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Submitted on 1 Jan 1984

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The improved Thomas-Fermi model: chemical and ionization potentials in atoms

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(Reçu le 7 juin 1983, accepté le 5 septembre 1983)

Abstract. — Analytical expressions for non-relativistic values of the chemical $\mu(N, Z)$ and ionization $I(N, Z)$ potentials are derived from the TF model including corrections for the exchange and inhomogeneity of electron density. These expressions reproduce well the smoothed ionization potential of an atom. It is shown that $I(N, Z)$ and $\mu(N, Z)$ in a weak ionization limit are determined mainly by quantum contributions due to the exchange and correlation and may be written as $A + B (Z - N)$. The relationship between $\mu$ and $I$ for atoms with a small ionization degree, $m = Z - N$, is found

$$\mu_{m+1} \approx - (2m+1)(2m+2)^{-1} I_{m+1}$$

which should be valid for atoms with s- and p-valence electrons. It is proved that the simple TF model gives an asymptotically exact value $I(N, Z)$ within $N/Z \to 0$ and the oscillation correction has a relative order $N^{-1/3}$.

1. Introduction.

Chemical and ionization potentials are important characteristics of an atom. The ionization potential $I$ of an atom with $N$ electrons and nucleus charge $Z$ is uniquely defined both in theory and in experiment. Determination of the chemical potential $\mu = \partial E/\partial N$ for isolated microscopic quantum systems (such as an atom or a molecule) is difficult since there is no exact continuous energy function $E(N)$. Recently, an interest to $\mu$ has increased essentially [1-4, 25-27] due to establishment of relationship between chemical potential and electronegativity [1].

As a tool for such investigation the Thomas-Fermi (TF) model including quantum corrections is used. This model has enabled us to obtain an accurate analytical expression for the non-relativistic atomic binding energy $E(N, Z)$ [5]. We shall demonstrate that this model is able to give asymptotic estimates even of such oscillating quantities as $I(N, Z)$ and $\mu(N, Z)$.

2. Basic equations.

In a simple TF model, the potential of a self-consistent atomic field is written as [6]

$$V(r) = - \frac{Z}{r} \psi(x) + \mu_{TF}$$

(1)
where \( \psi(x) \) is the screening function solution of the TF equation

\[
\psi''(x) = \psi^{3/2}(x) \cdot x^{-1/2}
\]

(2)

\[
\psi(x_0) = 0; \quad x_0 \psi'(x_0) = -1 + \frac{N}{Z}; \quad \psi(0) = 1;
\]

(3)

\( x \) is the dimensionless coordinate defined by the expression

\[
x = (9 \pi^2)^{-1/3} (128 \, Z)^{1/3} \cdot r.
\]

The quantity \( \mu_{TF} \) in (1) is the chemical potential in the TF model

\[
\mu_{TF} = V(r_0) = -\frac{Z - N}{r_0} = -\frac{(128 \, Z)^{1/3}}{9 \pi^2} \left( 1 - \frac{N}{Z} \right),
\]

(4)

\( x_0 \) is the boundary radius beyond which the electron density is zero. For a neutral atom \( \mu_{TF} = 0 \) since \( 1 - \frac{N}{Z} = 0 \) and \( x_0 \to \infty \). Here and below atomic units are used.

As is seen from (2) and (3) the solution of the TF equation and \( x_0 \) value are fully determined by the ratio \( N/Z \). It follows from (4) that \( \mu_{TF} \) (as well as other atomic properties in the TF model) can be presented in universal form

\[
\mu_{TF} \approx -0.110 \, 3(Z - N)^{4/3} \left[ 1 + 0.910 \, 2 \left( 1 - \frac{N}{Z} \right)^{2/3} + 0.824 \, 6 \left( 1 - \frac{N}{Z} \right)^{2/3} + \ldots \right].
\]

(8)

Here \( \sigma = (\sqrt{73} - 7)/2 \).

Recently [3], the first r.h.s. term of (8) has been obtained by using the same procedure but with a slightly different value of the quadratic term. The difference is due to the use [3] of only the first-order correction to the screening function of a neutral atom (see Appendix).

Equation 8 reproduces well the numerical values of \( \mu_{TF} \) [7] (the error being less than 2\%) only at small values of \( 1 - N/Z \leq 0.01 \) due to slow convergence of series (8). To illustrate this we should say that the use of the first term of (8) alone gives an error of 30\% even at \( 1 - N/Z = 0.01 \).

In order to obtain a good analytical estimate of \( \mu_{TF}(N, Z) \) in the entire range of \( 0 \leq N/Z \leq 1 \), we rearrange series (8) and (7). First of all, note that the expansion coefficients in (8) are very close to the coefficients of geometric progression. Bearing this in mind we write \( \mu_{TF} \) for \( N/Z \to 1 \) in the form

\[
\mu_{TF} \left( 0.88 \leq \frac{N}{Z} \leq 1 \right) \approx -0.110 \, 3(Z - N)^{4/3} \left[ 1 - 0.910 \, 2 \left( 1 - \frac{N}{Z} \right)^{2/3} \right]^{-1}.
\]

(9)

Introduction of this simple geometric approximation drastically improves the estimates (see Table I).

