |r_i - r_j|^k$ is expressed as:

$$\langle r_{12}^k \rangle = \int d^3r_1 \int d^3r_2 |r_1 - r_2|^k \rho_2(r_1, r_2).$$

The main part of $\langle r_{12}^k \rangle$ may be found using the simple separable approximation

where $\rho(r)$ is the one-particle density. Using this relation, we get an estimate of $\langle r_{12}^k \rangle$:

$$\langle r_{12}^k \rangle = \frac{1}{2} \int_0^{\infty} d^3r_1 \int_0^{\infty} d^3r_2 |r_1 - r_2|^k \rho(r_1) \rho(r_2).$$

We use the TF model [4] to estimate $\langle r_{12}^k \rangle$. In this model, $\rho(r)$ for an atom is related to the screening function, $\chi(x)$, by

$$\rho(r) = \frac{32 Z^2}{9 \pi^3} \frac{\chi''(x)}{x}.$$  

$$\chi(x) = - \frac{r}{Z} [V(r) - V_0]$$

for a neutral atom $r_0 \to \infty$, $V(r)$ stands for the total electrostatic potential, $V_0$ is the chemical potential.

For a neutral atom, the range of validity of (3) is $-3 < k < 3$. The upper boundary, $k = 3$, appears as due to the incorrect treatment of the electron density ($\rho(r \to \infty) \sim r^2$) at the periphery of the atom.

As the statistical density in the outer region better approximates the quantum one for positive ions [4], equation (3) holds for an ion if $-3 < k < \infty$, which completely coincides with the quantum range of $k$.

The spherical symmetry of $\rho(r)$ enables us to perform angular averaging of (3)

The interval, $-3 < k < 3$, includes 5 moments of the two-particle density, namely, $k = -2, -1, 0, 1, 2$. The zero moment is reduced to the normalization integral $Z^2/2$ and yields an asymptotically exact expression for the number of electron pairs at $Z \to \infty$; $\langle r_{12}^{-1} \rangle$ specifies the interelectron interaction. The
values of \( A(k) \) at \( k = -2, -1, 1, 2 \) obtained from the numerical solution of equation (5) are given in table I.

To estimate \( r_{12}^\lambda \) for an atom with an arbitrary ionization degree, we use the analytical expansion of the TF screening function in the parameter \( \lambda = (1 - N/Z)^{1/2} x_0^{1/2} \)

\[
\chi(x) = \left(1 - \frac{N}{Z}\right) \sum_{i=0}^{\infty} x_i \varphi_i(x/x_0).
\]

(9)

The functions \( \varphi_i(x/x_0) \) are determined from the hierarchy of differential equations in a closed form. Some of the first functions \( \varphi_i(x/x_0) \) are given in [5, 7]. Substituting (9) into (6) and using the expression for \( \lambda(Z, N) \) and \( x_0(Z, N) \) [5]

we get the series expansion in \( N/Z \) of \( r_{12}^\lambda \) for arbitrary values of \( k(-3 < k < \infty) \):

\[
\langle r_{12}^\lambda \rangle_{TF} = Z^{-k} N^{3/2} \sum_{i=0}^{\infty} A_i(k) (N/Z)i.
\]

(10)

This expansion \( \langle r_{12}^\lambda \rangle_{TF} \) has been obtained earlier [7]. The values of \( A_i(k) \) at \( k = -2, -1, 1, 2 \) are given in table I. It follows from table I that for \( k = 1, 2 \) expansion (10) converges slowly. This restricts the applicability of (10) to small \( N/Z \). Let us consider the relationship between some moments of the one- and two-particle density. It can be seen that for \( k = 2m, m > 0 \) (6) may be simplified to:

\[
\langle r_{12}^\lambda \rangle = \frac{1}{4(m+1)} \sum_{n=0}^{m} \left(\frac{2n+1}{2m+2}\right) \langle r^{2(m-n)} \rangle \langle r^{2n} \rangle.
\]

(11)

where \( \langle r^n \rangle \) are the one-particle averages determined within the statistical model [5]:

\[
\langle r^n \rangle = Z \mu^a \int_0^{\infty} \rho(x) x^{n+1/2} \chi^{1/2}(x) \, dx.
\]

(12)

In particular, for \( m = 1, 2 \) we have

\[
\langle r_{12}^\lambda \rangle = \langle r^3 \rangle N,
\]

(13)

\[
\langle r_{12}^\lambda \rangle = \langle r^4 \rangle N + \frac{5}{3} \langle r^2 \rangle^2.
\]

(14)

The approximation of \( \chi_{TF}(x) \) [17] is used to calculate \( A(-2) \).

Expressions (11), (13) and (14) relate the expectation values \( \langle r_{12}^{2m} \rangle \) to \( \langle r^m \rangle \) for an atom with an arbitrary ionization degree. Bearing this in mind, it is possible to find the first coefficients \( A_i(k) \) in (10) for \( k = 2m \) through the expansion \( \langle r^{2m-n} \rangle \) and \( \langle r^{2n} \rangle \) from [5]. For a neutral atom and \( m > 2 \), expressions (11)-(14) are invalid since the appropriate integrals diverge. Nevertheless, these expressions may be effective if the modified TF model with no self-interaction, namely the Fermi-Amaldi model, is adopted.

