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# Thomas–Fermi approach to density functional theory: binding energy for atomic systems

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## Abstract

In this work, we re-examine the Thomas–Fermi formalism as an approach to the calculation of atomic binding energies. We focus on the concept of electron density as the central magnitude, and the way in which the different contributions to the total energy can be evaluated from it. Total energies of simple atoms ( $Z = 2$  to 10) are calculated using three different analytical approximations for the electronic density, and the results are compared with those obtained within the Hartree–Fock model.

Keywords: Thomas–Fermi, density functional theory, atoms, molecules

(Some figures may appear in colour only in the online journal)

## 1. Introduction

From introductory quantum mechanics courses, it is generally assumed that the calculation of energy in quantum systems is indissolubly linked to the notion of wavefunctions [1, 2]. Courses based on more advanced textbooks tend to reinforce this concept [3, 4]. It should not

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be disregarded, however, that from the standpoint of atomic and molecular physics, the only exactly solvable system is the hydrogen atom, with nuclear charge  $Z$  and a single electron, in both the non-relativistic and relativistic approaches. Helium-like atoms, instead, are necessarily treated in an approximated way by means of the perturbation theory and/or the variational method [5]. In order to understand the difficulties involved in the study of the second simplest atom in the periodic table, a solved example can be found in [1]. For more complex atoms, the canonical method is based on the model of independent particles moving in a central field, generally known as the Hartree–Fock (HF) model, or, in the relativistic case, the Dirac–Fock (DF) model [6]. Some quantum mechanics textbooks give a brief summary of this subject but, for a thorough understanding, a more specific bibliography is necessary [7, 8]. For molecules, the problem turns out to be much more difficult since the central symmetry disappears, and the implementation of the HF model becomes more complex [8]. It should be noted that in the general case of  $N$  electrons, the wavefunction has  $3N$  degrees of freedom ( $6N$  when considering the spin), which makes difficult to treat with ‘chemical accuracy’ systems containing more than 10 active electrons. An estimation of this number is made in [9].

On the other hand, in 1927, Thomas and Fermi developed an alternative method, modified later by Dirac and Weizsacker, to deal with many-electron systems. A few classical textbooks discuss this topic [3], usually emphasizing the inadequacy of this method for the calculation of atomic binding energies. The important fact that the Thomas–Fermi (TF) method forms the conceptual basis for the powerful density functional theory (DFT) is, in our understanding, not sufficiently stressed in modern textbooks. The foundational papers of DFT, due to Walter Kohn and co-workers, appeared in 1964–65 [10, 11]. The main idea behind this theory is, basically, that all the information about a given quantum mechanical system can be obtained from the knowledge of its electronic density  $\rho(r)$  (a function with only three degrees of freedom, instead of the  $3N$  degrees of freedom of the wavefunction). Regarding this formalism, we can mention the didactical exposition in the book by Levine [8], and an excellent paper, also with a didactical approach, due to Capelle [12]. Another excellent text, that relates the DFT method with TF, is due to Parr and Yang [13]. The method of Kohn and co-workers has its roots in the method developed by Thomas and Fermi, and modified later by Dirac and Weizsacker. It is necessary to mention at this point that, in the lapse between 1927 and 1964, a very important contribution was a work by Slater in 1951 [14], where an approximated method to calculate the so-called exchange interaction was proposed.

The fundamental hypothesis underlying the DFT method is that *the knowledge of the electronic density  $\rho(r)$  in the ground state of any electronic system (with or without interactions) univocally determines the system*. The interested reader can resort to the above mentioned [8] and [12] for further details, particularly concerning with the way in which the DFT method is employed in practice to calculate several physical observables. The DFT method is, in principle, exact, since it takes into account the terms of ‘exchange’ and ‘correlation’ (whose meanings will be explained below). Also in principle, the DFT method do not need the concept of wavefunction, although Kohn and Sham introduced the so-called KS orbitals in order to have an initial estimation of the density.

It should be emphasized that the electron density,  $\rho(\mathbf{r})$ , is all that it is necessary to determine the exact energy of many electron systems. So, DFT has become an *ab initio* pillar of molecular and condensed matter physics. It is curious that, despite the formidable relevance of these theories, only a few papers on the subject have been published in journals devoted to didactical aspects of physics. As an example, Neal considered a system of two coupled harmonic oscillators in one dimension [15]. Later, the same author studied single-particle

systems in one spatial dimension [16]. Although theoretically interesting, no comparison with experiments was presented.

On the other hand, low  $Z$  neutral atoms provide both relatively simple systems (due to their spherical symmetry) and a lot of experimental data to compare the theoretical results, in particular, the total binding energies. More over, in low  $Z$  atoms, relativistic corrections can be neglected, to a great extent. The main aim of this work is to show how, by performing a reasonable choice for the analytical form of the electron density  $\rho(\mathbf{r})$  and avoiding the use of wavefunctions, it is possible to obtain the different contributions to the total energy of simple atomic systems. From the didactical point of view, it is important to stress that, whereas the canonical TF method needs a self-consistent procedure, our approach only needs the search of a minimum, with a few adjustable parameters. We consider that the implementation of this procedure is easier than a self-consistent method and, therefore, adequate for both graduate and undergraduate students of quantum mechanics, taking specialist courses.

