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ON THE NONRELATIVISTIC BINDING ENERGY FOR POSITIVE IONS

G. I. PLINDOV and I. K. DMITRIEVA

Nuclear Power Engineering Institute, Academy of Sciences BeSSR, Minsk, USSR

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Résumé. — L’énergie de liaison d’ions positifs peut être développée, sur la base de la théorie statistique, en série de puissances de la charge effective. L’expression analytique obtenue pour un atome avec un degré d’ionisation arbitraire donne des résultats en bon accord avec ceux obtenus par la méthode Hartree-Fock. Des formules permettant de calculer l’énergie de corrélation de l’atome sont proposées.

Abstract. — It is shown from statistical theory that the binding energy for positive ions may be expressed in a power series expansion of reciprocal effective charge. An analytical expression enabling one to calculate the nonrelativistic binding energy for an atom with an arbitrary degree of ionization in good agreement with the results of the SCF-method is obtained. Convenient formulae for the calculation of the correlation energy for an atom are presented.

The determination of the binding energy for heavy ions includes the calculation of pairwise interactions of fermions acting in the field of a Coulomb centre. Up till now an exact solution of this complicated problem has not been obtained. A good analytical evaluation of binding energy for ions in the ground state may be obtained within the statistical theory of the atom [1].

Recently Lieb rigorously proved [2] that the Thomas-Fermi (TF) theory gives an asymptotic exact description of the ion binding energy for a large number of electrons in the nonrelativistic approximation. Using this fact, we represent the binding energy of a heavy ion with $N$ electrons and with charge $Z$ as

$$E(N, Z) = E_{TF}(N, Z) + E_q(N, Z),$$

where $E_{TF}(N, Z)$ is the ion binding energy in the TF theory, $E_q(N, Z)$ corrections due to exchange, oscillations and other quantum effect.

The exact expression of $E_{TF}(N, Z)$ can be obtained on the basis of an analytical solution of the TF equation for the ion [1]

$$\psi''(x) = \psi^{3/2} x^{-1/2}$$

with the boundary conditions

$$\psi(0) = 1; \quad \psi(x_0) = 0; \quad x_0 \psi'(x_0) = -q = -(1 - N/Z).$$

Here $x$, $\psi(x)$ and $x_0$ are the dimensionless coordinate, the electrostatic potential and the ion radius respectively.

Previously we have shown [3] that the statistical potential of the ion may be found in the form of a functional series expansion

$$\psi(x) = q \sum_{\lambda=0}^{\infty} \lambda^N \psi_\lambda(x/x_0); \quad 0 \leq \lambda \leq \lambda_{cr},$$

where the $\lambda^2 = qx_0^2$ parameter has a simple physical meaning, namely, it is proportional to the product of an ion volume with its excess positive charge.

It is easy to show that the energy, as many other properties of an ion within the TF theory, may be written as a series in the parameter $\lambda$. Indeed, using an explicit expression of the ion binding energy [1] and substituting the expansion (3) we obtain (in atomic units)

$$E_{TF}(N, Z) = -\frac{3}{2} N(Z - \alpha N)^2 \times$$

$$\times \sum_{n=0}^{\infty} a_n(\alpha) \left(\frac{N}{Z - \alpha N}\right)^n.$$  (4)

Eq. (4) has the form of an energy expansion in reciprocal power series of the effective charge, $\alpha N$ playing the part of the screening parameter. For $\alpha = 0,$
this expression assumes the form of well known Z perturbation theory \[3a\]

\[ E_{TF}(N, Z) = - \frac{3}{2} \sqrt{2} N Z^2 \sum_{n=0}^{\infty} a_n(N/Z)^n. \] \[ (5) \]

March and White \[4a\] were the first to obtain the expression of nonrelativistic binding energy in the form (5) within the TF theory. However, they used Baker’s semiconvergent series, which does not represent by itself a solution of the equation for an ion, and prevented them from finding accurate values for the coefficient \(a_n\). Using expansion (3), valid at \(N/Z < 1\) we obtain values for first four coefficients \(a_n\):

\[ a_0 = 1; \quad a_1 = - 1 + \frac{256}{45 \pi^2}; \]
\[ a_2 = \frac{2}{3} + \frac{223}{30 \pi^2} - \frac{262}{205 \pi^4}; \]
\[ a_3 = 0.0024369. \]

The values of \(a_n\) \((n = 0, 1, 2)\) were presented earlier in \[3a, b\]. The value of \(a_3\) is given here for the first time.