For odd \( k \), we failed to find simple relations like (11) except for \( \langle r_{12} \rangle \) which may be expressed as (see appendix 1):

\[
\langle r_{12} \rangle = Z \langle r \rangle - \frac{1}{3} Z V_0 \langle r^2 \rangle - \frac{35}{12} N \langle k^2 \rangle
\]

(15)

where \( \langle k^2 \rangle \) is the mean squared azimuthal quantum number, \( \langle k^2 \rangle = \sum_i l(l+1) \), \( i \) stands for all occupied orbitals in the atom. Considering that, for a neutral atom in the TF model, \( V_0 = 0 \), we have from (15)

\[
\langle r_{12} \rangle = Z \left[ \langle r \rangle - \frac{35}{12} \langle k^2 \rangle \right].
\]

(16)

It is interesting to compare relations (11), (13)-(16) with those obtained with more exact quantum methods. In the Hartree model, the atomic wave function is equal to the product of the one-electron functions

\[
\psi(r_1, ..., r_n) = \psi_1(r_1) \psi_2(r_2), ..., \psi_N(r_n).
\]

Integrating the squared wave function over the \( (N-2) \) particle coordinates gives the two-particle density

\[
\rho_2(r_1, r_2) = \sum_i |\psi_i(r_1)|^2 |\psi_i(r_2)|^2 = \frac{1}{2} \left[ \rho(r_1) \rho(r_2) - \sum_i |\psi_i(r_1)|^2 |\psi_i(r_2)|^2 \right].
\]

(17)

The first term in the right hand side of (17) coincides with expression (3) while the second one is the self-interaction correction which cannot be exactly expressed through the electron density of an atom. However, for some expectation values, this correction may be easily obtained.

Table I. — Values of \( A(k) \) and \( A_i(k) \) (expressions (8) and (10)).

<table>
<thead>
<tr>
<th>( k )</th>
<th>(-2)</th>
<th>(-1)</th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>0.986015</td>
<td>0.484895</td>
<td>0.582663</td>
<td>1.28780</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>-0.601308</td>
<td>-0.207995</td>
<td>0.332247</td>
<td>1.41505</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>0.119206</td>
<td>-0.0083688</td>
<td>0.232843</td>
<td>1.29718</td>
</tr>
<tr>
<td>( A )</td>
<td>0.50964(*)</td>
<td>0.256248</td>
<td>2.42550</td>
<td>43.2403</td>
</tr>
</tbody>
</table>

(*) The approximation of \( \chi_{TF}(x) \) [17] is used to calculate \( A(-2) \).
Let us find the self-interaction correction for $\langle r_{12}^2 \rangle$. Since $\langle r_{12}^2 \rangle = \langle r_{1}^2 \rangle + \langle r_{2}^2 \rangle - 2 \langle r_{1} \cdot r_{2} \rangle$, it follows from (17) that in the Hartree method, $\langle r_{12}^2 \rangle$ is given as

$$\langle r_{12}^2 \rangle = (N-1) \langle r^2 \rangle. \quad (18)$$

The comparison of (13) and (18) shows that the allowance for the self-interaction reduces the right hand side of (13) by $(N-1)/N$. The same substitution into (11) yields the following modified relation

$$\langle r_{12}^{2n} \rangle = \frac{N-1}{4N(m+1)} \sum_{n=0}^{m} \left( \begin{array}{c} 2n+1 \\ 2m+2 \end{array} \right) \langle r^{2(m-n)} \rangle \langle r^{2n} \rangle \quad (19)$$

which may be used to obtain reliable estimates of the two-electron expectation values.

The expression (19) is exact (within the Hartree method) for the He isoelectronic series since the one-electron wave functions are equivalent in this case.


Equation (3) involves only the electrostatic electron interaction. To allow for the exchange interaction, the non-classical contribution due to the antisymmetry of the wave function must be eliminated. In the plane wave approximation, the exchange contribution to $\langle r_{12} k \rangle$ may be written [10] as

$$I(k) = \int_0^{\infty} (\sin y - y \cos y) y^{A-4} \, dy; \quad y = P_F(r) r_{12}.$$

The substitution of (21) into (23) gives an expression for a «two-particle» exchange correction as a function of the one-electron density

$$\langle r_{12}^{k+1} \rangle_{ex} = -\frac{3}{\pi} (3^{2-k}/k^3) I(k) \int r^{3-k} \rho(r) \, dr. \quad (25)$$

Expression (25) is valid as long as the integral $I(k)$ does not diverge. This is true for $-3 < k < 1$. This range includes three moments of the two-particle density $k = -2, -1, 0$. The values of $I(k)$ are equal to

$$I(-2) = \frac{\pi}{15}; \quad I(-1) = \frac{1}{4}; \quad I(0) = \frac{\pi}{6}.$$  

For the moments with $k \geq 1$, the domain $|r_1 - r_2| \geq P_F^{-1}(r_1)$ provides the main contribution to (22), and hence the approximation $P_F(r_1) \approx P_F(r_2)$ provides the main contribution to (22), and hence the approximation $P_F(r_1) \approx P_F(r_2)$ for these moments is not valid. The estimation of $\langle r_{12}^{k+1} \rangle_{ex}$ may only be made using (22).

The quantity $\langle r_{12}^{-1} \rangle_{ex}$

$$\langle r_{12}^{-1} \rangle_{ex} = -\frac{3}{4} \left( \frac{3}{\pi} \right) \int r^{6/3} \rho \, dr. \quad (26)$$
responsible for the exchange contribution to the inter-electron interaction was first obtained by Dirac [11]. As shown in [11], (26) also involves the electron self-interaction energy.

The exchange correction \( \langle r_{12}^0 \rangle_{\text{ex}}^{(2)} = - \frac{1}{2} \int \rho(r) d^3r \) involved into the zero moment results in the exact value of the normalization for the two-particle density \( N(N - 1)/2 \) (i.e. the error associated with the self-interaction in (3) is eliminated).

