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Tests and applications for atoms of an optimized semiexplicit density functional method

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Abstract We present a semiexplicit density functional for the energy of an N-electron system based on a modified Thomas–Fermi–Dirac approach. The resulting equations are analytically solved for a non-interacting electron atom, which gives insight about the precision that can be reached with the present method. The computational procedure and results for the application to real atoms are also described.

1 Introduction

Explicit density-functional methods, based on the old Thomas–Fermi model and its refinements [1–3], still attract research interest [4–6], and because of their simplicity, they have been applied to very complex systems such as clusters [7,8], nanostructures like quantum dots [9,10], as well as in different problems where atomic potentials take place, like scattering including polarization effects [11]. It can also be expected that they will be specially interesting in the future for the challenging study of very complex electronic systems, as biological systems, provided some of their deficiencies are corrected.

In recent work [12,13] we have performed quantum mechanical corrections in the Thomas–Fermi–Dirac atomic model with the result that average properties are described with a few percent errors with respect to Hartree–Fock estimates. It is interesting to know up to what level of accuracy this model is predictable, and to determine

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if some cancellation of errors gives more accurate results than what could be expected. For this purpose a test for a system exactly solvable and for which the present model can be also solved, is of obvious interest.

In this work we will improve the basis and application of this method as well as performing significative new tests. First, we will provide in Sect. 2 the theoretical basis of the method in the framework of density-functional theory, consisting of a semi-explicit density functional for the energy. Second, we will propose in Sect. 3 a scheme of resolution of the resulting equations for atoms which will correct some deficiencies of the previous approach. In Sect. 4 we will perform a test of the method for a exactly solvable system: the non-interacting electron atom. This test will give some information about the accuracy of the present approach, and will allow us to perform a further simplification in the resolution scheme. This simplified approach will be applied to real atoms in Sect. 5, and finally, some concluding remarks will be given in Sect. 6.

2 The semiexplicit energy functional

We obtain a density-functional for the energy of an N-electron system subject to a potential $v(\vec{r})$, containing the coulomb field of a nucleus located at the origin. For this purpose we split $\mathbb{R}^3$ in two regions of integration for a given r_0, i.e. $\mathcal{R}_1 = \{r \leq r_0\}$ and $\mathcal{R}_2 = \{r > r_0\}$.

For obtaining the energy functional we perform the following assumptions:

  (i)   the Hartree–Fock single-particle expression is the starting point, therefore no correlations are included.
 (ii)   the electronic wavefunctions, further from the nucleus than a distance r_0, are approximated by local plane waves, as in the Thomas–Fermi–Dirac model (exchange is included in region $\mathcal{R}_2$ semiclassically).
(iii)   exchange is neglected in region $\mathcal{R}_1$, which will be justified below.

The resulting energy functional is:

$$E[\rho] = E_1[\{\phi_i(\rho)\}] + E_2[\rho] + U_{12}[\{\phi_i(\rho)\}, \rho], \tag{1}$$

where

$$E_1 = T_1[\{\phi_i(\rho)\}] + V_1[\{\phi_i(\rho)\}] + U_{11}[\{\phi_i(\rho)\}], \tag{2}$$
$$E_2 = T_2[\rho] + V_2[\rho] + U_{22}[\rho] + K_2[\rho], \tag{3}$$

and the particular terms are:

$$T_1 = \sum_{i=1}^{N} \int_{\mathcal{R}_1} d\vec{r}\, \phi_i^*(\vec{r}) \left(-\frac{1}{2}\nabla^2 \right) \phi_i(\vec{r}), \tag{4}$$

$$V_1 = \sum_{i=1}^{N} \int_{\mathcal{R}_1} d\vec{r}\, \phi_i^*(\vec{r})v(\vec{r})\phi_i(\vec{r}), \tag{5}$$

$$U_{11} = \frac{1}{2} \sum_{i,j=1}^{N} \int_{\mathcal{R}_1} d\vec{r} \int_{\mathcal{R}_1} d\vec{r}'\, \phi_i^*(\vec{r})\phi_j^*(\vec{r}') \frac{1}{|\vec{r}-\vec{r}'|} \phi_i(\vec{r})\phi_j(\vec{r}'), \tag{6}$$

$$U_{12} = \sum_{i=1}^{N} \int_{\mathcal{R}_1} d\vec{r}\, \phi_i^*(\vec{r})\phi_i(\vec{r}) \int_{\mathcal{R}_2} d\vec{r}'\, \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}, \tag{7}$$