It is very important to stress that DFT makes two kinds of contribution to the science of many-body quantum systems, including the electronic structure of molecules, solids and plasma. The first is in the fundamental understanding. Theoretical chemists and physicists, by solving the Schrödinger equation, think in terms of a truncated Hilbert space of single-particle orbitals. In high accuracy calculations many Slater determinants are required; in some calculations of the order of  $10^9$  or so. DFT provides a complementary perspective, because it focuses on quantities in the real, three-dimensional coordinate space, principally on the electron density  $\rho(r)$ . These quantities are physical, independent of representation, and easily to visualize even for very large systems. The second contribution is practical. HF methods, when applied to many particle systems, encounter an exponential wall when the number of atoms  $N$  exceeds a critical value of  $N_0 \approx 10$ – $20$  for a system without symmetries [9]. Therefore, when  $N/N_0 \gg 1$ , such as large organic molecules, DNA, etc, HF methods are impractical. On the other hand, DFT can handle systems with a number of atoms of the order of  $10^2$ – $10^3$ . It is expected that wavefunction-based and density-based theories, in complementary ways, give us more accurate results but also a better understanding of the electronic structure of the matter. We think that the present paper could be considered as a starting point to subsequent reading on the subject.

## 2. Theory

### 2.1. Outline of the Thomas–Fermi theory

In an atom or molecule, each electron has three degrees of freedom (without counting the spin); for an  $N$  electron system,  $3N$  spatial variables are necessary. In atoms, assuming the independent particle model and a central force field, we can avoid the use of angular variables for the determination of physical observables (matrix elements such as the transition probabilities, etc), and calculate them in terms of the radial variable  $r$ . The angular variables can be treated by means of Racah algebra within the theory of angular momentum [7]. In molecules and solids, such separation of variables is not possible. In consequence, from the works by Thomas, Fermi and Dirac, later by Slater, and then by Hohenberg and Kohn, and Kohn and Sham, the electron density ( $\rho(\mathbf{r})$ ) was used instead of the many-body wavefunctions as the central concept of the theory [9, 12].

In this work we will employ the TF theory in the way it was understood and generalized throughout the years. This theory is described in several quantum mechanics books, for instance [3, 6, 17, 18]. The main idea is that the  $N$  electrons in an atom are described by an electron density  $\rho(r)$  inside a sphere of radius  $r_0$  (which may be infinite) [6]. The kinetic

energy density at a distance  $r$  of the nucleus is, as for a free electron gas, proportional to  $[\rho(r)]^{5/3}$ , whereas the potential energy is classically computed from a continuous charge distribution  $\rho(r)$ . The density  $\rho(r)$  is varied in order to minimize the total energy

$$E[\rho] = E_k[\rho] + E_{ne}[\rho] + E_{ee}[\rho] + E_W[\rho] \quad (1)$$

where

(1)  $E_k[\rho]$  is the electronic kinetic energy

$$E_k[\rho] = C_K \int_0^\infty 4\pi r^2 \rho^{5/3} dr \quad (2)$$

with  $C_K = 2.8712$ ,

(2)  $E_{ne}[\rho]$  is the interaction between the nucleus of charge  $Z$  and the  $N$  electrons

$$E_{ne}[\rho] = -4\pi Z \int_0^\infty r \rho(r) dr, \quad (3)$$

(3)  $E_{ee}[\rho]$  is the repulsion between the electrons, and is often written as the sum of two terms: a direct or Coulombian term  $J[\rho]$  and an exchange term  $K[\rho]$ , due to the Pauli exclusion principle (see the [appendix](#))

$$E_{ee}[\rho] = J[\rho] + K[\rho] \quad (4)$$

with

(a)  $J[\rho]$ , the Coulombian integral, given by

$$J[\rho] = \frac{1}{2} \int_0^\infty 4\pi r^2 V_e(r) \rho dr, \quad (5)$$

where  $V_e(r)$  is the potential experienced by each electron due to the remaining  $N - 1$  electrons, and is determined by the Poisson equation

$$\frac{d^2}{dr^2}(rV_e) = 4\pi\rho(r) \quad (6)$$

(b)  $K[\rho] \equiv E_x[\rho]$  the exchange integral, given by

$$K[\rho] \equiv E_x[\rho] = -C_X \int_0^\infty 4\pi r^2 \rho^{4/3} dr \quad (7)$$

where  $C_X = 0.7386$ ,

(4)  $E_W[\rho]$  is the Weizsacker correction to the kinetic energy

$$E_W[\rho] = c \frac{1}{8} \int_0^\infty 4\pi r^2 \frac{|\nabla\rho|^2}{\rho} dr. \quad (8)$$

(The constant factor  $c$  is often taken as  $1/5$  or  $1/9$  [13].)

With these definitions, we can write the total energy as

$$E[\rho] = E_k[\rho] + E_{ne}[\rho] + J[\rho] + K[\rho] + E_W[\rho]. \quad (9)$$

It should be noted that, within this approach, the correlation energy is not taken into account. This represents a small contribution to the total binding energy but is nonetheless necessary to obtain atomic and molecular energies with chemical accuracy, and also to find

the equilibrium geometry of the molecules. A general description of this term is given in [8] and [12].