Now we estimate a relative contribution of the « two-particle » exchange correction. Substituting (4) into (25) and integrating over the angle variables give

\[
\langle r_{12}^k \rangle_{\text{ex}}^{(2)} = - \frac{3}{\pi} \left( \frac{3}{32} \right)^{k/3} I(k) Z^{-1-2k/3} \times \int_0^{x_0} \frac{3-2k}{2} \chi^2 \left( \frac{x}{x_0} \right) x^{1+2k} dx. \tag{27}
\]

The comparison with (8) shows that the order of magnitude of the exchange correction relative value for a neutral atom decreases with increasing \( k \) for \( -3 < k < 1 \)

\[
\langle r_{12}^0 \rangle_{\text{ex}}^{(2)} / \langle r_{12}^0 \rangle_{\text{TF}} \sim Z^{-1-k/3}.
\]

Expression (27) contains only a part of the exchange correction to \( \langle r_{12}^k \rangle_{\text{TF}} \). The other part is related to the one-electron density \( \rho(r) \) versus the exchange interaction. This correction is stipulated by the contraction of the electron cloud. It leads to increasing one-electron expectation values \( \langle r^a \rangle \) for \( a < 0 \), and to decreasing \( \langle r^a \rangle \) for \( a > 0 \) [5].

The numerical estimate of \( \langle r_{12}^k \rangle \) with the total exchange correction may be obtained from (3) and (25), the one-particle density being calculated involving exchange. For an analytical estimation, we represent \( \chi(x_1) \) and \( \chi(x_2) \) as a series expansion in the exchange parameter \( \beta = \frac{1}{3} (6\pi Z)^{-2/3} \) in (6) and (7). Confining to the first order in \( \beta \)

\[
\chi(x) = \chi_TF(x) + \beta \chi_{ex}(x),
\]

we have \( -3 < k < 1 \)

\[
\langle r_{12}^k \rangle_{\text{TF}} \approx Z^{-2-3k} \left( \frac{9\pi^2}{128} \right)^{k/3} \int_0^{x_0} \int_0^{x_0} dx_1 \int_0^{x_0} dx_2 \chi_TF(x_1) \chi_TF(x_2) \times \left\{ (x_1 + x_2)^{k+2} - |x_1 - x_2|^{k+2} \right\} + \]

\[
+ \frac{(6\pi)^{1/3}}{8\pi(k+2)} \left( \frac{9\pi^2}{128} \right)^{k/3} Z^{-3} \int_0^{x_0} dx_1 \int_0^{x_0} dx_2 \chi_TF(x_1) \chi_{ex}(x_2) \]

\[
\times \left\{ (x_1 + x_2)^{k+2} - |x_1 - x_2|^{k+2} \right\} = \langle r_{12}^k \rangle_{\text{TF}} + \langle r_{12}^k \rangle_{\text{ex}}^{(1)}, \quad k \neq -2; \tag{28}
\]

\[
\langle r_{12}^{-2} \rangle_{\text{ex}} = Z^{8/3} \left( \frac{16}{9\pi^2} \right)^{2/3} \int_0^{x_0} \int_0^{x_0} dx_1 \int_0^{x_0} dx_2 \chi_TF(x_1) \chi_TF(x_2) \ln \frac{x_1 + x_2}{x_1 - x_2} + \]

\[
+ \frac{4}{3\pi^2} Z^2 \int_0^{x_0} dx_1 \int_0^{x_0} dx_2 \chi_TF(x_1) \chi_{ex}(x_2) \ln \frac{x_1 + x_2}{x_1 - x_2} = \langle r_{12}^{-2} \rangle_{\text{TF}} + \langle r_{12}^{-2} \rangle_{\text{ex}}^{(1)}. \tag{29}
\]

From (28) and (29) it follows that the relative value of \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} \) is, within \( -3 < k < 1 \), of the order of \( Z^{-2-3k} \), irrespective of \( k \). We have integrated (28) and (29) using the universal functions \( \chi_TF(x) \) and \( \chi_{ex}(x) \) and established that \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} \) changes its sign : within \( -3 < k < 0 \) the « one-particle » exchange correction \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} \) is positive, for \( k = 0 \) \( \langle r_{12}^k \rangle_{\text{ex}}^{(2)} = 0 \), and for \( 0 < k < 1 \) \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} < 0 \). Comparing (28) and (29) with (27), one may conclude that, for a heavy atom and \( k < -1 \), the « two-particle » exchange correction is predominant while it is the « one-particle » correction \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} \) within \( 1 > k > -1 \). Hence, within \( 0 \geq k \geq -1 \), the exchange corrections cancel strongly each other (for a neutral atom), and fine estimates of \( \langle r_{12}^k \rangle \) may be obtained using the simple TF model. At \( k > 1 \), the value of the integrals is determined by the behaviour of \( \chi_TF(x) \) and \( \chi_{ex}(x) \) at \( x \approx x_0 \), which hampers the analytical estimation.