$$T_2 = C_k \int_{\mathcal{R}_2} d\vec{r}\, [\rho(\vec{r})]^{5/3}, \tag{8}$$

being

$$C_k = \frac{3}{10} \left(3\pi^2\right)^{2/3}, \tag{9}$$

$$V_2 = \int_{\mathcal{R}_2} d\vec{r}\, v(\vec{r})\rho(\vec{r}), \tag{10}$$

$$U_{22} = \frac{1}{2} \int_{\mathcal{R}_2} d\vec{r} \int_{\mathcal{R}_2} d\vec{r}'\, \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}, \tag{11}$$

and

$$K_2 = C_e \int_{\mathcal{R}_2} d\vec{r}\, [\rho(\vec{r})]^{4/3}, \tag{12}$$

being

$$C_e = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}. \tag{13}$$

The terms of E_1 and U_{12} depend implicitly on ρ by means of the relationship:

$$\rho(\vec{r}) = \sum_{i=1}^{N} \phi_i^*(\vec{r})\phi_i(\vec{r}). \tag{14}$$

It may be expected that the integration of the exchange energy in region $\mathcal{R}_1$ give a small contribution, since the region is assumed to be small. Therefore, the $l \neq 0$ orbitals are negligible due to the r^l behavior for $r \to 0$, and because of the Kronecker delta in spin, only $n \neq n'$ appears in the sum for the contribution of region $\mathcal{R}_1$ to the exchange energy:

$$\sum_{n \neq n'} \int_{\mathcal{R}_1} d\vec{r} \, \phi_{ns}^*(\vec{r}) \phi_{n's}(\vec{r}) \int d\vec{r'} \, \phi_{n's}^*(\vec{r'}) \frac{1}{|\vec{r} - \vec{r'}|} \phi_{ns}(\vec{r'}), \tag{15}$$

and the overlap between ϕ_n and $\phi_{n'}$ in the integration in $\mathcal{R}_1$ must be small.

The minimization of $E[\rho]$ must be performed keeping the normalization condition fixed:

$$N = \sum_{i=1}^{N} \int_{\mathcal{R}_1} d\vec{r} \phi_i^*(\vec{r}) \phi_i(\vec{r}) + \int_{\mathcal{R}_2} d\vec{r} \rho(\vec{r}). \tag{16}$$

The functional derivative of the functionals restricted to the region of integration $\mathcal{R}_1$ is performed through the orbitals ϕ_i. This leads to the single-particle equations:

$$\left[-\frac{1}{2} \nabla^2 + V(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}), \quad \vec{r} \in \mathcal{R}_1, \tag{17}$$

whilst the functional derivative in the region $\mathcal{R}_2$ is done explicitly with respect to ρ and leads to:

$$\frac{5}{3} C_k [\rho(\vec{r})]^{2/3} + C_e [\rho(\vec{r})]^{1/3} + V(\vec{r}) + \lambda = 0, \quad \vec{r} \in \mathcal{R}_2. \tag{18}$$

In both expressions $V(\vec{r})$ denotes:

$$V(\vec{r}) = v(\vec{r}) + \int \frac{\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} \, d\vec{r'}. \tag{19}$$

For the resolution of Eqs. 17–18 the normalization condition and appropiate matching conditions for the density at r_0 should be imposed.

3 Description of isolated atoms

For isolated atoms, spherically symmetric solutions for $\rho(\vec{r})$ can be found. In the region $\mathcal{R}_1 = \{r < r_0\}$, an asymptotic solution of Eq. 17 can be found using an expansion of $V(r)$ in powers of r. In a previous work [12] we fitted the potential obtained from the Thomas–Fermi–Dirac model, which overstimates the screening of the nuclear charge, but this alternative can be improved using consistently Eq. 19 with the density of our present approach. We will use the expansion of this equation for small r, in terms of density quantitites:

$$V(r) = -\frac{Z}{r} + V_0 - V_2 r^2 + V_3 r^3 + O(r^4), \tag{20}$$

where

$$V_0 = \langle r^{-1} \rangle, \tag{21}$$

$$V_2 = \frac{2\pi}{3} \rho(0), \tag{22}$$

$$V_3 = \frac{2\pi}{3} \rho(0) Z = Z V_2, \tag{23}$$

and the Kato's cusp-condition ($\rho'(0) = -2Z\rho(0)$) has been used. It must be noted that no term on r appears, which is a difference with respect to our previous work [12], where a fit with $-Z/r + V_0 + V_1 r$ was utilized, and V_1 took into account effectively greater powers of r.