Then, we rearrange series (7) using the weak ionization limit

\[
\mu_{TF} = -18^{-1/3}(Z - N)^{4/3} \left\{ 1 - 0.361 \, 05 \frac{N}{Z} - 0.067 \, 67 \frac{N^2}{Z^2} - 0.035 \frac{N^3}{Z^3} + \ldots \right\}.
\]

(10)

One can see that summation (10) for \( N/Z = 1 \) does not give the correct value of the coefficient \(-0.110 \, 3\) of \( (Z - N)^{4/3} \). This results in essential inaccuracy of (10) for \( N/Z \approx 0.8 \). The error can be eliminated by using the
<table>
<thead>
<tr>
<th>N/Z</th>
<th>0.416 46 (*)</th>
<th>0.550 28 (*)</th>
<th>0.643 36 (*)</th>
<th>0.728 79 (*)</th>
<th>0.878 74 (*)</th>
<th>0.936 35 (*)</th>
<th>0.990 25 (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−μₜ₅ [11, 9]</td>
<td>0.278 34</td>
<td>0.150 95</td>
<td>0.093 49</td>
<td>0.055 55</td>
<td>0.014 05</td>
<td>5.079 × 10⁻³</td>
<td>3.173 × 10⁻⁴</td>
</tr>
<tr>
<td>−μₜ₅ [8, 7]</td>
<td>0.278 39</td>
<td>0.151 04</td>
<td>0.093 61</td>
<td>0.055 66</td>
<td>0.014 04</td>
<td>5.074 × 10⁻³</td>
<td>3.176 × 10⁻⁴</td>
</tr>
</tbody>
</table>

(*) μₜ₅ Z⁻⁴/₃, found from (11) are compared with μₜ₅ Z⁻⁴/₃ from [8].
(⁎) μₜ₅ Z⁻⁴/₃ derived from (9) are compared with μₜ₅ Z⁻⁴/₃ from [7].

[1, 3] Padé approximant of series (10)

\[ \mu_{TF} = -18^{-1/3}(Z - N)^{4/3} \left( \frac{Z}{N} \right)^{2/3} \left[ 1 - 0.361 05 \frac{N}{Z} - 0.067 67 \frac{N^2}{Z^2} - \frac{0.035 N^3}{Z^2 (Z - 0.738 8 N)} \right]. \] (11)

The coefficient in the denominator is chosen from the condition of matching (11) and (9) for N/Z = 0.88. Comparison shows that analytical approximations (9) and (11) perfectly reproduce the accurate values of μ for an atom with an arbitrary degree of ionization (Table I).

Consider quantum contributions to μ due to the exchange interaction and the inhomogeneity of electron density. As has been shown earlier [11], when taking into account the exchange interaction in the first order with respect to \( \beta = \frac{3}{2}(6 \pi Z)^{-2/3} \), the ion binding energy, as well as many other atomic properties, can be written as

\[ E = E_{TF} + E_{ex}. \] (12)

The exchange contribution, \( E_{ex} \), is written as [11]

\[ E_{ex} = -\frac{4}{\pi^2} \sqrt{3} N^{2/3} Z \sum_{k=0}^{\infty} \beta_k \left( \frac{N}{Z} \right)^k. \] (13)

When evaluating the chemical potential of an ion, we obtain the expression for μ with regard to the exchange

\[ μ = μ_{TF} + μ_{ex}, \] (14)

where \( μ_{TF} \) is determined by (7) and

\[ μ_{ex} = \frac{\partial E_{ex}}{\partial N} = -\frac{8}{3 \pi^2} \sqrt{3} N^{-1/3} Z \left( 1 - 0.920 3 \frac{N}{Z} - 0.010 2 \frac{N^2}{Z^2} + \cdots \right). \] (15)

We have failed to evaluate the accuracy of (15) for all N/Z because no data on \( μ_{ex} \) are available. Comparing the ratios of expansion coefficients (15) and (7) we may conclude that (15), like (7), gives sufficiently accurate \( μ_{ex} \) values for highly ionized atoms. The error should increase with N/Z. For more precise determination of \( μ_{ex} \) for N/Z > 0.5 we rearranged series (16) taking into account the behaviour of \( μ_{ex} \) for a weakly ionized atom. For this purpose we used the relation between μ and \( r_0 \) within the TF model with regard to the exchange [12]

\[ μ = -\frac{Z - N}{r_0} - \frac{1}{2 \pi^2}. \] (16)

It has been shown earlier [13] that the boundary radius, \( r_0 \), of a heavy ion with regard to the exchange in the first order in \( \beta \) may be presented as

\[ r_0(m, z) = a_0(m) \left( 1 + a_1(m) Z^{-4/3} + \cdots \right). \] (17)

Here, the \( a_i(m) \) are complex functions of \( m = Z - N \) which are determined from the hierarchy of algebraic equations obtained from the boundary conditions at \( r = r_0 \). Most important for studying an asymptotic form is the equation for \( a_0(m) \)

\[ 16 ma_0^2(m) + 81(5 + \sigma)a_0^2(m) - 162 \pi^2 (7 + \sigma) = 0. \] (18)

The solution of (18) for small \( m \) may be written as an expansion in \( m \), for large \( m \), in \( m^{-2/3} \). Taking into account that (16) includes \( r_0^{-1} \), it is convenient to obtain \( a_0^1(m) \) expansions in \( m^{-2/3} \) and \( m \)

\[ a_0^1(m) = \frac{2}{3 \pi} \left[ \frac{\pi}{3(7 + \sigma)} \right]^{1/3} m^{1/3} + \frac{5 + \sigma}{4 \pi} \left[ \frac{3}{(7 + \sigma)^2 \pi} \right]^{2/3} m^{-1/3} + \cdots \] (19a)
Comparison of \( a_0^{-1}(m) \) from (19a) and (19b) with the numerical solutions of (18) shows that (19a) reproduces accurate values within an error \(< 3\% \) at \( m > 2 \), while (19b), at \( m \leq 2 \).