Now we give an explicit expression for the exchange correction for \( \langle r_{12}^k \rangle \) and \( \langle r_{12}^k \rangle_{\text{ex}}^{(1)} \). Substituting \( \chi_{ex}(x) \) [5] into (28) and performing necessary transformations (see appendix 2) we obtain

\[
\langle r_{12}^{-1} \rangle_{\text{ex}}^{(1)} = \frac{2}{\pi(6\pi)^{1/3}} Z^{5/3} \int_0^{x_0} \chi_TF(x) dx. \tag{30}
\]

As \( \langle r_{12}^{-1} \rangle_{\text{ex}}^{(2)} \) differs from (30) only by the numerical factor \( (-3/2) \), we find that the total exchange correction, \( \langle r_{12}^{-1} \rangle_{\text{ex}} \), is equal to

\[
\langle r_{12}^{-1} \rangle_{\text{ex}} = - \frac{1}{\pi(6\pi)^{1/3}} Z^{5/3} \int_0^{x_0} \chi_TF(x) dx =
\]

\[
= -7.3607 \times 10^{-2} Z^{5/3}. \tag{31}
\]

This result immediately follows from the combination.
of the virial and Hellman-Feynman theorems

\[ \langle r_{12}^{-1} \rangle = \left(2 - Z \frac{\partial}{\partial Z}\right) E(Z) \quad (32) \]

provided that, for a neutral atom within the TF model,

\[ \frac{\partial E}{\partial N} = 0, \]

i.e.

\[ \frac{\partial E}{\partial Z} = \frac{dE}{dZ} - \frac{\partial E}{\partial N} \frac{dN}{dZ} \simeq \frac{dE}{dZ}. \quad (33) \]

Applying (32) and (33) to \( E_{ex}(Z) \) and taking into account \( E_{ex} = 0.22082 Z^{11/3} \), we obtain

\[ \langle r_{12}^{-1} \rangle_{ex} = \frac{1}{3} E_{ex} = -7.3607 \times 10^{-2} Z^{5/3}. \quad (34) \]

For the highly ionized atom, \( \langle r_{12}^{-1} \rangle_{ex} \) as a function of \( N \) and \( Z \) can be easily found through \( E_{ex}(N, Z) \), using (32):

\[ \langle r_{12}^{-1} \rangle_{ex}(N, Z) = -0.354049 N^{2/3} Z + 0.130332 N^{5/3} + 0.00090702 N^{8/3} Z^{-1} + \cdots, \]

using (32):

\[ \langle r_{12}^{-1} \rangle_{ex}(N, Z) = -0.354049 N^{2/3} Z + 0.260665 N^{5/3} + 0.00027211 N^{8/3} Z^{-1} + \cdots. \quad (35) \]

Contrary to \( \langle r_{12}^{-1} \rangle \), exchange corrections for \( \langle r_{12}^{-2} \rangle \) (27) and (29) have different orders with respect to \( Z \): the « two-particle » exchange correction \( \langle r_{12}^{-2} \rangle_{ex}^{(2)} \)
scales as \( Z^{7/3} \), while \( \langle r_{12}^{-2} \rangle_{ex}^{(1)} \sim Z^{6/3} \). As follows from (25) and (27), the leading correction is

\[ \langle r_{12}^{-2} \rangle_{ex}^{(2)} = -\frac{8}{5} \left(\frac{2}{9 \pi^2}\right)^{1/3} Z^{7/3} \times \int_0^{\infty} \chi_{TF}(x) x^{-1/2} dx = \frac{2}{3} E_{TF} \quad (36) \]

where \( E_{TF} \) is the electron binding energy in the TF model. The total exchange correction for a neutral atom calculated by the universal functions \( \chi_{TF}(x) \) and \( \chi_{ex}(x) \) is given by

\[ \langle r_{12}^{-2} \rangle_{ex} = -0.51250 Z^{7/3} + 0.2385 Z^{6/3}. \quad (37) \]

For the ionized atom, using \( E_{TF}(N, Z) \) from (13), we obtain the leading correction

\[ \langle r_{12}^{-2} \rangle_{ex}^{(2)} = -0.76315 N^{1/3} Z^2 (1 - 0.423595 N/Z + 0.0908051 N/Z^2 + 0.0024369 N^3/Z^3 + \cdots). \quad (38) \]

Expressions (34), (35), (37) and (38) give the exchange corrections for the averages \( \langle r_{12}^{-1} \rangle \) and \( \langle r_{12}^{-2} \rangle \) as an explicit function of the electron number and nuclear charge.

4. Expectation values \( \langle \delta^3(r_{12}) \rangle \).

Consider the operator \( \delta^3(r_{12}) \) whose expectation value is required to calculate the relativistic and radiative corrections for the binding energy. The approximate value of \( \langle \delta^3(r_{12}) \rangle \) is found from

\[ \langle \delta^3(r_{12}) \rangle_{ex} = \int d^3 r \int d^3 r' \delta^3(r_{12}) \rho_1(r_1, r_2) \]

\[ \approx \frac{1}{2} \int d^3 r \int d^3 r' \rho(r_1) \rho(r_2) \delta^3(r_{12}) = \frac{1}{2} \int \rho^2(r) d^3 r. \quad (39) \]

Here the action of \( \delta^3(r_{12}) \) on the function \( f(r_2) \) is reduced to the \( r_2 \rightarrow r_1 \) substitution.