Using Eq. 20 we can solve the single particle equation (17) up to order r^5 by means of:

$$\phi_i(r) = a_i \left(1 + b_i r + c_i r^2 + d_i r^3 + f_i r^4 + g_i r^5 \right), \tag{24}$$

obtaining all the parameters in terms of two arbitrary values, which we have chosen to be a_i and c_i, with the result for $|\phi_i(r)|^2$:

$$
\begin{aligned}
|\phi_i(r)|^2 = a_i^2 \Bigg[& 1 - 2Zr + (2c_i + Z^2)r^2 + \frac{Z}{3}(Z^2 - 10c_i)r^3 \\
& + \frac{1}{30}\left(48c_i^2 - 11Z^4 + 38Z^2 c_i - 6V_2 \right) r^4 \\
& - \frac{Z}{75}\left(168c_i^2 - 36V_2 - 42Z^2 c_i - Z^4 \right) r^5 \Bigg],
\end{aligned}
\tag{25}
$$

and

$$\epsilon_i = -3c_i + Z^2 + V_0. \tag{26}$$

As we will match electron densities, we will focus on the electron density in region $\mathcal{R}_1$

$$\rho_1(r) = \sum_{i=1}^{N} |\phi_i(r)|^2, \tag{27}$$

instead on the individual orbitals, by defining the global parameters $A = \sum_i a_i^2$ and $C = \sum a_i^2 c_i^2 / A$. The sum $\sum_i a_i^2 c_i^2$, which only appears in the forth and fifth-order terms, is approximated by AC^2 as it was justified in previous work [12]. We obtain:

$$\rho_1(r) = A \left[1 - 2Zr + (2C + Z^2)r^2 + \frac{Z}{3}(Z^2 - 10C)r^3 \right.$$
$$+ \frac{1}{30}(48C^2 - 11Z^4 + 38Z^2C - 6V_2)r^4$$
$$\left. - \frac{Z}{75}(168C^2 - 36V_2 - 42Z^2C - Z^4)r^5 \right]. \tag{28}$$

The method for solving the present approach reduces now to solve Eq. 18, obtaining the density in the region $\mathcal{R}_2$, which will be denoted $\rho_2(r)$. This resolution is similar to that of the Thomas–Fermi–Dirac model, but restricted to this region and using appropriate boundary conditions (see [12,13]).

We impose the matching conditions $\rho_1(r_0) = \rho_2(r_0)$ and $\rho_1'(r_0) = \rho_2'(r_0)$ to get the values of A and C. These parameters provide new values for the parameters of the potential. The new potential gives a new density and the process iterates until consistency is found with the correct normalization.

The energy is finally obtained by Eq. 1. We will split its expression in two terms:

$$E = \left(E_1 + \frac{1}{2}U_{12} \right) + \left(E_2 + \frac{1}{2}U_{12} \right), \tag{29}$$

where

$$E_1 + \frac{1}{2}U_{12} = \int_{\mathcal{R}_1} d\vec{r}\, e_1(r), \tag{30}$$

and the energy density can be written as:

$$e_1(r) = \sum_i \phi_i^* \left[\epsilon_i - \frac{1}{2}\left(V(r) + \frac{Z}{r} \right) \right] \phi_i. \tag{31}$$

If we substitute the potential given by Eq. 20, we will only use terms up to r^3 in ϕ_i for consistency. Using also Eq. 26 and the parameters A and C defined above, we can express:

$$e_1(r) = \left[-3C + Z^2 + V_0 - \frac{1}{2}(V_0 - V_2 r^2 + V_3 r^3) \right] \rho_1(r), \tag{32}$$

using the same approximation for AC^2 mentioned above.

The second term can be written as:

$$E_2 + \frac{1}{2}U_{12} = \int_{\mathcal{R}_2} d\vec{r}\, e_2(r), \tag{33}$$

where

$$e_2(r) = C_k[\rho(r)]^{5/3} + C_e[\rho(r)]^{4/3} + \frac{1}{2}\left[V(r) - \frac{Z}{r}\right]\rho(r), \tag{34}$$

and will be evaluated using numerical integration.

The only parameter which remains free is the value of the matching point r_0. In previous versions of this model [12], it was fixed by the condition $e_1(r_0) = e_2(r_0)$, i.e. the one that makes the energy density continuous. However, since the energy density is not uniquely defined, this condition does not seem to come from a fundamental argument. We will study the role of r_0 in a benchmark system that can be analytically solved.

4 Test of the model for a system of electrons in a bare coulomb field

For a system of non-interacting electrons attracted by a bare nucleus $v(r) = -Z/r$ (i.e. Bohr's atom), the exact solution is known and this model can be solved also exactly. Therefore, it is a benchmark system for testing the present approach.