The minimization of the expression (9) subject to the normalization condition

$$N = \int \rho(\mathbf{r}) d\mathbf{r} \quad (10)$$

result in an Euler type equation, that must be solved self-consistently, as we see in the section 3.1.

## 2.2. Calculation of the electron density

Several problems in atomic physics can be solved in terms of the so-called atomic screening function  $\chi(r)$ . This function is the quotient between the electrostatic potential  $U(r)$  due to all the charges (the nucleus and the remaining  $N - 1$  electrons, spherically averaged in such a way that the electronic density is  $\rho(r)$ ), and the potential due to the bare nucleus  $-Z/r$

$$\chi(r) = \frac{U(r)}{-Z/r}. \quad (11)$$

In terms of  $\chi(r)$ , equation (6) takes the form

$$\rho(r) = \frac{Z}{4\pi r} \chi''(r) \quad (12)$$

and, correspondingly

$$\chi(r) = \frac{4\pi}{Z} \int dr \left[ \int r \rho(r) dr \right].$$

With the replacements  $b = 0.885Z^{-1/3}$ ,  $x = r/b$ , the TF equation takes the universal form

$$\chi''_{\text{TF}}(x) = \frac{[\chi_{\text{TF}}(x)]^{3/2}}{x^{1/2}}, \quad (13)$$

which should be solved numerically (see [19] and references therein). It was the numerical character of the solution that suggested the inadequacy of the TF method for the calculation of binding energies. Instead, if appropriate analytical expressions are used for  $\rho(r)$ , the TF method gives very good results, as will be shown below.

**2.2.1. Moliere's approach.** In order to avoid the use of the numerical resolution of equation (13), Moliere [20] proposed an analytical representation for the screening function with the form

$$\chi_{\text{Mol}}(r) = \sum_{i=1}^3 B_i \exp(-\beta_i r/b) \quad (14)$$

with constant coefficients  $B_1 = 0.1$ ,  $B_2 = 0.55$ ,  $B_3 = 0.35$ ,  $\beta_1 = 6.0$ ,  $\beta_2 = 1.2$ ,  $\beta_3 = 0.3$  and  $b = 0.885Z^{-1/3}$ . The function (14) differs from the exact numerical solution by less than 0.002 in the range  $0 < x < 6$  [20]. Besides, by forcing the exponential behavior, the results are more accurate than those obtained using  $\chi_{\text{TF}}(x)$ . The electron density is obtained by means of equation (12), resulting in

$$\rho(r) = \frac{Z}{4\pi b^2 r} \sum B_i \beta_i^2 \exp(-\beta_i r/b).$$

Inserting this expression in equations (2)–(9), and integrating numerically, the different contributions to the binding energy are obtained.

**2.2.2. Moseley's law and Slater's screenings.** By 1927, the time by which the TF theory was developed, it was already known that the electrons in an atom accommodate in different (sub) shells; the main evidence for this fact was the experiments carried out by Moseley [21, 22]. After plotting the transition frequencies  $\nu$  for the  $p$  series, Moseley found an empirical law of the form

$$\nu^{1/2} = C_p(Z - \sigma_p) \quad (15)$$

where the constants  $C_p$  and  $\sigma_p$  are different for different series [21, 23]. As noted by Whitaker [21],  $Z - \sigma_p$  is not an effective charge, since this notion should be assigned to each of the levels of the transition. In the non-relativistic approximation (which will be used here for simplicity), the difference between the ionization potential and the energy for a level  $i = n_i, l_i; f = n_f, l_f$  is given by

$$\frac{T_i}{Ry} = \frac{(Z - s_i)^2}{n_i^2}, \quad \frac{T_f}{Ry} = \frac{(Z - s_f)^2}{n_f^2}. \quad (16)$$

Comparing equations (15) and (16) it can be inferred that the Moseley constant  $\sigma_p$  is in some way related to the screenings  $s_i$  and  $s_f$  of the initial and final states, respectively. In practice,  $\sigma_p$ ,  $s_i$  and  $s_f$  are often determined by fitting experimental data with the above expressions, or by using Sommerfeld's generalization of Bohr's model of the atom [22, 23]. For instance, we can assign effective charges to the different subshells from the experimental x-ray and photoelectric levels. The most well-known rules to determine the screenings are those due to Slater. Based on the experimental energy levels known at his time, Slater proposed a set of rules such as: (1) for an electron in a fully occupied  $1s$  subshell,  $s_{1s} = 0.30$ ; (2) for electrons in subshells  $ns$  or  $np$  ( $n > 1$ ), the screenings are given by  $s_i = 0.35x + 0.85y + 1.00z$ , where  $x$  is the number of remaining electrons in the same shell  $n_i$ ,  $y$  is the occupation of the shell with principal quantum number  $n_i - 1$ , and  $z$  is the occupation of the shell  $n_i - 2$  [5]. Although there are also rules for  $3d$  electrons, the given (1) and (2) are sufficient for our comparative purposes.