Within the plane wave approximation, the exchange interaction contribution due to the antisymmetry of the two-electron wave function may be easily calculated (similarly to equation (20))

\[ \langle \delta^3(r_{12}) \rangle_{ex} = -\int d^3 r \int d^3 r' \int_{0}^{P_{F}(r_1)} \frac{d^3 p}{(2 \pi)^3} \exp[-ip(r_1 - r_2)] \delta(r_1 - r_2) \times \]

\[ \times \int_{0}^{P_{F}(r_2)} \frac{d^3 p'}{(2 \pi)^3} \exp[-ip'(r_1 - r_2)] = -\frac{1}{36 \pi^4} \int P_F^6(r) d^3 r = -\frac{1}{4} \int \rho^2(r) d^3 r. \quad (40) \]

Thus, the exchange contribution involving the self-interaction correction decreases the total value of \( \langle \delta^3(r_{12}) \rangle \) by a factor of two:

\[ \langle \delta^3(r_{12}) \rangle = \langle \delta^3(r_{12}) \rangle_{TF} + \langle \delta^3(r_{12}) \rangle_{ex} = \frac{1}{4} \langle \rho(r) \rangle. \quad (41) \]

Expression (41) relates \( \langle \delta^3(r_{12}) \rangle \) to the expectation value of the one-particle operator \( \rho(r) \).

Let us show that this result may be obtained within the Hartree-Fock methods for a system of electrons with zero total spin in the ground state. Following the Fock idea [4], all electrons are divided into two groups with up and down spins, each group having \( N/2 \) electrons. The wave function of the system may be represented.
Here $\psi_k(i)$ are the orthonormalized one-electron functions of the $i$th electron in the $k$ quantum state.

Inserting (42) into (1) and considering that the terms corresponding to the different determinant coordinates are the only non-zero contributions to the sum, we have

$$\langle \delta^3(r_{12}) \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \int |\psi_i(r)|^2 |\psi_j(r)|^2 \, d^3r$$

$$= \frac{1}{4} \int \rho^2(r) \, d^3r = \frac{1}{4} \langle \rho(r) \rangle. \quad (43)$$

Within the HF method, expression (43) is exact for the total zero spin systems and must give a good estimate of the averages $\langle \delta^3(r_{12}) \rangle$ for non-zero spin atoms (in the ground state). $\langle \rho(r) \rangle$ cannot be estimated by the simple TF model since strongly bound electrons provide the leading contribution to this expectation value. A correct treatment of the strongly bound electron contribution to $\langle \rho \rangle$ using the Scott-Schwinger method [12,15] has been made in [6]. Using (43) and $\langle \rho \rangle$ from [6], which involves the exchange correction, we get for a neutral atom

$$\langle \delta^3(r_{12}) \rangle = \left[ \frac{1}{4} \langle \rho \rangle N - 0.029037 \right] Z^3 +$$

$$+ 0.029045 Z^{7/3}, \quad (44)$$

and for an ionized atom

$$\langle \delta^3(r_{12}) \rangle = \frac{1}{4} \langle \rho \rangle N Z^3 -$$

$$- (0.0428 N - 0.0438 N^{1/3}) Z^2$$

$$+ (0.0143 N^2 - 0.0174 N^{4/3}) Z + \cdots. \quad (45)$$

Here

$$\langle \rho \rangle N = \left[ \sum_{n,l} q_{nl} \psi_{nl}^2(r) \right] \, d^3r,$$

$\psi_{nl}$ stand for the hydrogen-like orbitals, and $q_{nl}$ are the occupation numbers.

We believe the accuracy of (44) and (45) is mainly determined by that of $\langle \rho \rangle$. It was shown [6], that the TF model allowing for the strongly bound electron contribution reproduced the HF values of $\langle \rho \rangle$ within some $\%$ for $N \geq 10$.

5. Discussion.

Let us use the results which follow from the statistical model in estimating the expectation values of $r_{12}^{-1}$ and $\delta^3(r_{12})$ for real atoms.

It should be quoted that the simple TF model (expressions (8) and (10)) yields exact asymptotic dependences (at $N \gg 1$) of $\langle r_{12}^{-1} \rangle$ on $N$ and $Z$. Taking into account (13) and using the one-electron expectation values [5], we state that the asymptotic relation, $\langle r_{12}^{-1} \rangle \cong Z^{5/3} - 0.029045 Z^{7/3}$, holds only for $Z$ far beyond the periodic table. By analogy with the TF description of $\langle r^{-1} \rangle$, expression (8) can be expected to give a good estimate of $\langle r_{12}^{-1} \rangle$ for a neutral atom. This is confirmed by the comparison with the numerical HF data [16]. Indeed, the error provided by (8) rapidly decreases with increasing $Z$, and for $Z \geq 24$ it does not exceed $6 \%$ (Fig. 1). We assume (8) and (10) to give a rough estimate of $\langle r_{12}^{-1} \rangle$ and $\langle r_{12}^3 \rangle$ for heavy many-electron atoms. Comparison with the only data available for the He isoelectronic series [3,8] shows that (10) points out to systematic trends for the expectation values to vary with $Z$-even for a system with such a small number of electrons.

Let us investigate how the inclusion of the exchange interaction affects the estimate of $\langle r_{12}^{-1} \rangle$. Combining (8) and (31) yields for a neutral atom

$$\langle r_{12}^{-1} \rangle = \langle r_{12}^{-1} \rangle_{\text{TF}} + \langle r_{12}^{-1} \rangle_{\text{ex}} =$$

$$= 0.256248 Z^{7/3} - 0.073607 Z^{5/3}. \quad (46)$$

Equation (46) reproduces the HF data [16] with an error less than $3 \%$ for all $Z \geq 38$, the deviation being highly oscillating (Fig. 1). From the earlier obtained expression for the oscillation correction to the binding energy [13]

$$E_{\text{osc}}(Z) = Z^{4/3} F(0.92 Z^{1/3})$$

and relation (32) it follows that the oscillation contri-
The first two terms of (48) are asymptotically exact, the third is not because the strongly bound electron contribution and the inhomogeneity of the electron density missed here are also of relative order $Z^{-2/3}$. Using (48) improves the estimate of $\langle r_{12}^{-2} \rangle$ even for the He atom (Table III).