Moreover, this theoretical system has also been also classically employed for comparing semiclassical methods with exact solutions for atomic properties depending on strongly bound electrons. In particular this comparison for the energy led to the following asymptotic expression for the energy of a neutral atom [14]:

$$E = -0.7687Z^{7/3} + \frac{1}{2}Z^2 - 0.294Z^{5/3}. \tag{35}$$

This formula, with errors less than 1% for most atoms, was obtained by adding to the Thomas–Fermi energy estimation the so-called Scott correction [14]. This was found by a comparison of the semiclassical and exact energies of a non-repulsive closed-shell electron atom, from the assumption that the main correction to the semiclassical estimation resides on the electrons closest to the nucleus. Then, this correction was estimated by neglecting the electron–electron interaction.

This is also the aim of this work, where we intend to improve the semiclassical methods in the near-nuclear region, and to correct the semiclassical estimations of all atomic properties in a similar way as the Scott correction improves the energy.

For these reasons we have solved the present model for a system of N electrons in a bare coulomb field. Assuming that the main deficiencies of the semiclassical approaches come from the description of the near-nuclear region, where the nuclear attraction dominates the electron–electron repulsions, we can estimate the accuracy of the present method for real atoms from the accuracy of its approach for these systems.

The energy of a closed-shell system of this type, can be easily expanded in powers of $N^{-1/3}$ when the number of electrons, N, is large:

$$E_{ex} \sim Z^2\left[-\left(\frac{3}{2}\right)^{1/3}N^{1/3} + \frac{1}{2} - \frac{1}{18}\left(\frac{3}{2}\right)^{2/3}N^{-1/3} + O\left(N^{-2/3}\right)\right]. \tag{36}$$

Other density-dependent properties, such as the density at the nucleus and the radial expectation values are easily obtained from the hydrogenic orbitals, and can be expanded in powers of $N^{-1/3}$:

$$\rho(0)_{\text{ex}} \sim \frac{2}{\pi} \zeta(3) Z^3, \tag{37}$$

$$\langle r^{-2} \rangle_{\text{ex}} \sim \frac{2\pi^2}{3} Z^2, \tag{38}$$

$$\langle r^{-1} \rangle_{\text{ex}} \sim 2 \left(\frac{3}{2}\right)^{1/3} Z N^{1/3} - Z - \frac{1}{6} \left(\frac{2}{3}\right)^{1/3} Z N^{-1/3} + O\left(Z N^{-2/3}\right), \tag{39}$$

$$\langle r \rangle_{\text{ex}} \sim \frac{3}{4} \left(\frac{3}{2}\right)^{2/3} Z^{-1} N^{5/3} + \frac{1}{8} \left(\frac{5}{2^{3/2} 3^{1/3}} - 3\right) Z^{-1} N + O\left(Z^{-1} N^{2/3}\right), \tag{40}$$

and

$$\langle r^2 \rangle_{\text{ex}} \sim \frac{9}{8} \left(\frac{3}{2}\right)^{1/3} Z^{-2} N^{7/3} + \frac{1}{16} \left(\frac{3}{2}\right)^{1/3} \left[7 - 9 \left(\frac{3}{2}\right)^{1/3}\right] Z^{-2} N^{5/3}$$
$$+ O\left(Z^{-2} N^{4/3}\right). \tag{41}$$

We will compare the estimations of the present approach with all these values. The original Thomas–Fermi method, applied to these systems, was able to take into account the first term of the expressions for E_{ex}, $\langle r^{-1} \rangle_{\text{ex}}$, $\langle r \rangle_{\text{ex}}$ and $\langle r^2 \rangle_{\text{ex}}$, however, the values for $\rho(0)_{\text{ex}}$ and $\langle r^{-2} \rangle_{\text{ex}}$ were infinity.

The present approach for these systems can be analitically solved. The U_{11}, U_{12}, U_{22} and K_2 terms in Eq. 1 are not present since they are caused by the repulsion among the electrons. The density in region $\mathcal{R}_1$ is given by

$$\rho_1(r) = A \left[1 - 2Zr + (2C + Z^2)r^2 + \frac{Z}{3}(Z^2 - 10C)r^3\right], \tag{42}$$

where we have neglected the fourth and fifth-order terms for symplicity and to keep consistency with the energy density, which now can be written as:

$$e_1(r) = A(Z^2 - 3C) \left[1 - 2Zr + (2C + Z^2)r^2 + \frac{Z}{3}(Z^2 - 10C)r^3\right]. \tag{43}$$