Combining (19a, b), (16) and (17) yields

\[
\mu(m, Z) = -\left\{ \frac{2}{3 \pi} \left[ \frac{\pi}{3(7 + \sigma)} \right]^{1/3} m^{4/3} + \frac{5 + \sigma}{4 \pi} \left[ \frac{3}{\pi(7 + \sigma)^2} \right]^{1/3} m^{2/3} + \ldots \right\} \times (1 - a_1(m) Z^{-\sigma/3} + \ldots) - \frac{\pi^2}{2}, \quad (m > 2). \tag{20}
\]

\[
\mu(m, Z) = -\frac{1}{2 \pi^2} \left[ \frac{3 - \sigma}{6} \right]^{1/2} m + \frac{8 m^2}{81(5 + \sigma)} + \ldots \times (1 - a_1(m) Z^{-\sigma/3} + \ldots), \quad (m \leq 2). \tag{21}
\]

Equations 20 and 21 give \( \mu(m, Z) \) for a weakly ionized heavy atom with regard to the exchange.

One can easily see that expression 20 has the form of partition (14). The first term in (20) is \( \mu_{TF} \) for a heavy atom when only the first order in the ionization is taken into account (see Appendix), the second one is the main part of \( \mu_{ex} \) at \( N/Z \sim 1 \)

\[
\mu_{ex}(N, Z) \approx -\frac{5 + \sigma}{4 \pi} \left[ \frac{3}{\pi(7 + \sigma)^2} \right]^{1/3} (Z - N)^{2/3} \left( 1 - 0.068 23 N^2 \frac{N}{Z(Z - 0.735 5 N)} \right). \tag{20a}
\]

We suppose that corrections of higher orders in the ionization do not change essentially the coefficient in (20a), like asymptotic form for \( \mu_{TF} \) (8).

The chemical potential of a neutral atom and single (double)-charged ions (21) cannot be written in the form of equation 14, since the exchange contribution is not a small correction. Comparison of (9) and (21) shows that the exchange interaction leads to a change in a limiting form of \( \mu(N/Z \rightarrow 1) \).

Expression 20a enables us to rearrange series (15) by taking outside the dependence \( (Z - N)^{2/3} \). Using the [1, 2] Padé-approximants of the rearranged series we arrive at

\[
\mu_{ex}(N, Z) \approx -\frac{8}{3 \pi^2} \left( \frac{2}{3} \right)^{1/3} (Z - N)^{2/3} \left( 1 - 0.253 6 \frac{N}{Z} - \frac{0.068 23 N^2}{Z(Z - 0.735 5 N)} \right). \tag{22}
\]

The coefficient in the denominator is chosen from the coupling condition of (20a) and (22).

Let us now discuss the contribution to \( \mu \) due to the effect of the electron density inhomogeneity. The correction to the binding energy due to this effect coincides fully in its form with (13) differing only in the factor 2/9 [5]. Bearing this in mind we write

\[
\mu = \mu_{TF} + \mu_{q}, \tag{23}
\]

where

\[
\mu_{q} = \frac{11}{5} \mu_{ex}. \]

Expressions 14 or 23 where \( \mu_{TF} \) and \( \mu_{ex} \) are determined from (11) and (22) permit evaluation of \( \mu \) in a wide range of \( N/Z \left( 0 \leq N/Z < 1 - \frac{2}{Z} \right) \).

The weak ionization limit, \( Z - 2 \leq N \leq Z \), with allowance for inhomogeneity preserves the form of (21) with changed coefficients whose accurate values cannot be obtained because of the absence of a generally accepted scheme for taking into account the inhomogeneity at the boundary of a weakly ionized atom. However, it is known that the effect of the inhomogeneity leads to a slight (as compared to the allowance for the exchange alone) decrease in \( r_0 \) and to a small increase in \( |\mu| \).

Let us consider the linkage of \( \mu \) with the ionization potential

\[
I(N, Z) = -\int_{N-1}^{N} \mu(y, z) \, dy = E(N-1, Z) - E(N, Z). \tag{24}
\]

The Taylor expansion of the second part of equality 24 at a point \( N - 1/2 \) yields an approximate relation

\[
I(N, Z) \approx -\frac{\delta E}{\delta N} \left. \right|_{N-1/2} - \frac{1}{24} \frac{\delta^3 E}{\delta N^3} \left. \right|_{N-1/2} + \ldots
\]

which allows

\[
I(N, Z) \approx -\mu(N - 1/2, Z). \tag{25}
\]

Relation 25 is obtained from the condition of a continuous dependence \( \mu(N) \) which is always fulfilled within the TF model. Making use of all the expressions for \( \mu \) we can easily evaluate \( I \).
3. Results and discussion.

Now we show that the obtained functions $\mu(N, Z)$ and $I(N, Z)$ allow a number of important conclusions for real atomic systems.

First of all it follows from the TF model that the ionization $I_{m+1}(Z)$ and chemical $\mu_{m+1}(Z)$ potentials of a heavy weakly ionized atom decrease with increasing $Z$ and tend to a finite value depending on the multiplicity $m = Z - N$. This conclusion is valid both with [10] and without introducing the exchange [13].

In the simple TF model (8) and (24) yield

$$I_{m+1}^{\text{TF}}(Z) = 0.047 \left( [m + 1]^{7/3} - m^{7/3} \right) + 0.038 Z^{-\sigma Z} \left[ [m + 1]^{7/3} - m^{7/3} \right] + \cdots$$  \hspace{2cm} (26)

From (8) and (26) we obtain the limiting form of $I_{m+1}^{\text{TF}}$ and $\mu_{m+1}^{\text{TF}}$ as $Z \to \infty (m \ll Z)$

$$I_{m+1}^{\text{TF}}(Z \to \infty) \approx 0.047 [m + 1]^{7/3} - m^{7/3}$$  \hspace{2cm} (27)

$$\mu_{m+1}^{\text{TF}}(Z \to \infty) \approx -0.110 m^{4/3}.$$  \hspace{2cm} (28)

It is easy to see from (8) and (26) that the limiting values are attained at $Z$ far outside the periodic table.