With the screenings  $s_i$  as obtained from Slater's rules, it is possible to calculate the effective charges  $Z_i^{\text{eff}} = Z - s_i$  corresponding to each subshell  $i = n_i, l_i$ . Taking into account for a moment the exact wavefunction of hydrogenic atoms ( $\psi_{\text{hyd}} \propto e^{-Zr/n_i}$ ), and the concept of screened charges within the framework of the screened hydrogenic model (where the effective charge seen by an electron at subshell  $i$  differs from the nuclear charge by the corresponding screening due to the remaining electrons,  $Z_i^{\text{eff}} = Z - s_i$ , see below equations (18)–(19)), we can identify the parameters  $k_i$  with the effective charges and screenings:

$$k_i = 2Z_i^{\text{eff}}/n_i \equiv 2(Z - s_i)/n_i$$

(the factor 2 appears because  $\rho(r) \propto |\psi|^2$ ). The parameters  $A_i$  seen below in equations (18)–(19) are again obtained from the normalization conditions (see equation (20), below). With these values it is possible to evaluate the different contributions to the total atomic energy.

**2.2.3. Our alternative approach.** A function directly related with the electronic density  $\rho(r)$  is the so-called radial distribution function,  $D(r)$

$$D(r) = 4\pi r^2 \rho(r)$$

This function satisfies the normalization condition

$$\int_0^\infty D(r) dr = N \quad (17)$$

with  $N$  the total number of electrons. Plotting  $D(r)$  versus  $r$  provides us information about the electron distribution in the different shells.

As an alternative to Moliere's approach, and basing our choice in the analytical solutions for hydrogenic atoms and the concept of effective charge for each subshell, the following simple analytical expression for the radial distribution function is proposed

$$D(r) = A_1 r^2 \exp(-k_1 r) \quad (18)$$

for atoms with one shell (He), and

$$D(r) = A_1 r^2 \exp(-k_1 r) + A_2 r^4 \exp(-k_2 r) \quad (19)$$

for atoms with two shells (Li to Ne). The generalization to atoms with three or more shells is straightforward. This shell partitioning is similar to the idea of Kohn and Sham to express the density in terms of the auxiliary Kohn–Sham orbitals [11]. But, whereas the Kohn and Sham equations must be solved self-consistently, in our approach we search for a minimum of the total energy jointly with a fulfillment of the virial theorem (see section 3.2).

In contrast to Moliere's model, the parameters  $A_i$ ,  $k_i$  are not constants, but depend on the system under consideration. For a given system, their values were determined by a variational procedure, minimizing the total energy (9). It should be noted that these parameters are not independent, since the normalization condition (17) should be satisfied. Furthermore, for atoms with  $n = 2$  ( $Z = 3$  to 10), we imposed two separate conditions

$$\int_0^\infty A_1 r^2 \exp(-k_1 r) d^3r = 2, \quad \text{and} \quad \int_0^\infty A_2 r^4 \exp(-k_2 r) d^3r = N - 2. \quad (20)$$

This double normalization condition is restrictive and could be removed, but we keep it in order to reduce the number of unknowns.

### 3. Comparison between the different methods

In Moliere's approach the coefficients  $B_i$  are fixed and only depend on  $Z$  through the parameter  $b = 0.885Z^{-1/3}$ . This makes Moliere's approach the less appropriate one, because is an analytical approximation to the numerical solution of the original TF method. It is well known that the pure TF method is not very appropriate from the quantitative point of view, although improves for higher  $Z$  [3, 17].

With regard to the use of Slater's rules, its coefficients were estimated from the available experimental data in about 1930. Although better results can be achieved, this is not immediate, because the new, improved rules, arise only after comparison with experimental data. The interested reader may consult [5].

In the next two subsections we indicate briefly how to perform the procedures using both: (1) the Thomas–Fermi–Dirac self-consistent approach according to the classic text by Parr and Yang [13], and (2) our search for the minimum of the total energy and, together, the fulfillment of the virial theorem.



**Table 1.** Different contributions to the binding energy, as obtained using the universal TF function in the form presented by Moliere [20].

Element	$E_k^{\text{Mol}}$	$E_{n-e}^{\text{Mol}}$	$E_{e-e}^{\text{Mol}}$	$E_x^{\text{Mol}}$	$E_W^{\text{Mol}}$	$E_{\text{TOT}}^{\text{Mol}}$	$E_{\text{TOT}}^{\text{exp}}$	$E_{\text{TOT}}^{\text{Mol}}/E_{\text{TOT}}^{\text{exp}}$	Virial
He	2.95	-7.77	2.60	-0.93	1.12	-2.03	-2.90	0.70	-1.49
Li	7.60	-20.01	6.69	-1.82	2.13	-5.42	-7.48	0.725	-1.56
Be	14.85	-39.16	13.09	-2.17	3.36	-10.03	-14.20	0.71	-1.55
B	24.99	-65.91	22.04	-3.15	4.78	-17.25	-24.23	0.71	-1.58
C	38.24	-100.86	33.72	-5.78	6.37	-28.31	-37.86	0.75	-1.63
N	54.79	-144.52	48.32	-5.52	8.12	-38.80	-54.42	0.71	-1.62
O	74.82	-197.35	65.98	-6.89	10.01	-53.42	-75.00	0.71	-1.63
F	98.49	-259.77	86.85	-8.38	12.05	-70.76	-99.50	0.71	-1.64
Ne	125.94	-332.17	111.05	-13.53	14.22	-94.49	-129.05	0.73	-1.67