The contribution to the energy of region $\mathcal{R}_1$ is therefore given by:

$$E_1 = 4\pi \int_0^{r_0} r^2 e_1(r)\,dr$$

$$= 4\pi A(Z^2 - 3C)r_0^3 \left[\frac{1}{3} - \frac{Z}{2}r_0 + \frac{1}{5}(2C + Z^2)r_0^3 + \frac{Z}{18}(Z^2 - 10C)r_0^4 \right], \tag{44}$$

and the fraction of electrons in this region is:

$$N_1 = 4\pi \int_0^{r_0} r^2 \rho_1(r)\,dr$$

$$= 4\pi A r_0^3 \left[\frac{1}{3} - \frac{Z}{2}r_0 + \frac{1}{5}(2C + Z^2)r_0^3 + \frac{Z}{18}(Z^2 - 10C)r_0^4 \right], \tag{45}$$

which is a particular case of the one-electron radial expectation values, given by:

$$\langle r^k \rangle_1 = 4\pi \int_0^{r_0} r^{k+2}\rho_1(r)$$

$$= 4\pi A r_0^{k+3} \left[\frac{1}{k+3} - \frac{2Z}{k+4}r_0 + \frac{2C+Z^2}{k+5}r_0^2 + \frac{Z^3 - 10ZC}{3(k+6)}r_0^3 \right]. \tag{46}$$

The description of region $\mathcal{R}_2$ is reduced to:

$$\frac{5}{3}C_k[\rho_2(r)]^{2/3} - \frac{Z}{r} + \lambda = 0, \qquad \vec{r} \in \mathcal{R}_2, \tag{47}$$

which gives:

$$\rho_2(r) = \frac{1}{3\pi^2}\left(\frac{2Z}{r}\right)^{3/2}\left(1 - \frac{r}{r_l}\right)^{3/2}, \qquad r \le r_l, \tag{48}$$

where $r_l = Z/\lambda$ and represents the atomic radius.

Integrals of ρ_2 can be calculated in powers of $t = r_0/r_l$, assuming this ratio is small. In particular, for the radial expectation values of orders greater than -2, we obtain:

$$\langle r^k \rangle_2 = \frac{4}{3\pi}(2Z)^{3/2}\left[\int_0^{r_l} r^{k+\frac{1}{2}}\left(1 - \frac{r}{r_l}\right)^{3/2}dr - \int_0^{r_0} r^{k+\frac{1}{2}}\left(1 - \frac{r}{r_l}\right)^{3/2}dr \right]$$

$$= \frac{4}{3\pi}(2Z)^{3/2}\left[\frac{\Gamma(k+3/2)\Gamma(5/2)}{\Gamma(k+4)}r_l^{k+\frac{3}{2}} - \frac{(r_0/r_l)^{k+\frac{3}{2}}}{k+\frac{3}{2}} \right.$$

$$\times \ _1F_2(k + 3/2; -3/2, k + 5/2; r_0/r_l)\Bigg]$$

$$= \frac{4}{3\pi}(2Z)^{3/2}\frac{\Gamma(k+3/2)\Gamma(5/2)}{\Gamma(k+4)}\left(\frac{r_0}{t}\right)^{k+\frac{3}{2}}$$

$$\times \left[1 - \frac{\Gamma(k+4)}{(k+\frac{3}{2})\Gamma(k+3/2)\Gamma(5/2)}t^{k+\frac{3}{2}} + O\left(t^{k+\frac{5}{2}}\right)\right], \tag{49}$$

where $_1F_2$ denotes a hypergeometric function. For $\langle r^{-2}\rangle$, since the above decomposition is not possible, we will make use of a linear transformation formula for the hypergeometric function obtained:

$$\langle r^{-2}\rangle_2 = \frac{4}{3\pi}(2Z)^{3/2}\int_{r_0}^{r_l} r^{-\frac{3}{2}}\left(1 - \frac{r}{r_l}\right)^{3/2}dr$$

$$= \frac{8}{15\pi}(2Z)^{3/2}r_l^{-1/2}\left(1 - \frac{r_0}{r_l}\right)^{5/2}\ _1F_2(5/2; 3/2, 7/2; 1 - r_0/r_l)$$

$$= \frac{8}{15\pi}(2Z)^{3/2}r_l^{-1/2}\left(1 - \frac{r_0}{r_l}\right)^{5/2}\left[5\left(\frac{r_l}{r_0}\right)^{1/2}\ _1F_2(1; 2, 1/2; r_0/r_l)\right.$$

$$\left. - \frac{15\pi}{4}\ _1F_2(5/2; 3/2, 3/2; r_0/r_l)\right]$$

$$= \frac{8}{3\pi}(2Z)^{3/2}r_0^{-1/2}\left[1 - \frac{3\pi}{4}t^{1/2} + O(t)\right]. \tag{50}$$