Introducing the exchange interaction changes the functional form of $I_{m+1}(Z \to \infty)$ and $\mu_{m+1}(Z \to \infty)$ for small $m$, which makes impossible the derivation of the weak ionization limit from the TF model. Taking the limit $Z \to \infty$ from (21) and (24) at $m = \text{const.}$ $(0 \leq m \leq 2)$ we get

$$I_{m+1}(Z \to \infty) \approx 0.153 + 0.211 m + 0.017 m^2,$$  \hspace{2cm} (29)

$$\mu_{m+1}(Z \to \infty) \approx -0.051 - 0.194 m - 0.017 m^2.$$  \hspace{2cm} (30)

Thus, allowance for the exchange leads to an essential increase of the limiting value $I_{m+1}(Z \to \infty)$. This is physically substantiated by decreasing electron-electron repulsion due to the exchange interaction which leads to decreasing mean distance of electrons from the nucleus. In particular, for a neutral atom we have

$$I_1^{\text{TF}}(Z \to \infty) \approx 1.3 \text{ eV}; \quad I_1(Z \to \infty) \approx 4.2 \text{ eV}.$$  \hspace{2cm}

Taking account of the exchange results in increasing the non-zero chemical potential of a neutral atom.

It is of interest that $I_{m+1}(Z \to \infty)$ for $0 \leq m \leq 2$ calculated within the Fermi-Amaldi model [10] approaches the values obtained from (29).

In order to understand how much the obtained relations describe the reality, we consider experimental ionization potentials of neutral and single-(double)-ionized atoms (Fig. 1). Let us point out the main trends in $I_{m+1}(Z)$ variation:

1) $I_{m+1}(Z)$ is a periodic function; an oscillation period is determined by $n_m$, maximum value of the main quantum number;

2) inside one column of the periodic table, $I_{m+1}(Z)$ decreases with increasing $Z$;

3) an oscillation amplitude falls with increasing $Z$;

4) the ratio for noble gases and isoelectron ions characterizing a relative oscillation amplitude decreases with increasing $Z$.

The TF model cannot, naturally, describe periodic properties (trend 1). Nevertheless this model reproduces correctly trend 2. Taking into consideration that with increasing $Z$ the ionization potential is smoothed (trend 3) and that the TF model reproduces well the behaviour of the smooth part $I_{m+1}(Z)$ one may predict that for ions of small multiplicity with sufficiently large $Z$, the value of $I_{m+1}$ is independent of $Z$. Bearing in mind the relation for $I$ and $\mu$ (25), it is natural to suppose that the chemical potential of a heavy ion does not depend on $Z$ either. Approximate values of $I_{m+1}(Z \to \infty)$ and $\mu_{m+1}(Z \to \infty)$ are given by (29) and (30).

These values can be refined by taking into account the contribution due to correlation effects. Using an asymptotic expression of the correlation energy $E_{\text{cor}} \approx -0.05 N$ [11] we obtain $(0 \leq m \leq 2)$:

$$I_{m+1}(Z \to \infty) \approx 0.203 + 0.211 m + 0.017 m^2,$$  \hspace{2cm} (31)

$$\mu_{m+1}(Z \to \infty) \approx -0.101 - 0.194 m - 0.017 m^2.$$  \hspace{2cm} (32)

It can be easily seen that (31) and (32) yield approximate
relationships

\[ I_{m+1} \approx (m + 1) I_1, \quad (33) \]

\[ \mu_{m+1} \approx (2m + 1) \mu_1. \quad (34) \]

As (33) and (34) are obtained by including main quantum effects, it may be expected that they are valid for real atoms. Indeed, as shown in [14], a linear relation between successive ionization potentials for small m (33) is obeyed approximately for real atoms. It is most accurately obeyed for s and p-valence electrons. This was explained in [15] based on detailed studies of accurate quantum energies of valence electrons.

Taking into account the relationship between \( I \) and \( \mu \) (25), one may expect that (34) is also fulfilled for s- and p-valence electrons. This is confirmed by the analysis of sufficiently accurate \( \mu \) values for the ions of small ionization degree [4].

Combining (25), (31) and (32) we can establish the relationship between the ionization and chemical potentials of the ions with small ionization degree:

\[ \mu_{m+1} \approx - \frac{2m + 1}{2m + 2} I_{m+1}. \quad (36) \]

These relationships allow \( \mu_{m+1} \) for real atoms with s- and p-valence electrons to be found.

From equation 32, one more interesting corollary follows. By integrating (32) we get

\[ \Delta E = E(m, Z) - E(0, Z) \approx 0.101 m + 0.097 m^2 + \frac{0.006 m^3}{2} \approx 0.1 m(m + 1), \quad (37) \]

\[ 0 \leq m \leq 2. \]

Thus, the TF model, with exchange and correlation effects taken into account, enables one to obtain a qualitatively correct dependence of the binding energy on \( m \) in the weak ionization limit. The r.h.s. coefficient in (37) for real ions is a function of \( Z \) [15].