Consider $\langle r_{12}^{+} \rangle$ for an atom with an arbitrary ionization degree. It is easily seen that (10), (35) and (38) have the form of a $Z^{-1}$ expansion [2]:

$$\langle r_{12}^{+} \rangle = Z^{-k} \sum_{i=0}^{\infty} B_i(N, k) Z^{-i}.$$  

(49)

The dependence of the leading term on $Z$ exactly coincides with the quantum one based on the scaling [3]. The $N$ dependence was not studied earlier even for the leading coefficient. This is due to the mathematical difficulties associated with multi-dimensional integral calculations which hamper even numerical estimates.

Table II. — Expectation values $Z^k \langle r_{12}^k \rangle$ for two-electron atoms (expressions (8) and (10)).

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$k = -2$</th>
<th>$k = -1$</th>
<th>$k = 1$</th>
<th>$k = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.809 (0.4605)</td>
<td>0.646 (0.5129)</td>
<td>7.42 (2.724)</td>
<td>436 (9.48)</td>
</tr>
<tr>
<td>10</td>
<td>1.382 (0.6225)</td>
<td>1.12 (0.6028)</td>
<td>4.18 (2.276)</td>
<td>16.36 (6.51)</td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.565 (0.6667)</td>
<td>1.22 (0.6250)</td>
<td>3.70 (2.188)</td>
<td>12.98 (6.00)</td>
</tr>
</tbody>
</table>

The HF data [8] are given in brackets.
Table III. — Expectation values of two-electron operators for the He isoelectronic series with allowance for the exchange (expressions (46), (48), (53), (44) and (45)).

<table>
<thead>
<tr>
<th>Z</th>
<th>$Z^{-2} \langle r_{12}^2 \rangle$</th>
<th>$Z^{-1} \langle r_{12}^1 \rangle$</th>
<th>$Z^{-3} \langle \delta^3(r_{12}) \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.472 (0.4605)</td>
<td>0.5289 (0.5129)</td>
<td>0.0290 (0.0235)</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.6037 (0.6667)</td>
<td>0.6598 (0.6250)</td>
<td>0.03979 (0.03979)</td>
</tr>
</tbody>
</table>

The HF data are given in brackets: *from reference [8]; bfrom reference [19].

The accuracy may be appreciably improved by the Padé-approximants. For example, using the neutral atom value of $\langle r_{12}^{-1} \rangle$ as a reference point, we obtain the [1, 3] Padé-approximant

$$\langle r_{12}^{-1} \rangle_{TF} = 0.484895 N^{4/3} Z - 0.207995 N^{7/3} - \frac{8.3688 \times 10^{-3} N^{10/3}}{Z - 0.59477 N}$$

(51)

which reproduces the exact TF values within 0.5%.

Equation (51) yields reliable semi-quantitative estimates of $\langle r_{12}^{-1} \rangle$ for isoelectronic series as compared to the HF data. The accuracy of (51) decreases as the ionization degree increases. Typical results for Ar and Se isoelectronic series are presented in figure 3.

The inclusion of the exchange correction improves the estimate of $\langle r_{12}^{-1} \rangle$. It should be quoted that, unlike the one-electron expectation values, the exchange contribution changes even the leading coefficients of the $Z^{-1}$ expansion (49). This is due to the «two-particle» exchange correction $\langle r_{12}^{1} \rangle^{(2)}$. Combining (10) and (23) and substituting the $N/Z$ expansion of $\langle p^{-k} \rangle$ from [6] we get

$$B_0(k, N) = A_0(k) N^{2/3} k^{+2} + A_{02}^m(k) N^{1+k/3} - 2 \leq k < 1$$

(52)

where

$$A_{02}^m(k) = -4(3-k) \left(\frac{3}{2}\right)^{k/3} \times I(k) \Gamma\left(\frac{3-k}{2}\right) \Gamma\left(\frac{3+k}{2}\right).$$

In particular

$$B_0(-1, N) = 0.484895 N^{4/3} - 0.354049 N^{2/3}$$

$$B_0(-2, N) = 0.986034 N^{2/3} - 0.76315 N^{1/3}.$$
Following the trends of $\langle r_{12}^4 \rangle_{\text{ex}}^{(2)}$ variation with increasing $k$, it may be seen that its relative contribution falls off. We assume, therefore, that this correction may be neglected as compared to the « one-particle » exchange correction $\langle r_{12}^4 \rangle_{\text{ex}}^{(1)}$. The latter is allowed for in (19) when using the HF one-electron averages.

Now we discuss the expectation values of $\delta^3(r_{12})$. As follows from (39) and (49), the simple TF model, with correct treatment of the strongly bound electron contribution, gives an exact asymptotic $Z$ dependence of $\langle \delta^3(r_{12}) \rangle$ but overestimates the numerical values by a factor of two as compared with the HF data. This effect may be eliminated by taking into account the exchange and self-interaction. Analytical expression (44) containing the exchange term allows to give an approximate estimate of the HF values of $\langle \delta^3(r_{12}) \rangle$, even for the He atom (Table III).

For ionized atoms, the accuracy of the analytical estimate (45) must increase with the ionization degree since (45) is exact for a high ionization limit.