The energy density in this region can be written as:

$$e_2(r) = C_k\rho_2^{5/3} - \frac{Z}{r}\rho_2 = -\left[1 - \frac{3}{5}\left(1 - \frac{r}{r_l}\right)\right]\frac{Z}{r}\rho_2(r), \tag{51}$$

and the integration in region $\mathcal{R}_2$ gives:

$$E_2 = -\frac{Z^{5/2}r_0^{1/2}}{2^{1/2}}t^{-1/2}\left[1 - \frac{64}{15\pi}t^{1/2} + O\left(t^{5/2}\right)\right]. \tag{52}$$

The conditions of continuity of ρ and ρ' are applied now. Using $\rho_1(r_0)/\rho_1'(r_0) = \rho_2(r_0)/\rho_2'(r_0)$ and defining $\mu = Zr_0$ and $y = C/Z^2$ we find:

$$\frac{1 - 2\mu + (2y+1)\mu^2 + (1 - 10y)\mu^3/3}{2 - 2(2y+1)\mu - (1 - 10y)\mu^2} = \frac{2}{3}\mu(1 - t), \tag{53}$$

and from $\rho_1(r_0) = \rho_2(r_0)$ the value of A can be obtained:

$$A = \frac{1}{3\pi^2}\left(\frac{2Z}{r}\right)^{3/2}\frac{(1-t)^{3/2}}{1-2\mu+(2y+1)\mu^2+(1-10y)\mu^3/3}. \tag{54}$$

The definitions of μ and y are inspired from the numerical scaling found for r_0 and C in the previous work, and as we will see immediately, these new parameters will result independent of Z and N, at first order.

The parameter t can be found from the normalization condition:

$$N = N_1 + N_2 = N_1 + \frac{1}{3\sqrt{2}}\left(\frac{\mu}{t}\right)^{3/2}\left[1 - \frac{32}{3\pi}t^{3/2} + O\left(t^{5/2}\right)\right], \tag{55}$$

which can be solved for t and shows up how this parameter scales with $N^{-2/3}$. For large N:

$$t = \frac{\mu}{3^{2/3}2^{1/3}}N^{-2/3}\left[1 + O\left(\frac{N_1}{N}\right)\right]. \tag{56}$$

Now we solve the problem completely in terms of μ, the only parameter which will remain free for the moment. We will assume that this parameter behaves asymptotically as a constant when $N \to \infty$, and solve all the parameters as power series of $1/N$.

The parameter y is obtained from Eq. 53, which leads to:

$$y = \frac{3\mu^3 + 7\mu^2 - 10\mu + 3}{2\mu^2(15\mu - 7)}\left[1 + O\left(N^{-2/3}\right)\right], \tag{57}$$

and using Eq. 54 we obtain:

$$A = \rho(0) = \frac{\sqrt{2}(15\mu - 7)}{\pi^2\mu^{3/2}(6\mu^3 - 20\mu^2 + 21\mu - 6)}Z^3\left[1 + O\left(N^{-2/3}\right)\right]. \tag{58}$$

Then, giving a value for μ, all the parameters required for evaluating the density-dependent quantities are obtained. We will here test two different approaches for determining this value:

(i) Determination of $r_0 = \mu/Z$ from the continuity of the energy density. This will provide a test of the procedure employed in previous works. Utilizing $e_1(r_0)/\rho_1(r_0) = e_2(r_0)/\rho_2(r_0)$ we find:

$$(3y - 1)\mu = -\frac{3}{5}(1 - t) + 1. \tag{59}$$

This can be solved by using:

$$\mu = \mu_0 + \mu_2 N^{-2/3}, \tag{60}$$

where μ_0 and μ_1 do not depend on N. Using Eqs. 56, 57 we find that μ_0 satisfy:

$$105\mu_0^3 - 115\mu_0^2 + 122\mu_0 - 45 = 0, \tag{61}$$

which has only one real root, $\mu_0 = 0.495617$, very approximate to the values obtained from the numerical solution of the approach for normal atoms. Using this value of μ, we obtain for the energy

$$E = -\left(\frac{3}{2}\right)^{1/3} Z^2 N^{1/3} + 0.520106 Z^2 + O\left(Z^2 N^{-2/3}\right), \tag{62}$$

where the leading correction to the TF energy is appropriate in order (Z^2), with a coefficient approximate to the exact one $(1/2)$. No corrections of order $N^{-1/3}$ appear.