Relationships (29) through (37) follow from (21) and are valid only for the ions of small ionization degree. With increasing \( m \), the dependence of \( I_{m+1}, \mu_{m+1} \), and \( E \) on \( m \) for heavy atoms changes. Using (20), (23) and (26), we derive, for \( 3 < m \leq Z \):

\[ \mu_{m+1} \approx \mu_{m+1} = -0.110 m^{4/3} - 0.141 m^{2/3} - 0(Z^{-a/3}), \quad (38) \]

\[ I_{m+1} \approx I_{m+1} = 0.110(m + 1/2)^{4/3} + 0.141(m + 1/2)^{2/3} + 0(Z^{-a/3}), \quad (39) \]

\[ \Delta E = 0.0473 m^{7/3} + 0.0845 m^{5/3} + 0(Z^{-a/3}). \quad (40) \]

From (39) and (38) it follows that the linear relation between successive \( I_m \) (or \( \mu_m \)) breaks down when \( m \) increases.

Equations 38 through 40 involve both the electrostatic (TF) contribution and quantum corrections due to exchange interaction and electron density inhomogeneity (correlation corrections with the order \( m^0 \) are neglected in these equations). It is seen that for \( m > 3 \) the TF contribution prevails even for the energy difference. In contrast to this, for \( 0 \leq m \leq 2 \) the quantum contribution is dominant \(^{(1)}\).

The oscillation contribution, being rather significant for the ions of small ionization degree, cannot be taken into account within the TF model. This is the reason why expressions 31, 32, 38-40, reproducing correctly the trends of \( I, \mu, \Delta E \) variation, do not give accurate quantitative values for the ions with great \( Z \) and small \( m \).

The question is how much correctly the improved TF model reproduces the dependence of \( I \) and \( \mu \) on \( N \) and \( Z \) for an atom with an arbitrary degree of ionization. We shall show now that for a highly ionized atom the simple TF model gives the main part of \( \mu(N, Z) \) and \( I(N, Z) \), while the quantum oscillations define the leading correction of the relative order \( N^{-1/3} \).

It is well known [16] that the ionization potential of the isoelectronic series may be calculated by using a \( Z^{-1} \) expansion

\[ I(N, Z) = Z^2 \sum_{k=0} b_k(N) Z^{-k}. \quad (41) \]

Now represent the chemical ion potential in the form of a \( Z^{-1} \) expansion

\[ \mu(N, Z) = Z^2 \sum_{k=0} d_k(N) Z^{-k}. \quad (42) \]

Using expressions 7, 15, 23 and 25, we write the coefficients of \( Z^{-1} \) expansions of \( I(N, Z) \) and \( \mu(N, Z) \) within the TF model allowing for the contributions of the exchange interaction and electron density inhomogeneity

\[ b_0(N) = -d_0(N - 1/2); \quad (43a) \]

\[ d_0(N) = d_0^{TF}(N); \quad d_k(N) = d_k^{TF}(N) + d_{k-1}^{(1)}(N), \quad k > 0. \quad (43b) \]

The first coefficients are specified from the equations

\[ d_0^{TF}(N) = -18^{-1/3} N^{-2/3}; \quad d_1^{TF}(N) = 0.6465 53 N^{1/3}; \]

\[ d_2^{TF}(N) = -0.243 04 N^{1/3}; \quad d_3^{TF}(N) = -0.088 48 N^{-1/3}; \]

\[ d_4(N) = 0.265 49 N^{2/3}. \quad (44) \]

Exact values of \( b_0(N) \) and \( d_0(N) \) may be determined from the non-interacting electrons model.

The binding energy of atoms with \( N \) electrons in

\(^{(1)}\) This behaviour is not considered in reference 3 whose author has incorrectly extended TF dependence (40) to the weak ionization limit. The same error is made in the derivation of the function \( \mu(Z \rightarrow \infty) \sim Z^{-1/3} \) for neutral atoms [25].
this model is
\[ E_0(N, Z) = - Z^2 \sum_{l=1}^{\infty} 2(2l + 1) n^{-2} = \]
\[ = - Z^2 (n_m - 1 + p) \quad (45) \]
where \( p \) is the fractional occupation of the outermost shell (0 \( \leq p \leq 1 \)).

Taking into account the \( N - n_m \) link [11].

\[ N = \frac{1}{3} n_m (n_m - 1) (2n_m - 1) + 2 n_m^2 p \quad (46) \]
and eliminating \( n_m \) from (46) and (45) we arrive at
\[ E_0(N, Z) = - Z^2 \left\{ \sqrt{2} \frac{3}{2} N - \frac{1}{2} + \frac{p^2 - p + \frac{1}{2}}{(1/2) N^{1/3}} + \right. \]
\[ + \left. \frac{p(1 - p)(2p - 1)}{3(2/3) N^{2/3}} + \ldots \right\} \]
whence follows the exact value
\[ d_0(N) = -18^{-1/3} N^{-2/3} - \frac{2p - 1}{3N} - \frac{1}{3} \left( \frac{2}{3} \right)^{1/3} N^{-4/3} \left( p^2 - p + \frac{7}{12} \right). \quad (47) \]

The exact value of \( b_0(N) \) is given by the ionization potential of a hydrogen-like atom \( b_0 = \frac{4}{3} n_m^{-2} \). Using (46), we expand \( b_0(N) \) in powers of \( N^{-1/3} \).

\[ b_0(N) = (18 N^2)^{-1/3} \left[ 1 + \left( \frac{2}{3} \right)^{1/3} N^{-1/3} (2p - 1) + \right. \]
\[ + \left. \left( \frac{2}{3} \right)^{2/3} N^{-2/3} (p^2 - p - \frac{7}{12}) + \ldots \right] \quad (48) \]

Comparison of (47) and (48) allows the conclusion that for a highly-ionized atom up to the terms of \( \sim N^{-1} \) the following equality is valid
\[ \mu_0(N, Z) = - I_0(N, Z). \quad (49) \]