The investigation of the convergence of expansion (5) up to the value of \(N/Z = 1\) is of great importance. It is a strong argument for the convergence of this expansion for ions with values of \(N/Z\) sufficiently close to 1, that the solution (3) on which expansion (5) is based correctly allows for both singular points of the TF equation for an ion and coincides with Baker’s series at \(x \rightarrow 0\) and with the expansion first obtained by Kobayashi \[5\] at \(x \rightarrow x_0\) (1):

\[ \psi(x) = qy + \frac{4}{35} (qx_0)^{3/2} y^{7/2} + \frac{2}{63} (qx_0)^{3/2} y^{9/2} + \]
\[ + \frac{1}{66} (qx_0)^{3/2} y^{11/2} + \frac{1}{175} 2^2 x_0^2 y^6 + \ldots, \]
\[ y = 1 - x/x_0. \]

A limit for the neutral atom requires a special consideration. Nevertheless, expansion (5), even with the first three coefficients \(a_n\), can be successfully used for the calculation of the binding energy \(E_{TF}(N, Z)\) up to \(N/Z = 1\). The error in this limiting case is about 0.6 %. The consideration of \(a_3\) and introduction of the simple geometric approximation

\[ E_{TF}(N, Z) = - \frac{3}{2} \sqrt{2} N Z^2 \left\{ 1 - 0.42360 \frac{N}{Z} + \right. \]
\[ \left. + 0.09085 \frac{N^2}{Z^2} + 0.0024369 \frac{N^3}{Z^3} \right\} \]
\[ (7) \]

decreases the maximum error to 0.01 % which is illustrated by the data of table I.

\[ \text{(1)} \] The problem whether the combination of these two semiconvergent series proposed by March \[4b\] is an approximate analytical solution of the TF equation for an ion requires further investigation.

### Table I

| Values of the ion binding energy in the TF theory, \(E' = E_{TF} Z^{-7/3}\) |
|------------------|------------------|------------------|------------------|------------------|
| \(N/Z\)          | 0.356            | 0.615            | 0.897            | 0.926            | 1.000           |
| \(E_{ext}[5]\)   | 0.698            | 0.754            | 0.768            | 0.768            | 0.768           |
| \(E(N, Z)\)eq.(7) | 0.698            | 0.754            | 0.768            | 0.768            | 0.768           |

We now return to the expression for the ion binding energy (1) and evaluate \(E_q(N, Z)\). The exact analytical expression of \(E_q(N, Z)\) may be evidently obtained only for the model of noninteracting electrons \[36\]

\[ E_q(N, Z) = \]
\[ = Z^2 \left\{ 1 - \frac{(1/2-p)^2}{(3/2 N)^{1/3}} + \frac{2 p - 1}{3(3/2 N)^{2/3}} + \ldots \right\}. \]
\[ (8) \]

Here \(0 \leq p \leq 1\) is a degree of filling the last shell; expression (8) takes into account both shell effects and corrections for inhomogeneity of the electron density.

The inclusion of electron interactions leads to the necessity of summing over multiparticle diagrams which can be performed only numerically. However, Scott \[6\] showed that a good analytical approximation of the neutral atom binding energy may be obtained with inclusion of an exchange interaction within the TF theory. It is easy to obtain an expression for the ion exchange energy in a series in \(N/(Z - \alpha N)\), using a similar approach

\[ E_{ex}(N, Z) = - \frac{4}{\pi^2} \frac{3}{3} \left( Z - \alpha N \right) N^{2/3} \times \]
\[ \times \sum_{k=0}^{\infty} b_k(z) \cdot \left( \frac{N}{Z - \alpha N} \right)^k. \]
\[ (9) \]

At \(z = 0\) we recover the expansion of \(Z^{-1}\) perturbation theory \[3b\] with the following values of \(b_k\):

\[ b_0 = 1; \quad b_1 = \frac{31}{16} \frac{1024}{45 \pi^2}; \quad b_2 = - 0.0024908. \]

The first two coefficients are given in \[3b\]; the accurate value of \(b_3\) is given here for the first time. It markedly differs from 0.0077 used by March \[4b\]. Thus

\[ E_{ex}(N, Z) = - \frac{4}{\pi^2} \frac{3}{3} \left( Z N^{2/3} \times \right) \]
\[ \times \left\{ 1 - \left( \frac{1024}{45 \pi^2} - \frac{31}{16} \frac{N}{Z} - 0.0024908 \frac{N^2}{Z^2} \right) \right\}. \]
\[ (9a) \]

Expression \(9a\) describes well even an exchange energy of a neutral atom \[6\]; the error in this case is \(\sim 0.3\ %\).