### 3.1. The Thomas–Fermi–Dirac self-consistent approach

As we have seen above, the minimization of equation (9) with condition (10) requires the introduction of the Lagrange multiplier  $\mu_{\text{TFD}}$ , with the physical significance of the *chemical potential* [13]

$$\mu_{\text{TFD}} = \frac{5}{3}C_K\rho^{2/3}(\mathbf{r}) - \frac{4}{3}C_x\rho^{1/3}(\mathbf{r}) - \phi(\mathbf{r}) \quad (21)$$

with

$$\phi(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

For neutral atoms,  $\mu_{\text{TFD}} = 0$  [13] and, therefore

$$\phi(\mathbf{r}) = \frac{5}{3}C_K\rho^{2/3}(\mathbf{r}) - \frac{4}{3}C_x\rho^{1/3}(\mathbf{r}).$$

The self-consistent procedure consists in the following steps [13]: (1) make an initial guess of the density  $\rho_0(\mathbf{r})$ , (2) compute the electrostatic potential  $\phi_0(\mathbf{r})$  from this guessed  $\rho_0(\mathbf{r})$ , (3) use this  $\phi_0(\mathbf{r})$  in (21) to solve for a new density  $\rho_1(\mathbf{r})$  whose normalization determines the value of  $\mu_{\text{TFD}}$ , (4) insert  $\rho_1(\mathbf{r})$  in step (1) and repeat until self-consistency is reached.

The design and implementation of a self-consistent method is not a trivial task, therefore we turn to the alternative point of view.

### 3.2. Our approach

Given the equations (18) and (19), then: (1) for each possible value of  $k_1$  and  $k_2$ : (2) we calculate  $A_1$  and  $A_2$  according to equation (20) and made a table of  $\rho(\mathbf{r})$  between  $r = 0$  and  $r = r_{\text{max}}$ , (3) Integrals (2) to (8) are calculated, (4) The total energy  $E_{\text{tot}}(k_1, k_2)$  (9) and the virial are calculated and stored. Then, we search for both, the minimal value of  $E_{\text{tot}}$  and the virial, where we expect a value close to 2.00.

The implementation of this cycle is easier than a self-consistent method and, therefore, more adequate for undergraduate students of quantum mechanics.

## 4. Results

Tables 1 to 4 contain the different contributions to the total binding energies of simple neutral atoms as obtained with four different procedures. In all the cases, the last column indicates the value assumed by the virial

$$\text{virial} = \frac{E_{\text{POT}}}{E_{\text{KIN}}} = \frac{E_{\text{ne}} + E_{\text{ee}} + E_x}{E_k + E_W},$$

with  $E_{\text{POT}}$  the total potential energy, calculated as the sum of the nucleus–electron, electron–electron, and exchange contributions, and the total kinetic energy  $E_{\text{KIN}}$  being the sum of the classical TF kinetic energy and the Weizsacker correction.

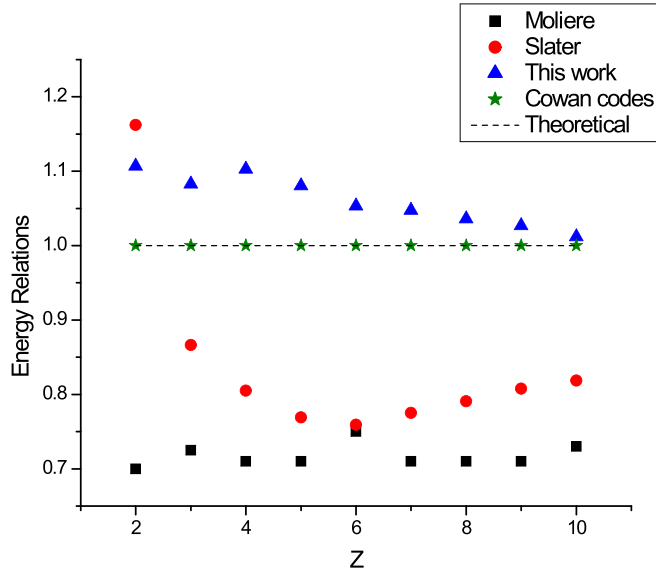
In table 1 we present the different contributions to the energy using the universal screening function proposed by Moliere (section 2.2.1). The values obtained applying Slater’s rules (section 2.2.2) for the calculation of the subshell screenings  $s_i$  and the effective charges

**Table 2.** Different contributions to the binding energy, as obtained using the Slater rules for the screenings section 2.2.3.

Element	$E_k^{\text{Sla}}$	$E_{n-e}^{\text{Sla}}$	$E_{e-e}^{\text{Sla}}$	$E_x^{\text{Sla}}$	$E_W^{\text{Sla}}$	$E_{\text{TOT}}^{\text{Sla}}$	$E_{\text{TOT}}^{\text{exp}}$	$E_{\text{TOT}}^{\text{Sla}}/E_{\text{TOT}}^{\text{exp}}$	Virial
He	2.74	-6.80	1.28	-0.91	0.32	-3.37	-2.90	1.16	-2.10
Li	6.95	-17.11	4.44	-1.53	0.78	-6.48	-7.48	0.87	-1.84
Be	13.30	-33.32	9.45	-2.30	1.45	-11.43	-14.20	0.80	-1.77
B	22.06	-56.21	16.45	-3.24	2.32	-18.63	-24.23	0.77	-1.76
C	33.62	-86.92	25.55	-4.38	3.38	-28.74	-37.86	0.76	-1.78
N	48.47	-126.45	36.88	-5.73	4.65	-42.18	-54.42	0.78	-1.79
O	67.12	-175.81	50.57	-7.31	6.13	-59.31	-75.00	0.79	-1.81
F	90.17	-236.00	66.77	-9.14	7.81	-80.38	-99.50	0.81	-1.82
Ne	118.28	-308.00	85.61	-11.22	9.71	-105.62	-129.05	0.82	-1.83

**Table 3.** Our results: different contributions to the total energy as obtained with the method proposed in section 2.2.2.

