

DIFFERENTIAL EQUATIONS FOR TOTAL ENERGY OF ATOMS AND ATOMIC IONS WITHIN THOMAS–FERMI APPROXIMATION

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Abstract

An approach to the calculation of the total energy of atoms and atomic ions as a function of atomic number Z and number of electrons N , based on the solution of second-order differential equations together with auxiliary conditions, is presented. Some applications of the equations to the description of real atoms are also shown. Physical consequences of the approach are indicated. Attention is paid to the methodological aspects of the approach, which give the analytical form of the results and are very convenient for further treatment.

1. Introduction

The Hohenberg–Kohn theorem [1] states the one-to-one correspondence between the positive electrostatic field and the ground-state electronic density ρ . The total energy of the system is given by the functional $E[\rho]$, which generally depends on the function $V(\mathbf{r})$ defining the field. If the functional $E[\rho]$ is defined, both the density function and the energy can be determined with the help of the variational principle.

The Density Functional Theory (DFT) postulates the variational equation with isoperimetric constraints fixing the number of electrons N in the system. The Lagrange multiplier defines the chemical potential μ of the electron gas. This means that the field and the number of particles determine the chemical potential and the total ground energy of the system.

In the case of atoms or atomic ions, where the field is explicitly defined by the nuclear charge Z , the total energy is fixed solely by Z and N . One can expect the existence of the function $E(Z, N)$ resulting from the general functional $E[\rho]$. Such a function exists within Nonrelativistic Thomas–Fermi (NTF) theory. The NTF theory is a very useful tool in studies of atomic and molecular properties, mainly as a convenient charge density and energy model [2]. The atomic (ionic) binding energy function $E(Z, N)$ has been determined numerically [3, 4], and can in principle be defined analytically in the case of large N as the Z^{-1} expansion [5–8]. Approximate analytical results have also been established for the weak and strong ionization limits [4].

The regularities in the experimental atomic/ionic binding energies are still not clear within the density functional theory [9], and it is expected that the modifications of the T-F scheme should be helpful in elucidation of the problem.

In the previous note [10], we have paid attention to the equation [9,11]:

$$N \left(\frac{\partial \mu}{\partial N} \right)_Z + Z \left(\frac{\partial \mu}{\partial Z} \right)_N = p\mu, \quad (1)$$

where $p = 4/3$, $\mu(Z, N)$ is the chemical potential of the atom or positive ion with nuclear charge eZ and the number of electrons N , which is equivalent to the more general second-order differential equations of the hyperbolic type:

$$N \frac{\partial^2 E}{\partial N^2} + Z \frac{\partial^2 E}{\partial N \partial Z} - p \frac{\partial E}{\partial N} = 0. \quad (2)$$

The general solution of this equation in the generalized coordinates resulting from the characteristic equation of (2) is of the form:

$$E(\eta, \xi) = F(\eta) G(\xi), \quad (3)$$

where $\xi = Z$, $\eta = \ln(Z/N)$. Independent of the chosen boundary conditions,

$$G(\xi) = a_1 \xi^{p+1}, \quad (4)$$

where a_1 is a constant.

The function $F(\eta)$ depends on the boundary conditions imposed on the general solution. Assuming that the energy of the atomic system changes by the same value due to the small change of charge of the electronic cloud as due to the change of the nuclear charge [12],

$$\frac{\partial E}{\partial Z} = - \frac{\partial E}{\partial N}, \quad (5)$$

and using the energy scale defined by the boundary condition $E(\xi, 0) = 0$, the solution for $F(\eta)$ is obtained:

$$F = a_2 (1 - e^{-\eta})^{p+1}, \quad (6)$$

which together with (3) and (4) gives the relation

$$E(Z, N) = a(Z - N)^{p+1}, \quad (7)$$

with $a = A/\vartheta_0$ in the weak ionization limit, where:

$$\vartheta_0 = \lim_{\eta \rightarrow 0} x_0(\eta)(1 - e^{-\eta})^{-1/3} = \text{const},$$

$$A = \frac{12}{7} (2/9\pi^2)^{1/3}, \quad x_0 \text{ is the T-F radius of the ion.}$$

The same results have also been obtained in an independent way [13]. Here, we present further results concerning in particular the boundary conditions (5).