Combining eq. (7), (8) and (9a) we obtain an ana-
Table II gives the values of $E(N, Z)$ for isoelectronic sequences calculated using formula (10), compared with the results of the SCF-method [7]. It is evident that good agreement is obtained for ions with closed electron shells even at a small value of $N$. For ions with unclosed shells good agreement is achieved only for a large number of electrons. A further improvement may be obtained by allowing for shell effects and inhomogeneity in the density.

Let us note that the analytical solution (3) of the TF equation allows a good evaluation of such small quantities as the correlation energy of an ion, equal to the difference of the exact and Hartree-Fock values of the nonrelativistic ion binding energy.

To evaluate the correlation energy it seems convenient to use the expression obtained by Wigner [1] based on the free electron gas approximation

$$E_{\text{cor}}(N, Z) = -\alpha_1 \int \frac{\rho^{2/3}(r)}{\alpha_2 + \rho^{1/3}(r)} \, dr$$

(11)

where $\rho(r)$ is the electron density of the ion;

$$\alpha_1 = 0.056 \, 47; \quad \alpha_2 = 0.121 \, 6.$$  

It will be shown that for an atom with an appreciable degree of ionization the main part of the correlation energy $E_{\text{cor}}(N, Z)$ may be represented as an expansion in reciprocal powers of the effective charge. Indeed, after simple transformations expression (11) reduces to

$$E_{\text{cor}}(N, Z) = -\alpha_1 N \left[ 1 - \frac{4}{9} \alpha_2 \frac{3}{\pi} \frac{\langle r^2 \rangle}{N} - \frac{\pi}{8} \frac{3}{\alpha_2^2} \frac{q^2}{Z^{1/3}} - \alpha_2^2 f(\alpha_2, N, Z) \right].$$

(12)

It is easy to be convinced that for $N/Z \geq 1$ two last terms in brackets can be expanded in a series in $Z - \alpha N$, their main terms being $N^{4/3}/Z^2$ and $N^{1/3}/Z$ correspondingly. The function $f(\alpha_2, N, Z)$ containing the nonanalytical dependence $N^{5/3} Z^{-5} \ln (N^{1/3} Z^{-1})$ at small values of $N/Z$ may be neglected since its main part goes as $\sim N^{2/3} Z^{-2}$.

We obtain a simple and convenient formula for the calculation of $E_{\text{cor}}(N, Z)$ using an explicit dependence $\langle r^2 \rangle$ and $x_0$ on $N$ found in [8] and [3a]

$$E_{\text{cor}}(N, Z) = -0.056 \, 5 \, 0.06 \, N \left[ 1 - \frac{0.366 \, N^{1/3}}{Z} \right] \times \left[ 1 + 0.576 \frac{N}{Z} + 0.382 \frac{N^2}{Z^2} + 0.274 \frac{N^3}{Z^3} + \cdots \right].$$

(13)

As can be seen from figure 1, eq. (13) reproduces fairly well quantum mechanical values of the correlation energy [8b] at $N/Z \geq 0.4$. The discrepancy increases
with an increase of the $N/Z$ ratio; that is due to both the approximations made in deriving formulae (11) and (13), and the slowly converging series given in round brackets of eq. (13). Taking into account the latter we obtain $E_c(Z)$ for a neutral atom using the corresponding value of $\langle r^2 \rangle$. The analysis performed shows that the function $f(\alpha_2, N, Z)$ is of order $Z^{-1}$ at $N/Z \sim 1$. Thus

$$E_{cor}(Z) = -0.0565Z + 0.128Z^{1/3} - B. \quad (13a)$$

This expression reproduces fairly well the data of Clementi [7b] for the correlation energy of a neutral atom at $B = 0.083$. As is seen from figure 1, the error does not exceed 10% in the range of $Z$ from 10 to 18, the deviation evidently indicating an appreciable contribution from the oscillation effects.

References