Let us consider the structure of the $Z^{-1}$ expansion coefficients of $\langle \delta^3(r_{12}) \rangle$

$$\langle \delta^3(r_{12}) \rangle = Z^3 \sum_{i=0}^{\infty} D_i(N) Z^{-i}. \quad (54)$$

The leading coefficient, $D_0 = \frac{1}{4} \langle \rho \rangle \gamma_0(N)$, includes a logarithmic dependence on $N$ and has the asymptotic structure (at $N \gg 1$):

$$D_0(N) = d_0 \ln N + d_1. \quad (55)$$

The form of the subsequent coefficient is

$$D_i(N) = a_i N^{i_1} + b_i N^{i-2/3} \quad (56)$$

where $a_i$ and $b_i$ are equal to $1/4$ of the $Z^{-1}$ expansion coefficients of $\langle \rho \rangle^2$ [5]. In particular

$$a_1 = -0.0428, \quad b_1 = 0.0438,$$

$$a_2 = 0.0143, \quad b_2 = -0.0174.$$  

Note that the ratio $D_2(N)/(N \cdot D_1(N))$ rapidly reaches its asymptotic value ($-0.33$). This fact may be used to approximately estimate $D_2(N) \approx -0.33 \cdot N D_1(N)$ for the many-electron atom ($N \gg 10$).

It is of interest to relate $\langle \delta^3(r_{12}) \rangle$ to the experimentally measured quantity, namely, the averaged intensity, $I(q)$, of the elastic X-ray scattered by an atom. To this end, we use the relationship between $I(q)$ and $\langle \rho \rangle$ from [20]:

$$\langle \rho \rangle = \frac{1}{Z^2} \int_0^{\infty} q^2 I(q) \, dq. \quad (57)$$

Substituting (57) into (41) we get

$$\langle \delta^3(r_{12}) \rangle = \frac{1}{8 \pi^2} \int_0^{\infty} q^2 F^2(q) \, dq. \quad (58)$$

Here $q$ stands for the magnitude of momentum transfer, $I(q)$ is related to the atomic form-factor, $F(q)$, by $I(q) = F^2(q)$. The precision of (58) is completely determined by that of (41), which is exact for the non-zero spin atom within the HF model. The contribution of the correlation effects may essentially change (58), especially for neutral atoms. To examine (58), we compare (Fig. 4) the values of $\langle \delta^3(r_{12}) \rangle$ [21] obtained using accurate correlated wave functions with those of (58), the integrals in the right hand side of (58) being calculated by means of $F(q)$ [1] obtained from just the same wave functions. The comparison shows that, for He isoelectronic sequence, the accuracy of (58) is fast increased with the ionization degree. We believe (58) to give a good estimate of $\langle \delta^3(r_{12}) \rangle$ for highly ionized atoms and semi-quantitative one for neutral many-electron atoms.

### 6. Conclusion.

We have adopted the TF model allowing for the exchange interaction to consider the expectation values $\langle r_{12}^4 \rangle$ and $\langle \delta^3(r_{12}) \rangle$ for atoms. Moreover, when estimating $\langle \delta^3(r_{12}) \rangle$, the strongly bound electron contribution has been taken into account. Especially, we have paid attention to the derivation of analytical dependences of the expectation values on the natural atomic parameters, namely, the nuclear charge $Z$ and number of electrons $N$.

Two significant effects remain beyond our consideration, namely, quantum oscillation and inhomogeneity of the electron density. As previously shown [5], if the latter is a small part of the exchange contribution, the oscillation effects may prove to be very important. We have found the oscillation amplitude of $\langle r_{12}^4 \rangle$ to be of the same relative order, $Z^{-2/3}$, as the exchange

![Fig. 4. $\langle \delta^3(r_{12}) \rangle/\delta_0$ as a function of $Z$ for He isoelectronic series; $\delta_0 = (8 \pi^2)^{-1} \int_0^{\infty} F^2(q) \, dq$. ——, HF data; ---, correlated data.](image-url)
correction. We assume that, for the expectation values with positive exponents \( k > 2 \), which are determined by the periphery of an atom, quantum oscillations play more appreciable role as for one-electron averages \( \langle r^2 \rangle \) at \( a > 2 \) [5]. The analytical estimation of the oscillation contribution requires another technique, different from the TF model. A part of such a contribution to averages \( \langle r_{12}^2 \rangle \) may be taken into account by using (19) which relates the expectation values of one- and two-electron operators.

**Appendix I.** — Let us derive the expression for \( \langle r_{12} \rangle \) in terms of the expectation values of one-particle operators. From (6) we have

\[
\langle r_{12} \rangle = \frac{1}{2} Z^2 \mu \left\{ \int_0^{\infty} \chi^{3/2}(x) x^{3/2} \left[ \int_0^{\infty} y^{1/2} \chi^{1/2}(y) dy \right] dx + \int_0^{\infty} \chi^{3/2}(x) x^{1/2} \left[ \int_x^{\infty} y^{3/2} \chi^{1/2}(y) dy \right] dx \right. \\
- \frac{1}{3} \int_0^{\infty} \chi^{3/2}(x) x^{-1/2} \left[ \int_0^{\infty} y^{5/2} \chi^{1/2}(y) dy \right] dx - \frac{1}{3} \int_0^{\infty} \chi^{3/2}(x) x^{5/2} \left[ \int_x^{\infty} \chi^{1/2}(y) y^{1/2} dy \right] dx \right\}
\]

\[
= \frac{1}{2} Z^2 \mu \left( i_1 + i_2 - \frac{1}{3} i_3 - \frac{1}{3} i_4 \right) . 
\]  

(A.1)