It should be noted that for closed shells (49) is destroyed since \( \mu_0(N, Z) \) undergoes a break and becomes ambiguous. We may choose \( \mu_0(N, Z) \) for an ion with a closed shell in the form
\[ \mu_0(N, Z) = \frac{1}{2} \left( \frac{\partial E_0}{\partial N} \right)_+ + \frac{\partial E_0}{\partial N} \right)_- = \]
\[ = - Z^2 \left\{ (18 N^2)^{-1/3} + \frac{7}{36} \left( \frac{2}{3} \right)^{1/3} N^{-1/3} + \ldots \right\}. \quad (49a) \]

It is seen from (47) and (44) that the first term in the exact \( d_0(N) \) expansion with respect to \( N^{-1/3} \) coincides with \( d_0^{TF}(N) \), while the second, the oscillation term, has a relative order \( N^{-1/3} \). Thus, the TF model gives asymptotically (at \( N \gg 1 \)) exact expressions \( \mu(N, Z) \) and \( I(N, Z) \) at \( N/Z \ll 1 \).

Evaluation of the oscillation contribution to consequent coefficients of \( Z^{-1} \) expansion is very difficult since inclusion of the interelectronic interaction requires the summation of multiparticle diagrams which does not yield explicit dependence \( b_k(N) \) at \( k > 0 \). Numerical estimation of \( b_1(N) \) may be based on the summation of hydrogen-like radial integrals [17]. An approximate analytical estimate is given by using the expression for the oscillation contribution to the second term of \( Z^{-1} \) expansion of binding energy [11].

\[ E_{osc}^{TF}(N, Z) = A Z N^{2/3} (p - 1). \]

Differentiating this expression, we represent the main part of the oscillation contribution to \( b_1(N) \) as
\[ b_1^{osc}(N) \approx - \left( \frac{2}{3} \right)^{2/3} \left( p - \frac{1}{2} \right) A_1 \left( N - \frac{1}{2} \right). \quad (50) \]

Analysis of the numerical values shows (Fig. 2) that linear dependence (50) fairly describes \( b_1^{osc}(N) \) assuming that \( A_1(N - 1/2) \) is a slowly varying function
\[ A_1(N - 1/2) \approx 2.15 - 2.07 (N - 1/2)^{-1/3}. \quad (51) \]

Comparison of (47) and (50) with (44) indicates that, with the TF model giving the main part \( b_2(N) \) at \( N \gg 1 \), the oscillation contribution may be very pronounced at moderate \( N \) especially at the beginning of a shell. We think that the main part of the oscillation contribution to subsequent coefficients of \( Z^{-1} \) expansion has also relative order \( N^{-1/3} \) and is proportional to \( (p - 1/2) \).

Combining (47), (50) and (51) we represent the oscillation contribution to \( I(N, Z) \) of a many-electron highly ionized atom as
\[ I_{osc}(N, Z) \approx \frac{1}{3 N_1} Z^2 (2p - 1) \times \]
\[ \times \left[ 1 - 2.46 \frac{N_1 - 0.95 N^{2/3}}{Z} \right]. \quad (52) \]

with \( N_1 = N - 1/2 \).

Fig. 2. — The plot of \( b_1^{osc}(N) = b_1(N) - d_1^{TF}(N - 1/2) + d_0(N - 1/2) \) for \( N \leq 28 \); \( b_1(N) \) are calculated by using hydrogen-like integrals [17].
The main part of $I_{\text{osc}}(N, Z)$ has a shell structure and depends linearly on $p$. $I_{\text{osc}}(N, Z)$ is the result of the substitution of a discrete dependence on quantum numbers by a continuous dependence on $N$.

It follows from (52) and figure 2 that $I_{\text{osc}}$ for a highly ionized atom is a periodic function of $n_m \simeq \frac{1}{2} N - 1/2$. When $n_m$ increases by unity, maximum $I_{\text{osc}}$ shifts to minimum, which is consistent with the critical values $N_c = 3, 11, 29, 61, \ldots$

Taking into account that an oscillation period of a weakly ionized atom is also determined by $n_m$ (trend 1, page 89) — we may present $I_{\text{osc}}$ for an atom with an arbitrary degree of ionization as

$$I_{\text{osc}}(N, Z) \simeq A(N_1, \frac{N_1}{Z}) \times$$

$$\times F\left[k\left(N_1 \frac{N_1}{Z}\right) N_1^{1/3}\right] I_{\text{TF}}(N, Z).$$  (53)

Here, $k(N_1/Z) N_1^{1/3} = n_m$; $F(x)$ is the periodic function, $A(N_1, \frac{N_1}{Z})$ is the relative amplitude of oscillations.

Now let us discuss a change of $A(N, N/Z)$ and $n_m$ along isoelectronic series. As $N/Z$ increases for $N < 18$, the oscillation period changes slightly. Electron shells rearrange along isoelectronic series due to electronic interaction. This is followed by increasing $n_m$ [19] and, as a result, by decreasing the oscillation period. The most pronounced change occurs around a neutral atom. At some $N/Z$, a new quantity, $N_c$, appears. For a neutral atom $N_c = 19, 37, 55, 87, \ldots$

Now consider the dependence of the oscillation amplitude on $N$ and $N/Z$. From (41) and (44) the expression of $I(N, Z)$ for a highly ionized atom within the TF model with corrections for the exchange and inhomogeneity results

$$I(N, Z) = 18^{-1/3} N_1^{-2/3} Z^2 \times$$

$$\times \left(1 - \frac{1.6944}{N_1 - 0.75604 N_1^{1/3}}\right)$$

$$+ \frac{0.63695 N_1^2 - 0.6958 N_1^{4/3}}{Z^2} + \cdots \right).$$  (54)