Element	$E_k^{\text{our}}$	$E_{n-e}^{\text{our}}$	$E_{e-e}^{\text{our}}$	$E_x^{\text{our}}$	$E_W^{\text{our}}$	$E_{\text{TOT}}^{\text{our}}$	$E_{\text{TOT}}^{\text{exp}}$	$E_{\text{TOT}}^{\text{our}}/E_{\text{TOT}}^{\text{exp}}$	Virial
He	2.64	-6.78	1.27	-0.91	0.57	-3.21	-2.90	1.11	-2.00
Li	6.96	-17.60	3.21	-1.82	1.15	-8.10	-7.48	1.08	-2.00
Be	13.75	-34.76	6.41	-2.96	1.89	-15.66	-14.20	1.10	-2.00
B	23.27	-59.10	11.05	-4.30	2.81	-26.18	-24.23	1.08	-2.00
C	36.00	-91.26	17.32	-5.83	3.90	-39.88	-37.86	1.05	-2.00
N	51.85	-131.74	25.31	-7.55	5.15	-57.00	-54.42	1.05	-2.00
O	69.86	-178.80	34.27	-9.39	6.38	-77.69	-75.00	1.04	-2.00
F	94.01	-239.69	46.85	-11.51	8.17	-102.18	-99.50	1.03	-2.00
Ne	120.55	-308.00	60.67	-13.73	9.95	-130.57	-129.05	1.01	-2.00



**Figure 1.** Ratios  $E_{TOT}^{calc}/E_{TOT}^{exp}$  for the different methods of calculation.

**Table 4.** Different contributions to the binding energy, as obtained with the Hartree–Fock method [6].

Element	$E_k^{HF}$	$E_{n-e}^{HF}$	$E_{e-e}^{HF}$	$E_x^{HF}$	$E_{TOT}^{HF}$	$E_{TOT}^{exp}$	$E_{TOT}^{HF}/E_{TOT}^{exp}$	Virial
He	2.88	-6.77	2.06	-0.89	-2.90	-2.90	1.000	-2.00
Li	7.46	-17.18	4.08	-1.53	-7.44	-7.48	0.995	-2.00
Be	14.60	-33.66	7.16	-2.31	-14.67	-14.20	1.033	-2.00
B	24.77	-57.05	11.67	-3.27	-24.65	-24.23	1.017	-2.00
C	37.80	-88.28	17.82	-4.40	-37.83	-37.86	0.999	-2.00
N	54.57	-128.56	26.15	-5.75	-54.52	-54.42	1.002	-2.00
O	75.23	-178.77	36.88	-7.31	-75.05	-75.00	1.001	-2.00
F	100.12	-239.88	50.31	-9.10	-99.76	-99.50	1.003	-2.00
Ne	129.58	-312.85	66.76	-11.11	-129.00	-129.05	1.000	-2.00

are shown in table 2. In table 3 the contributions obtained with our simple variational procedure are displayed. During the iterative procedure, the convergence to the minimum in energy is accompanied by the simultaneous fulfillment of the virial theorem:  $virial \equiv -2$ . It is remarkable that, as shown in table 3, the results of our model approach closely the experimental values as  $Z$  increases,  $E_{TOT}^{TF}/E_{TOT}^{exp} \rightarrow 1$ . This is a reasonable result since the TF theory has a statistical nature, and its predictive character improves as the number of electrons increases. Finally, in table 4, we present, for comparative purposes, the results obtained within the Hartree–Fock model, as obtained using the suite of computational codes due to Cowan [6].

The results included in the tables are plotted in figures 1 and 2. In figure 1, we show the ratio  $E_{TOT}^{calc}/E_{TOT}^{exp}$  as a function of the atomic number  $Z$  for the four employed methods. In figure 2 is represented the value of the virial.

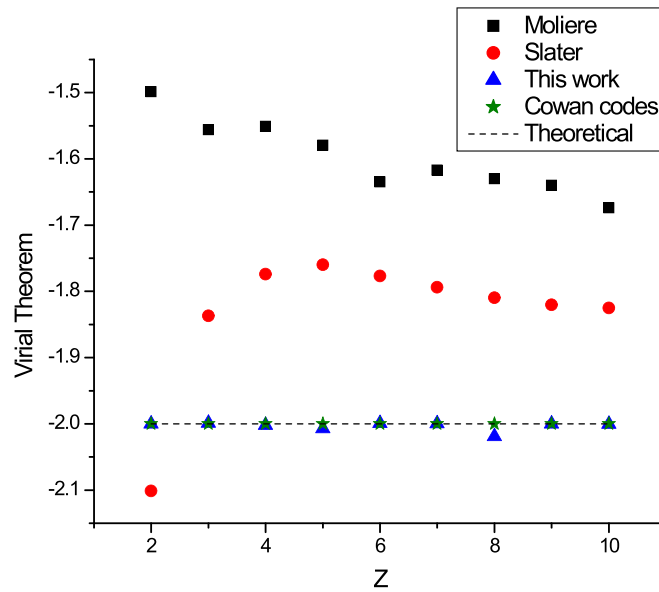


Figure 2. The virial  $E_{\text{POT}}/E_{\text{KIN}}$ , as calculated with the different methods.