(ii) Try to match the expansion of the energy. This can be done by means of the following expression for μ:

$$\mu = \mu_0 + \mu_1 N^{-1/3} + \mu_2 N^{-2/3}, \tag{63}$$

with coefficients to be determined by matching the exact energy, given by Eq. 36. This can be fulfilled with $\mu_0 = 0.494375$ and $\mu_1 = -0.00432188$. μ_2 can be chosen arbitrarily because it contributes to the next term $(Z^2 N^{-2/3})$.

With these choices of μ_0 and μ_1 the rest of parameters are given by:

$$r_0 = Z^{-1}\left[0.494375 - 0.00432188 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{64}$$

$$t = r_0/r_l = N^{-2/3}\left[0.188496 - 0.00164839 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{65}$$

$$C = Z^2\left[0.637823 - 0.129338 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{66}$$

and

$$A = \rho(0) = Z^3\left[0.783352 - 0.024852 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{67}$$

which completes the description of the density. The values for the density-dependent properties obtained from this method, to be compared to Eqs. 37–41, are:

$$\langle r^{-2} \rangle = Z^2\left[6.51392 - 3.55347 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{68}$$

$$\langle r^{-1} \rangle = Z N^{1/3}\left[12^{1/3} - 1.04777 N^{-1/3} + O\left(N^{-2/3}\right)\right], \tag{69}$$

$$\langle r \rangle = Z^{-1} N^{5/3}\left[\frac{3}{4}\left(\frac{3}{2}\right)^{2/3} + O(N^{-1})\right], \tag{70}$$

and

$$\langle r^2 \rangle = Z^{-2} N^{7/3} \left[\frac{9}{8} \left(\frac{3}{2} \right)^{1/3} + O(N^{-1}) \right]. \tag{71}$$

Therefore, with these parameters, the energy is reproduced up to three orders, the leading terms for $\rho(0)$ and $\langle r^{-2} \rangle$ are provided with constant errors of 2.3 and 1%, respectively, the second term of $\langle r^{-1} \rangle$ is given with a constant error of 4.8%. The first order of the radial expectation values of positive order, which were reproduced by the original Thomas–Fermi theory are not modified by the present corrections. This gives us an idea of the accuracy that the application of this method can provide when applied to real systems.

The scaling of r_0, the point beyond which local plane waves has been used for representing the electron wavefunctions, as Z^{-1}, is the same as the one Schwinger found [15] for the validity of this approximation.

5 Application to real atoms: computational procedure and results

The computational procedure is simplified if r_0 is fixed from the start. We can use an expansion of the type of Eq. 64, but the optimal coefficient of $N^{-1/3}$ for the energy may change when including electron–electron interaction. In addition to this we can include a coefficient for $N^{-2/3}$ for a better matching of the energies for small values of N.

We will describe a computational approach for obtaining the energy, density and potential of an atom:

The resolution of Eq. 18, as in the standard Thomas–Fermi–Dirac approach is performed via the function $\chi(x)$ defined by

$$V(r) + \lambda - \frac{1}{2\pi^2} = -\frac{Ze^2}{r} \chi(x), \tag{72}$$

which is found by solving the differential equation

$$\frac{d^2\chi}{dx^2} = x \left[\beta + \left(\frac{\chi}{x} \right)^{1/2} \right]^3, \tag{73}$$

where $x = r/b$, b is a scale factor:

$$b = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{2/3} Z^{-1/3}, \tag{74}$$

and

$$\beta = \frac{3}{2} \frac{1}{(6\pi Z)^{2/3}}. \tag{75}$$

The density in region $\mathcal{R}_2$ is found by the relationship

$$\rho_2(r) = \frac{2^{3/2}}{3\pi^2} \left\{ \frac{1}{\sqrt{2\pi}} + \sqrt{\frac{Z}{r}} [\chi(r/b)]^{1/2} \right\}^3, \quad r < r_l, \tag{76}$$

and the constraints for the resolution are:

1. Usual condition in the atomic limit $r_l = bx_l$:

$$\chi(x_l)/x_l = \beta^2/16. \tag{77}$$

2. Value of the potential at r_0:

$$V(r_0) = -\frac{Z}{r_0}\chi(x_0) - \lambda + \frac{1}{2\pi^2} = -\frac{Z}{r_0} + \frac{N_1}{r_0} + \langle r^{-1} \rangle_2, \tag{78}$$

   where

$$\langle r^{-1} \rangle_2 = \frac{Z}{b} \left[\chi'(x_l) - \chi'(x_0) \right]. \tag{79}$$