Using TF equation (5) we transform \( i_1 \) and \( i_4 \) as:

\[
i_1 = \int_0^{\infty} \chi^{3/2}(x) x^{3/2} \left[ \int_0^{\infty} y \chi'(y) dy \right] dx = \int_0^{\infty} \chi^{3/2}(x) x^{3/2} [x \chi'(x) - \chi(x) + 1] \\
= \int_0^{\infty} \chi^{3/2}(x) x^{3/2} dx - 2 \int_0^{\infty} \chi^{5/2}(x) x^{3/2} dx
\]  

(A.2)

\[
i_4 = \int_0^{\infty} \chi^{3/2}(x) x^{5/2} \left[ \int_x^{\infty} \chi'(y) dy \right] dx = - \frac{q}{x_0} \int_0^{\infty} \chi^{3/2}(x) x^{5/2} dx - \int_0^{\infty} \chi^{3/2}(x) \chi'(x) x^{5/2} dx \\
= - \frac{q}{x_0} \int_0^{\infty} \chi^{3/2}(x) x^{5/2} dx + \int_0^{\infty} \chi^{5/2}(x) x^{3/2} dx
\]  

(A.3)

\( i_2 \) and \( i_3 \) are integrated by parts

\[
i_2 = \int_0^{\infty} \chi''(x) x \left[ \int_0^{\infty} \chi^{3/2}(y) y^{3/2} dy \right] dx = (x \chi'(x) - \chi(x)) \left[ \int_0^{\infty} \chi^{3/2}(y) y^{3/2} dy \right] + \\
+ \int_0^{\infty} [\chi^{3/2}(x) \chi'(x) x^{5/2} - \chi^{5/2}(x) x^{3/2}] dx = i_1 , 
\]  

(A.4)

\[
i_3 = \int_0^{\infty} \chi''(x) dx \int_0^{\infty} \chi^{3/2}(y) y^{5/2} dy = \chi'(x) \left[ \int_0^{\infty} \chi^{3/2}(y) y^{5/2} dy \right] \bigg|_0^{\infty} - \int_0^{\infty} \chi^{3/2}(x) \chi'(x) x^{5/2} dx = i_4 . 
\]  

(A.5)

When deriving (A.2)-(A.5), we used the boundary conditions of the TF equation

\[
\chi(0) = 1 , \quad \chi(x_0) = 0 , \quad x_0 \chi'(x_0) = -1 + \frac{N}{Z} = -q .
\]

Summing up (A.2)-(A.5), from (A.1) we find

\[
\langle r_{12} \rangle = Z^2 \mu \left( \int_0^{\infty} \chi^{3/2}(x) x^{3/2} dx + \frac{q}{3x_0} \int_0^{\infty} \chi^{3/2}(x) x^{5/2} dx - \frac{7}{3} \int_0^{\infty} \chi^{5/2}(x) x^{3/2} dx \right)
\]

which, allowing for (12), the relationship between the boundary radii and chemical potential

\[
V_0 = -q/x_0
\]
and the statistical expression [18]

\[ \langle k^2 \rangle = \frac{4}{5} \frac{Z^2 \mu^2}{N} \int_0^\infty \chi^{5/2}(x) x^{3/2} \, dx \]

results in equation (15).

**Appendix 2.** — To calculate \( r^{-1/2} \chi_{et}^{(1)} \) for a neutral atom, it is necessary to calculate the integral

\[ L = 2 \int_0^\infty dx_1 \chi_{TF}(x_1) \left[ \int_0^{x_1} \chi_{et}^{''}(x_2) x_2 \, dx_2 + x_1 \int_{x_1}^\infty \chi_{et}^{''}(x_2) \, dx_2 \right]. \quad (A.6) \]

Integrating the expression in parenthesis by parts two times, we transform (A.6) to get

\[ L = 2 \int_0^\infty dx_1 \chi_{TF}(x_1) \left[ x_1 \chi_{et}^{''}(\infty) - \chi_{et}(x_1) \right]. \quad (A.7) \]

The dimensionless potential, \( \chi_{et}(x) \), is found from the equation [14]

\[ \chi_{et}^{''}(x) = \frac{3}{2} \chi_{TF}^{1/2}(x) x^{-1/2} \chi_{et}(x) + 3 \chi_{TF}(x) \quad (A.8) \]

with the boundary conditions

\[ \chi_{et}(0) = 0, \quad \chi_{et}(\infty) = 0, \quad \chi_{et}^{'}(\infty) = 0. \quad (A.9) \]

Integrating (A.7) by parts and using (A.8) and (A.9) yield

\[
L = -2 \int_0^\infty \chi_{TF}^{''}(x) \chi_{et}(x) \, dx = -2 \chi_{TF}^{'}(x) \chi_{et}(x) \bigg|_0^\infty + 2 \chi_{TF}(x) \chi_{et}^{'}(x) \bigg|_0^\infty - 2 \int_0^\infty \chi_{TF}(x) \chi_{et}^{''}(x) \, dx
\]

\[ = -2 \chi_{et}^{'}(0) - 3 \int_0^\infty \chi_{TF}^{3/2}(x) x^{-1/2} \chi_{et}(x) \, dx - 6 \int_0^\infty \chi_{TF}^2(x) \, dx. \quad (A.10) \]

Substituting the TF equation into the second integral of the right hand side of (A.10) gives

\[ L = 4 \chi_{et}^{'}(0) + 12 \int_0^\infty \chi_{TF}^2(x) \, dx. \quad (A.11) \]

Considering that [14]

\[ \chi_{et}^{'}(0) = -\frac{5}{2} \int \chi_{TF}^2(x) \, dx \]

we have finally

\[ L = 2 \int_0^\infty \chi_{TF}^2(x) \, dx. \]
References