2. Generalization of boundary conditions

In the generalized coordinates, eq. (5) is

$$(e^\eta - 1) \frac{\partial E}{\partial \eta} = \xi \frac{\partial E}{\partial \xi}, \tag{8}$$

from which, after elimination of $G(\xi)$, results

$$\frac{dF}{d\eta} + \frac{p+1}{1-e^\eta} F = 0. \tag{9}$$

It is supposed that the right-hand side of (9) in the general case is different from zero and is a function of N/Z . Therefore, the equation

$$\frac{dF(\eta)}{d\eta} + P(\eta)[F(\eta) + Q(\eta)] = 0 \tag{10}$$

is proposed as the most obvious generalization of (9).

The solution of (10) may be expressed as

$$F(\eta) = \exp \left\{ - \int_{\eta_0}^{\eta} P(\beta) d\beta \right\} \left[F(\eta_0) - \int_{\eta_0}^{\eta} P(\alpha) Q(\alpha) \left\{ \exp \int_{\eta_0}^{\alpha} P(\beta) d\beta \right\} d\alpha \right]. \tag{11}$$

It may be proved that eq. (10) contains the boundary conditions for the exact Thomas–Fermi solution.

Assuming as before

$$P(\eta) = \frac{p+1}{1-e^\eta}, \tag{12}$$

we have from (10)

$$(1 - e^\eta) \frac{dF}{d\eta} + (p+1)F = -(p+1)Q. \quad (13)$$

Multiplying both sides by G/ξ and introducing

$$\frac{\partial G}{\partial \xi} = (p+1) \frac{G}{\xi}, \quad (14)$$

the equation:

$$\frac{1}{\xi} \frac{\partial E}{\partial \eta} + \frac{\partial E}{\partial \xi} - \frac{e^\eta}{\xi} \frac{\partial E}{\partial \eta} = -(p+1) \frac{G}{\xi} Q \quad (15)$$

is obtained.

On the other hand, the T–F energy may be expressed in our coordinate system as

$$E_{\text{TF}} = -A \phi(0) \xi^{p+1} \left[1 - \frac{\phi(\eta)}{\phi(0)} - \frac{(1 - e^{-\eta})^2}{\phi(0)x_0(\eta)} \right], \quad (16)$$

where $\phi(0) = (\partial\phi/\partial x)_{\eta=0, x=0}$; $\phi(x)$ is the T–F potential in dimensionless coordinates. Eliminating x_0 from this equation through the identity [4],

$$\frac{(1 - e^{-\eta})^2}{x_0} \frac{\partial x_0}{\partial \eta} - x_0 \frac{\partial \phi}{\partial \eta} = -(p-1)e^{-\eta}(1 - e^{-\eta}), \quad (17)$$

it is possible to derive the equation

$$\frac{1}{\xi} \frac{\partial E_{\text{TF}}}{\partial \eta} (1 - e^\eta) + \frac{\partial E_{\text{TF}}}{\partial \xi} = -(p+1)A \phi(0) \xi^p \left[1 - \frac{\phi(\eta)}{\phi(0)} \right], \quad (18)$$

which is formally identical to (14), under the condition

$$Q = 1 - \frac{\phi(\eta)}{\phi(0)}, \quad (19)$$

which defines function $Q(\eta)$ in (10).

The knowledge of this function, together with (10) and (14), is sufficient for the definition of the function $E(N, Z)$ in the T–F method. The boundary condition of (2) in the T–F limit as expressed by (10) has a clear physical meaning. It defines the relation between the chemical potential $\mu(\eta)$ and the electrostatic potential at the nucleus $\chi(\eta)$:

$$\mu + \chi = a(p + 1)\xi^p(1 - Q) \quad (20)$$

as a function of $Q(\eta)$ and ξ .