Combining (54) and (52) allows approximate expansion of $A(N_1, N_1/Z)$ for $N/Z \ll 1$

$$A\left(N_1, \frac{N_1}{Z}\right) = \left(\frac{3}{2} N_1\right)^{-1/3} \times$$

$$\times \left(1 - 0.77 N_1 - 2.34 N_1^{2/3} + 0.76 N_1^{1/3}\right).$$  (55)

It follows from (55) that the variation of $A(N, N/Z)$ along isoelectronic series is different for great and small $N$. With $N < 18$, the second term of expansion (55) is positive and $A(N/Z)$ grows with $N/Z$ (Fig. 3). As a measure of $A(N, N/Z)$, the parameter

$$\lambda(N, Z) = \frac{I(N - 1, Z - 1) - I(N, Z)}{I(N - 1, Z - 1) + I(N, Z)}$$

is assumed for $N = N_c$. This is valid since for $N = N_c - 1$ the function $F$ reaches a maximum, while for $N = N_c$, it is minimum.

For $N > 20$, the coefficient of $Z^{-1}$ in (55) changes sign, which results in decreasing $A(N, N/Z)$ along an isoelectronic series. Near a neutral atom, as follows from the analysis of experimental $I(N, Z)$ values, the relative amplitude of oscillations abruptly increases irrespective of $N$ (Table II). Thus, the oscillation contribution, like other quantum effects, i.e. exchange interaction and electron density inhomogeneity, increases for a weakly ionized atom. But, in contrast to exchange and inhomogeneity, the relative oscillation amplitude for many-electron ions is minimum at $N/Z \neq 0$.

Fig. 3. — Relative oscillation amplitude vs. $N/Z$ for the Ne isoelectronic series.

Table II. — $\lambda(N, Z)$ for neutral and weakly ionized atoms.

<table>
<thead>
<tr>
<th>$N$</th>
<th>11</th>
<th>19</th>
<th>37</th>
<th>55</th>
<th>87</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0.615</td>
<td>0.568</td>
<td>0.540</td>
<td>0.514</td>
<td>0.474</td>
</tr>
<tr>
<td>1</td>
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<td>0.454</td>
<td>0.428</td>
<td>0.393</td>
<td>0.378</td>
</tr>
<tr>
<td>2</td>
<td>0.476</td>
<td>0.346</td>
<td>0.335</td>
<td>0.316</td>
<td>0.293</td>
</tr>
</tbody>
</table>

$I(N, Z)$ are according to [23].
This raises hopes that the TF model with allowance for exchange and inhomogeneity may give a satisfactory estimate of \( I(N, Z) \) and \( \mu(N, Z) \) in a wide range of \( N \) and \( Z \). We have compared \( I(N, Z) \) (11), (22), (25) with experimental data [19] to verify that an error of the improved TF model does not exceed 30% for \( 12 \leq N \leq 29 \) and \( Z > N + 4 \). A typical dependence of the error on \( Z - N \) is plotted in figure 4. Taking into account that \( \Delta(N, N/Z) \) falls with increasing \( N \) one may assert that the improved TF model gives a semi-quantitative estimate of non-relativistic values of \( I(N, Z) \) and \( \mu(N, Z) \) for all atoms with \( N \geq 12 \) at \( Z \geq N + 4 \).

The existence of quantum oscillations leads to a complex configuration (hills and ravines) of \( I(N, Z) \) and \( \mu(N, Z) \) surfaces for real atoms. There is a physical problem implying a study of heavy-ion penetration through matter [20] for which a smoothed ionization potential for an atom with arbitrary \( Z \) and degree of ionization must be known. From experimental conditions averaging is performed with respect to angular momentum for many different, but energetically close, states of ionization. The improved TF model gives this very potential, \( I(N, Z) \). We have calculated \( I(N, Z) \) for a wide range of ions with \( Z > 20, N < Z - 2 \) by using expressions 9, 11, 22, 23 and 25. Comparison with realistic \( I(N, Z) \) values [18, 19] shows that, with the exception of the system having a small electron number \( (N \sim 2 \div 4) \), the improved TF model yields a reliable estimate of smoothed ionization potentials. The asymptotic behaviour of the expressions displays the growing accuracy with increasing \( Z \) and \( N \) (Fig. 5).

4. Conclusion.

Based on expressions previously obtained for non-relativistic binding energy, analytical expressions of \( \mu(N, Z) \) and \( I(N, Z) \) are derived within the TF model, including corrections for exchange interaction of electrons and inhomogeneity of electron density ((9), (11), (22), (23), (25)). These expressions fairly reproduce the smoothed ionization potential for arbitrary \( N \) and \( Z \).

It follows from the TF model that for heavy ions with small ionization degree, \( m \), the values of \( I_{m+1}(Z) \) and \( \mu_{m+1}(Z) \) decrease with increasing \( Z \) and tend to the limit determined by \( m \) (27), (28). The effect of exchange interaction (and other quantum effects) changes the weak ionization limit for \( \mu \), \( I \) and \( \Delta E \) (equations 29, 30, 37). Based on these equations, approximate relationships between \( I_{m+1} \) and \( \mu_{m+1} \) (36)-(39) are derived which may be useful to estimate the chemical potential for ions with s-p-valence electrons.