## 5. Conclusions

In this work we presented calculations of the binding energies of simple atoms (He to Ne) as obtained within the framework of the Thomas–Fermi model, which constituted the seed of the successful density functional theory developed years later. The present work focuses on the concept of electronic density  $\rho(r)$  (or, equivalently, the radial distribution function  $D(r)$ ), avoiding the concept of wavefunction, and uses instead reasonable semi-empirical guesses for the analytical form of  $\rho(r)$ , based on the form of the analytical solution for hydrogenic atoms (1926), and the concept of different screened charges for different subshells, first suggested by Moseley in 1913 [21].

Regarding the results obtained with Moliere’s approach (which are equivalent to the ones obtained by numerical resolution of the TF equation), it can be seen that  $E_{\text{TOT}}^{\text{Mol}}/E_{\text{TOT}}^{\text{exp}} \approx 0.75$ . This confirms that, in its original formulation, the TF theory is not well suited for the calculation of binding energies. However, when using better approximations for  $\rho(r)$ , such as those obtained by a variational procedure, then  $E_{\text{TOT}}/E_{\text{TOT}}^{\text{exp}} \approx 1$ . By looking at the numerical results detailed in the tables and figures, it can be concluded that our very simple method gives values for the total energy and the virial comparable with the Hartree–Fock results. We can conclude that, as a first approximation to the study of modern DFT, the TF deserves to be treated to some extent.

Finally, it is necessary to highlight two important points. Firstly, the TF model, when treated as a variational method, gives results comparable with Hartree–Fock. Second, students should know that, whereas in the formulation of DFT the central magnitude is the electronic density  $\rho(\vec{r})$  instead of the wavefunction  $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ , Kohn and Sham (KS) were forced to employ the so-called KS orbitals in order to have an initial estimation of the density. In the atomic case, the KS orbitals, although they do not have *a priori* physical meaning, are similar to the HF orbitals [8, 12].

It is important to stress that, besides its value as a computational tool for both simple and complex systems (atoms, solids, plasma), DFT has great conceptual relevance. In fact, several parameters of interest in theoretical chemistry (such as chemical potential, electronegativity differences driving electron transfer, hardness and softness, affinity, etc), find a clear interpretation in the DFT framework [13].

### Appendix. Many-electron systems: the exchange interaction

We know from quantum mechanics that all the information about a given physical system is contained in its wavefunction  $\Psi$ . Non-relativistically, this wavefunction is calculated from the Schrödinger equation  $\hat{H}\Psi = E\Psi$ . For a system with  $M$  nuclei and  $N$  electrons (a molecule, for instance), the Hamiltonian takes the form

$$\hat{H} = \sum_{i=1}^N \left\{ -\frac{\nabla_i^2}{2} - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right\} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (22)$$

The first summation goes over the  $N$  electrons in the molecule and includes the one-electron operators for the kinetic energy and the attraction between electrons and nuclei, with  $r_{iA} = |\vec{\mathbf{r}}_i - \vec{\mathbf{R}}_A|$  the distance between the  $i$ th electron and the  $A$ th nuclei. The second term accounts for the repulsion between pairs of electrons,  $r_{ij}$  being the distance between electrons  $i$  and  $j$ . The last summation in equation (22) represents the repulsions between all pairs of nuclei,  $Z_A$  being the nuclear charge of atom  $A$ ; and  $R_{AB}$  the distance between nucleus  $A$  and  $B$ . For an isolated atom the last term disappears, and  $r_{iA}$  should be thought of as  $|\vec{\mathbf{r}}_i - \vec{\mathbf{R}}|$ ; with  $\vec{\mathbf{R}}$  being the nuclear position, taken to be the zero of the coordinate system.

The prototypical case of a many-electron atom is He [1], [5]. For  $Z = 2$ , the hamiltonian (22) takes the form

$$\hat{H} = \left( -\frac{\nabla_1^2}{2} - \frac{2}{r_1} \right) + \left( -\frac{\nabla_2^2}{2} - \frac{2}{r_2} \right) + \frac{1}{r_{12}} \equiv \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}. \quad (23)$$

Because, due to the Pauli principle, the wavefunction must be antisymmetric, we construct the spatial symmetric and antisymmetric combinations as

$$\psi_S(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad (24)$$

and

$$\psi_A(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]. \quad (25)$$

(The square root is a normalization constant.)