3. The weak ionization limit

Within the T–F method (the function $P(\eta)$ defined by (12)), the functional (11) assumes a simpler shape:

$$F = (1 - e^{-\eta})^{p+1} \left[1 - (p + 1) \int_{\eta}^{\infty} \frac{e^{-\beta}}{(1 - e^{-\beta})^{p+2}} Q(\beta) d\beta \right]. \quad (21)$$

In the weak ionization limit: $Q = 0$, i.e. $\phi(\eta) = \phi(0)$. Substituting this value into (21), eq. (7) is obtained. The known numerical values [3,4] of $\phi(\eta)$ indicate that this approximation is excellent up to $\eta = 0.5$ and very good up to $\eta = 1$. In other words, the symmetry of energy changes with respect to the changes of Z and N , as expressed by (5), holds approximately even for the moderately ionized atoms. This is probably the reason that a relation similar to (7) holds very well for atomic ions with partially filled valence shells [14]. The relation between chemical potential and electrostatic potential is very simple in this limit and depends only on the ionization degree of the ion

$$\mu = \chi \frac{(1 - e^{-\eta})^p}{1 - (1 - e^{-\eta})^p}. \quad (22)$$

The chemical potential itself is a function of both the coordinates η, ξ which has been discussed earlier [10].

4. Neutral atom limit

The chemical potential of a neutral atom expected by T–F theory is equal to zero, which is a serious shortcoming of the theory if it is used as the model for the real atomic structure. In the light of the results of this work, this is an effect of boundary conditions which determine the function $E(Z, N)$ in the T–F limit, particularly the behaviour of the energy with respect to Z and N for neutral atoms.

To illustrate the possibility of modification of the function $E(N, Z)$, let us assume the condition in the form

$$\kappa \frac{\partial E}{\partial Z} + \frac{\partial E}{\partial N} = 0, \quad (23)$$

which is equivalent to the function $Q(\eta)$ defined by

$$Q = (1 - \kappa e^{-\eta})^p (\kappa - 1). \quad (24)$$

Substituting this function into (21), one can obtain

$$E(\eta, \xi) = a \xi^{p+1} (1 - \kappa e^{-\eta})^{p+1}. \quad (25)$$

In this case, the limit $\lim_{\eta \rightarrow 0} (\partial E / \partial \eta)$ is different from zero and relates the chemical potential to the value of κ :

$$\mu = -a \kappa (p + 1) \xi^p (1 - \kappa)^p. \quad (26)$$

Simultaneously,

$$\lim_{\eta \rightarrow \eta_0} E(\eta, \xi) = 0,$$

where $\eta_0 = \min\{\eta\}$; therefore, for $0 < \kappa < 1$, negative ions with charge

$$q \geq Z \left(\frac{1}{\kappa} - 1 \right)$$

are stable.

As an illustration, the application of a modified eq. (25) for the valence shells of chosen atoms is shown. The parameter κ which ensures the correct value of the chemical potential of a neutral atom is expected to improve the agreement between experimental values $E_{Z,N}$ and the theoretical relation. Equation (25), if satisfied, should give the linear relation between $\ln E$ and $\ln(Z - \kappa N)$ at constant Z . The minimal net error of linear regression for optimal κ value as measured by $1 - R^2$ (R is the correlation coefficient) is typically fifty times lower than that for $\kappa = 1$ (fig. 1). The optimal value of κ allows us to estimate the chemical potential of neutral atoms from (26). The obtained values are in agreement with other values obtained in independent ways (table 1).

The data for atoms with three valence electrons (B, Al) are only tentative (statistics with zero degree of freedom). The obtained energy parameters are different from the T-F values. The a value is systematically higher than the T-F value but, according to expectations, values for the third period are lower than for the second period, p oscillates around the T-F value.