Within the quantum model of non-interacting electrons it is proved that the simple TF model gives an asymptotically exact dependence of \( I(N, Z) \) for \( N/Z \ll 1 \), while the oscillation contribution is a leading correction of relative order \( N^{-1/3} \). The study of isoelectronic series shows that the oscillation period decreases with increasing \( N/Z \) but the relative amplitude has a minimum at an intermediate value \( 0 < N/Z < 1 \). Owing to this the improved TF model gives a reliable semi-quantitative estimate of non-relativistic \( I(N, Z) \) values (the error being less than 30\%) for all atoms with \( N > 12, Z \geq N + 4 \).
Appendix.

The TF expression for \( X_0 \) at \( q \ll L \)

Solution of TF equation (2, 3) for a weakly ionized atom may be represented as \([10]\)

\[
\psi(X) = \psi_0(X) + \sum_{n=1}^{\infty} C^n \psi_n(X) , \quad (A.1)
\]

where \( \psi_0(X) \) is the solution of the TF equation for a neutral atom; parameter \( C \) depends on \( N/Z \), its explicit form is given below.

Substituting (A.1) into equation 2 and equating the expressions with equal exponents \( C \) we derive a recurrent system of second-order differential equations

\[
\psi'_2(X) - \frac{1}{2} \psi^{1/2}_2(X) X^{-1/2} \psi_2(X) = 0 ,
\]

\[
\psi'_1(X) - \frac{1}{2} \psi^{1/2}_1(X) X^{-1/2} \psi_1(X) = \psi'_0(X)/(X^{-1/2}) = F_2(X) . \quad (A.2)
\]

The first equation of system (A.2) has been derived by Fermi when investigating the first-order correction function; its solution is written in quadratures [21]

\[
\psi_1(X) = \alpha_1 I_1(X) + \beta I_2(X) \quad (A.3)
\]

where

\[
I_2(X) = \psi_0(X) + \frac{1}{2} X \psi'_0(X),
\]

\[
I_1(X) = I_2(X) \int_0^X I_2^{-2}(x) \, dx . \quad (A.4)
\]

Solution to the \( n \)-th equation of system (A.2) satisfying the conditions \( \psi(0) = \psi_0(0) = 1 \) and \( C = \psi'(0) - \psi_0'(0) \), is \([10]\)

\[
\psi_1(X) = I_1(X),
\]

\[
\psi_n(X) = \int_0^X F_n(X') \{ I_1(X) I_2(X') - I_1(X') I_2(X) \} \, dX', \quad n > 1 . \quad (A.5)
\]

The relationship between \( C, X_0 \) and \( N/Z \) is determined from boundary conditions \([3]\)

\[
\sum_{n=0}^{\infty} C^n \psi_n(X_0) = 0 ; \quad \sum_{n=0}^{\infty} C^n \psi_n(0) = - \left( 1 - \frac{N}{Z} \right) X_0^{-1} . \quad (A.6)
\]

Using asymptotic expansions of \( \psi_0(X) [22], I_1(X) \) and \( I_2(X) \) at \( X \gg 1 [10] \)

\[
\psi_0(X) = 144 X^{-3} \sum_{n=0}^{\infty} A_k X^{-k} \sigma
\]

\[
I_1(X) = \left[ 48 \sigma A_1(7 + 2 \sigma) \right]^{-1} X^{4 + \sigma} \sum_{k=0}^{\infty} B_k X^{-k} \sigma
\]

\[
I_2(X) = - 48 \sigma X^{-3} \sum_{k=1}^{\infty} kA_k X^{-k} \sigma
\]

proves that all \( \psi_n(X \gg 1) \) are of the form

\[
\psi_n(X \gg 1) = a_n X^{n(\sigma - 3) - 3} (1 + \gamma_1 X^{-\sigma} + \gamma_2 X^{-2\sigma} + \ldots) . \quad (A.8')
\]

In formulae A.7 and A.8 \( A_0 = B_0 = 1 ; A_k \) and \( B_k \) are determined from the recurrent relations and are expressed in terms of \( A_1 = - 13.270 974 \) [22], \( a_1 = [48 \sigma A_1(7 + 2 \sigma)]^{-1} \); \( B_k \) and \( \gamma_n \) values are given in [10].

Introducing (A.8) into (A.6) and substituting \( CX_0^{-\sigma} = D \), we obtain the system \((q = 1 - N/Z)\)

\[
\sum_{n=0}^{\infty} D^n a_n [ (7 + n + n \sigma - 3) \gamma_1 X_0^{-\sigma} + \ldots ] = - qX_0^3 . \quad (A.9)
\]

Solution of system (A.9) gives the weak ionization limit for \( X_0 \) and \( D \)

\[
X_0 = a_0 q^{-1/3} (1 + a_1 q^{n/3} + a_2 q^{2n/3} + \ldots) , \quad (A.10)
\]

\[
D = D_0 (1 + D_1 q^{n/3} + D_2 q^{2n/3} + \ldots) . \quad (A.11)
\]

Insertion of each consequent term of expansion (1) leads to readimation of \( a_0 \) and \( D_0 \).

For the first order we obtain

\[
X_0 = [144(7 + \sigma)]^{1/3} (1 - 0.870 95 q^{4/3} + 0.138 46 q^{2n/3} + \ldots) , \quad (A.12)
\]

and introducing the second one we have

\[
X_0 = 10.248 q^{-1/3} (1 - 0.910 16 q^{4/3} + 0.030 73 q^{2n/3} + \ldots) . \quad (A.12)
\]

More accurate \( a_k \) values may be obtained when using an increasing number of terms of the asymptotic series (A.1). The author of [3] has noticed this and has believed erroneously that the first term in (A.10) gives the weak ionization limit for \( X_0(q \rightarrow 0) \). At our request S. K. Pobrebynya has calculated \( a_0 \) by using 20 orders to found \( a_0 = 10.232 0 \) that differs slightly from the value given in (A.12).
References