3. Potential at r_l:

$$V(r_l) = -\frac{Z}{r_l}\chi(x_l) - \lambda + \frac{1}{2\pi^2} = -\frac{Z}{r_l} + \frac{N}{r_l}. \tag{80}$$

4. Normalization condition:

$$N = N_1 + Z \left[x_l\chi'(x_l) - x_0\chi'(x_0) - \chi(x_l) + \chi(x_0) \right]. \tag{81}$$

The procedure is as it follows: given particular values of Z, N and r_0, we perform a loop for determining the scaled atomic radius x_l. For each x_l, we set an initial value (very small) for $\chi'(x_l)$, and, fixing $\chi(x_l)$ from Eq. 77, we solve numerically the differential equation from x_l to $x_0 = r_0/b$ with a fourth order Runge–Kutta method. We then calculate $\rho_2(r_0)$, $\rho_2'(r_0)$, and find C and A from the matching conditions $\rho_1(r_0) = \rho_2(r_0)$ and $\rho_1'(r_0) = \rho_2'(r_0)$. After that, N_1 is evaluated, λ is obtained from Eq. 80, and the loop is stopped when Eq. 78 holds within a small error. Now, the normalization condition is applied for defining a new $\chi'(x_l)$, and we start again the loop in x_0. The procedure is repeated until $\chi'(x_l)$ converges to a stable value. With this technique, we can solve tens of atoms in a few seconds.

We have applied this procedure and we are able to match very approximately the formula for the energy given by Eq. 35 with the use of:

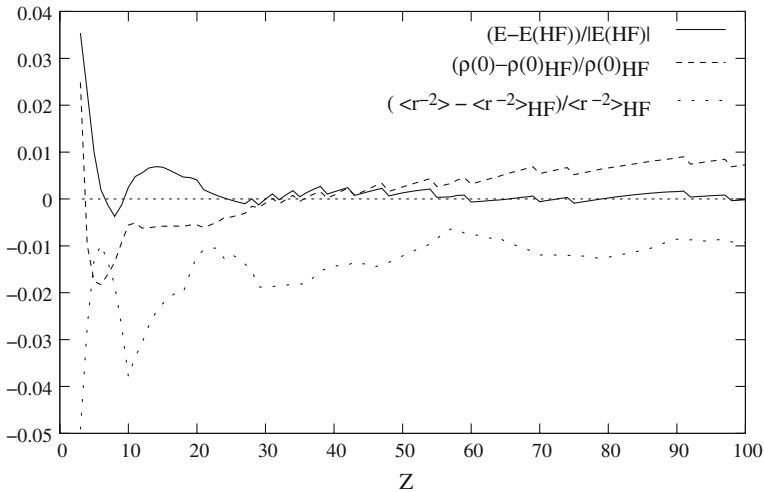$$r_0 = Z^{-1} \left(0.494375 + 0.006Z^{-1/3} + 0.03Z^{-2/3} \right). \tag{82}$$

Fig. 1 Plot of the relative differences of present work estimations with respect to Hartree–Fock values for the energy (*solid line*), density at the nucleus (*dashed line*) and $\langle r^{-2} \rangle$ (*dotted line*) of neutral atoms

Results for the energy, $\rho(0)$ and $\langle r^{-2} \rangle$ when using this choice of r_0 are illustrated in Fig. 1 for atoms from $Z = 3$–100 by their relative differences with respect to Hartree–Fock values obtained from the wavefunctions of Koga et al. [16].

6 Concluding remarks

In this work we have presented a modified Thomas–Fermi–Dirac method arising from the minimization of a semiexplicit density functional. Also, we have performed some improvements on its application, by means of different changes on the constraints.

The weakest assumption of this method, the choice of the matching point has been studied in detail. The test for the Bohr's atom shows up that the scaling of r_0 as Z^{-1} gives a correction for the energy by means of a term which scales exactly as the Scott correction in Thomas–Fermi theory. But the present model does not only provide estimations for the energy. For the lowest-order radial expectation values this test also shows that the main corrections to Thomas–Fermi theory are incorporated with the appropriate scaling. The remaining errors seem to be of the order of shell effects. This is clear for the energy, which from the analysis of the non-interacting electron atom, the relative errors should be expected of the order of N^{-1}, of the same order as these effects [17]. As correlation effects are of the same order, it seems that we have optimized the semiclassical description of atoms. This could serve as a partial tool for the approach of more complex problems.

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