The above expressions must be multiplied, respectively, by the antisymmetric and symmetric spin-functions  $\chi_A(1, 2)$  and  $\chi_S(1, 2)$  to obtain

$$\Psi_{\text{total}}(1, 2) = \psi_S(1, 2)\chi_A(1, 2) \quad \text{or} \quad \Psi_{\text{total}}(1, 2) = \psi_A(1, 2)\chi_S(1, 2). \quad (26)$$

Replacing with functions (26) in (23) we obtain

$$E = \int \Psi_{\text{tot}}^* \widehat{H} \Psi_{\text{tot}} \, d\tau = E_a + E_b + \int \Psi_{\text{tot}}^* \widehat{H}_{12} \Psi_{\text{tot}} \, d\tau;$$

the last term is fundamental for our purposes; due to the form of  $\psi_S(1, 2)$  and  $\psi_A(1, 2)$ , a direct (but not trivial) calculation gives

$$\int \Psi_{\text{tot}}^* \widehat{H}_{12} \Psi_{\text{tot}} \, d\tau = J \pm K$$

where  $J$  is called the Coulombian integral

$$J = \iint \frac{1}{r_{12}} |\psi_a(1)|^2 |\psi_b(2)|^2 \, d\tau_1 \, d\tau_2,$$

which has the classical interpretation of the interaction energy of the two electrons, assuming they are spatially distributed with densities  $\rho_1 = -|\psi_a(1)|^2$  and  $\rho_2 = -|\psi_b(2)|^2$ . The exchange integral  $K$  is

$$K = \iint \frac{1}{r_{12}} \psi_a^*(1) \psi_b^*(2) \psi_b(1) \psi_a(2) \, d\tau_1 \, d\tau_2$$

and has no classical interpretation: it is a manifestation of the Pauli principle.

In the HF model, the resulting numerical equations, essential to solve many-electron problems, are integral and non-linear, due to the exchange terms [6]. In the Hartree–Fock–Slater theory, the exchange terms are non-local and approximated by a statistical free-electron approximation, similar to that used in the Thomas–Fermi–Dirac theory (see equation (7) above). Later, in the Kohn and Sham theory, the Slater term is viewed as a special case of DFT, and other approaches were developed [8].

### A.1. The correlation energy

Two kinds of electron correlation exist. In the first, the correlations among the positions of the various electrons are only partially taken into account through the Pauli exclusion principle: this principle keeps the electrons of parallel spin apart. The second type of correlation involves mainly electrons of different spins and the effect is due to Coulomb repulsion. It is customary to define the correlation energy as

$$E_c \equiv E_{\text{average}}^{\text{exp}} - (E_{\text{average}}^{\text{HF}} + E_{\text{relat}}). \quad (27)$$

In the above equation,  $E_{\text{average}}^{\text{exp}}$  is the experimental total binding energy,  $E_{\text{average}}^{\text{HF}}$  is the mean value of the atomic Hamiltonian given by equation (22) with  $M = 1$ ; for the two-electron case, the appropriate equation is (23). On the other hand,  $E_{\text{relat}}$  is given by the sum of mass-velocity plus Darwin and spin–orbit corrections [6]. For light atoms,  $E_{\text{relat}}$  can be calculated by the perturbation theory and satisfies  $E_{\text{relat}} \ll E_{\text{average}}^{\text{HF}}$ .

Several methods have been developed for the theoretical calculation of correlation energies; however, each of these involves a major computational effort. Old calculations made mainly by E Clementi in the 1960s indicated that, empirically, for atoms,  $\bar{e}_c \cong -0.08Ry/\text{electron}$  [6]. In newer papers, based on the free-electron-gas (‘jellium’) model, the Coulomb electron correlation is obtained in terms of the radius  $r_s$  of a sphere whose volume is the local average volume per electron:  $\rho = 3/(4\pi r_s^3)$ . In particular, Barbiellini obtained the approximate expression  $\bar{e}_c = -3.121Z_c/\sqrt{r_s}$ , with  $Z_c$  being the total charge redistributed by the Coulomb hole [24]. By comparison with Monte Carlo simulations, Barbiellini found that  $Z_c = 0.0407$ , therefore



$$\bar{\epsilon}_c = -\frac{0.127}{\sqrt{r_s}} \text{Ry/electron}; \quad (28)$$

in the range  $r_s = 1 - 6$ , the values given by expression (28) are in good agreement with other conventional theories.

For more complex systems (molecules and solids), a number of theoretical and numerical works have been carried out. In the DFT theory the term  $E_{xc}$  (exchange plus correlation energies) is estimated using different approximate functionals. More accurate correlation and exchange functionals are steadily being developed; for classic papers, the reader can consult the book by Parr and Yang [13]; more modern works were published throughout the years. As examples, two very recent articles must be referenced: the one by Sun *et al* [25] and the other by Cohen and Mori-Sánchez [26]. Sun *et al* propose that the ground-state energy, electron density and related properties of ordinary matter can be computed efficiently when the exchange–correlation energy as a functional of the density is approximated semilocally. For this, they propose the first meta-generalized-gradient approximation (meta-GGA). On the other hand, in the paper of Cohen and Mori-Sánchez, the asymmetric two-site Hubbard model is studied, which has a two-dimensional universe of density matrices. The exact functional becomes a simple function of two variables whose three dimensional energy landscape can be visualized and explored. Additionally, the extensive bibliography cited in these articles is an important guide for newer papers, published principally in this century.

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