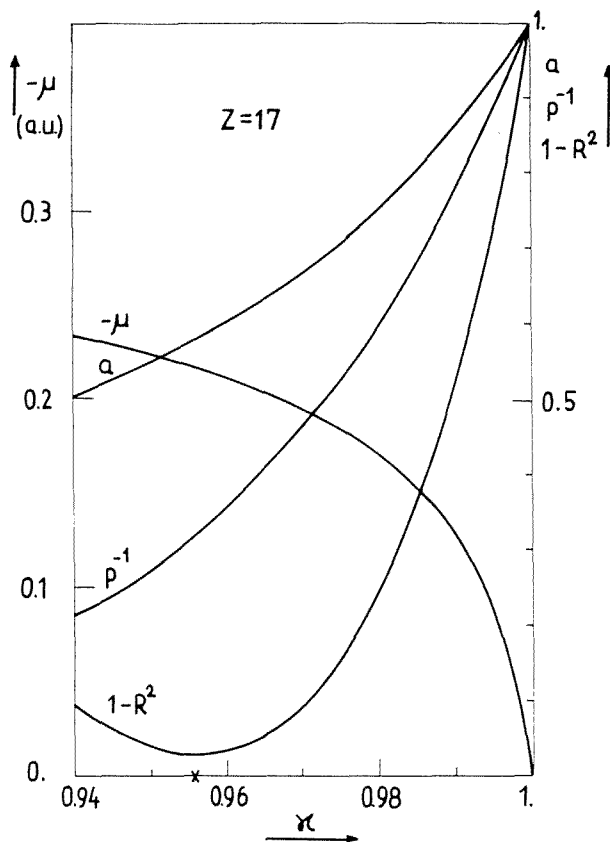


Fig. 1. The effect of adjustment of eq. (25) to the experimental energy of chlorine ions. The energy parameters a , p and the net error of fitting are expressed in relation to the analogous values for $\kappa = 1$. The best fit (optimal κ) corresponds to the minimum of $1 - R^2$.

Table 1

Optimal κ values, remaining energy parameters a and p , and chemical potential μ calculated for valence shells of some second and third period elements. Comparative values are in brackets

Element	κ	a	p	$-\mu$ [a.u.]
B	1.04	0.41	0.73	(<0) [0.12 ^b]
C	0.93	0.20	1.30	0.15 [0.11 ^a , 0.19 ^b]
N	0.89	0.16	1.50	0.22 [0.26 ^b]
O	0.96	0.29	1.20	0.16 [0.13 ^a , 0.33 ^b]
F	0.93	0.22	1.39	0.26 [0.25 ^a , 0.40 ^b]
Ne	0.92	0.23	1.39	0.34 [0.38 ^b]
Al	1.02	0.35	0.67	(<0) [0.08 ^b]
Si	0.94	0.061	1.72	0.11 [0.11 ^a , 0.13 ^b]
P	0.93	0.072	1.60	0.17 [0.08 ^a , 0.18 ^b]
S	0.97	0.17	1.22	0.15 [0.15 ^a , 0.24 ^b]
Cl	0.96	0.13	1.34	0.21 [0.23 ^a , 0.30 ^b]
Ar	0.95	0.16	1.29	0.26 [0.26 ^a]

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5. Concluding remarks

Studies of the function $E(Z, N)$ in the NTF approximation by means of differential eqs. (2) and (10) give some additional insight into the problem. This may be summarized as follows:

- (1) The solution of eq. (2) in the coordinates η, ξ suggests the variable $\ln(Z/N)$ as the most suitable for investigation of the NTF approximation.
- (2) The mathematically simplest boundary conditions lead to an energy scale counted from the infimum of the function $E(Z, N)$, which may be compared with the "chemical" manner of energy counting from the equilibrium point. In our case, this is the point for which the chemical potential is equal to zero.
- (3) Boundary conditions for weakly ionized atoms in the NTF approximation illustrate some interesting features of the atomic structure. The small change of nuclear charge gives nearly the same energetical effect as the small change of number of electrons. Because in the spirit of the Hohenberg–Kohn theorem [1] Z defines the positive electrostatic field, N the total negative charge, relation (5) or, more generally (10), is one of the aspects of field–space charge correspondence.

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