Modified Thomas-Fermi-Dirac approach for the evaluation of atomic ground-state properties

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Atomic ground-state properties are evaluated by means of a modified semiclassical approach with a quantum-mechanical treatment of the near-nuclear region. The results for the energy and lowest-order radial expectation values are close to Hartree-Fock results, improving the Thomas-Fermi-Dirac-Weizsäcker estimates. [S1050-2947(99)01603-0]

I. INTRODUCTION

The great impact of the Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) methods for the study of fermionic systems is well known, providing simple schemes for adequate estimations of average properties [1]. For atoms, the discrepancies between TF(D) and Hartree-Fock (HF) results are mainly attributed to the description of the electron and energy density near the nucleus, where the electron cloud differs most from a local Fermi gas.

A great effort has been made to correct this deficiency [2–7], a very popular example being the gradient expansion of the energy functional [4–7]. Although providing adequate features for the electron density and great improvement on the energy values, there are several problems in its application: First, the gradient expansion cannot be extended beyond fourth order (the so-called Hodges term [8]) because the sixth-order term diverges for atoms; second, if we wish to retain as much as possible the simplicity of the original theory, the complication of the integro-differential equation that appears in this scheme usually restricts this method to the inclusion of the second-order term (the Thomas-Fermi-Dirac-Weizsäcker approach [4–6]) and for a good comparison to HF energies, the prefactor of the Weizsäcker term obtained from theoretical grounds (1/9) has to be replaced by 1/5 [4]. In addition to this, the values of the density close to the nuclei are much less accurate than those of the energy even when including the fourth-order correction [7].

A simpler alternative approach for correcting the density was proposed by Ashby and Holzman [2], replacing the TF density at short distances by a hydrogenic one (considering the $1s$ orbital for an effective nuclear charge), which matches the former at a point where the kinetic-energy density also matches.

In this work we propose an improvement of this procedure, based on the inclusion of electron exchange and a different treatment of the short-range density from the exact small-r limit of the s orbitals, according to a three-term expansion of the one-electron potential. Also, the boundary conditions differ from this reference. The description of our method now follows (atomic units are used throughout the paper).

II. THEORY

We will adopt, from an inner radius r_0 up to an atomic radius r_l, the electron and energy densities obtained from the standard TFD procedure [1], which is based on the relations

$$\rho_{TFD}(r) = \frac{2^{3/2}}{3\pi}\left[\frac{1}{\sqrt{2}\,\pi} + \sqrt{\frac{1}{2\,\pi^2} - V(r) + \epsilon_F}\right]^3 \quad (1)$$

for the density in terms of the potential, defined by

$$V(r) = -\frac{Z}{r} + \int \frac{\rho_{TFD}(r')}{|\vec{r}-\vec{r'}|}\, d\vec{r'}, \quad (2)$$

and for the energy density

$$\epsilon_{TFD} = C_k \rho_{TFD}^{5/3} - \frac{Z}{r}\rho_{TFD} + \frac{1}{2}\rho_{TFD}$$

$$\times \int \frac{\rho_{TFD}(r')}{|\vec{r}-\vec{r'}|}\, d\vec{r'} - C_e \rho_{TFD}^{4/3}$$

$$= C_k \rho_{TFD}^{5/3} - \frac{1}{2}\frac{Z}{r}\rho_{TFD} + \frac{1}{2}V(r)\,\rho_{TFD} - C_e \rho_{TFD}^{4/3}, \quad (3)$$

where

$$C_k = \frac{3}{10}(3\pi^2)^{2/3}, \quad (4)$$

$$C_e = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}. \quad (5)$$

All the quantities can be expressed in terms of the screening function $\phi(x)$, defined by

$$V(r) - \epsilon_F - \frac{1}{2\pi^2} = -\frac{Z}{r}\phi(x), \quad (6)$$

where x is related to the radial coordinate by

$$r = bx, \quad (7)$$

with

$$b = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3} Z^{-1/3} = 0.885\,341 Z^{-1/3}. \quad (8)$$

The values of $\phi(x)$ are obtained from the resolution of the TFD differential equation

$$\frac{d^2\phi}{dx^2} = x\left[\beta + \left(\frac{\phi}{x}\right)^{1/2}\right]^3, \tag{9}$$

where

$$\beta = \frac{3}{2}\frac{1}{(6\pi Z)^{2/3}}, \tag{10}$$

with the condition

$$\phi(0) = 1, \tag{11}$$

which provides the proper small-r limit for $V(r)$, and the condition at a limiting x_l,

$$\frac{\phi(x_l)}{x_l} = \frac{\beta^2}{16}, \tag{12}$$

for null pressure of the electron cloud at the atomic radius $r_l = bx_l$, the cutoff density. The fraction of electrons lying between r_0 and r_l, which are described by this TFD procedure, is given by

$$N_2 = Z[x_l\phi'(x_l) - x_0\phi'(x_0) - \phi(x_l) + \phi(x_0)], \tag{13}$$

where $x_0 = r_0/b$.

The Fermi energy ϵ_F is fixed by the constraint that the potential at the atomic radius be equal to $-(Z-N)/r_l$, where N is the total number of electrons, which implies that

$$\epsilon_F + \frac{1}{2\pi^2} = -\frac{Z-N}{r_l} + \frac{1}{32\pi^2}. \tag{14}$$

These complete the expressions required for the TFD description of the density in the range $r_0 \leq r \leq r_l$. For the near-nuclear region $r \leq r_0$, we base our description of the internal $\rho_I(r)$ and $\epsilon_I(r)$ upon the expansion of the potential for small values of r,

$$V(r) = -\frac{Z}{r} + V_0 + V_1 r + O(r^2), \tag{15}$$

and the corresponding one for the one-electron s-state wave functions (n stands for the principal quantum number)

$$\psi_n(r) = a_n[1 + b_n r + c_n r^2 + d_n r^3 + O(r^4)]. \tag{16}$$

Substituting these expressions in the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2 + V(r)]\psi_n = \epsilon_n\psi_n \tag{17}$$

for $V(r)$ given above and comparing the different terms in r, we find the relations

$$b_n = -Z, \tag{18}$$

$$c_n = \tfrac{1}{3}(Z^2 - \epsilon_n + V_0), \tag{19}$$

$$d_n = \tfrac{1}{18}[-Z^3 + 4Z(\epsilon_n + V_0) + 3V_1] = \tfrac{1}{6}(Z^3 - 4Zc_n + V_1). \tag{20}$$

Then the electron density is given by

$$\rho_I = \sum_n |\psi_n|^2 = \sum_n a_n^2\left[1 - 2Zr + (2c_n + Z^2)r^2 \right. $$
$$\left. + \frac{1}{3}(Z^3 - 10Zc_n + V_1)r^3 + O(r^4)\right], \tag{21}$$

where the sum runs over all occupied orbitals (the ocupation number is implicitly included in the coefficients a_n) and we have kept the parameter c_n instead of $\epsilon_n + V_0$ for simplicity. If we define the total parameters

$$A = \sum_n a_n^2, \tag{22}$$

$$C = \frac{\sum_n a_n^2 c_n}{\sum_n a_n^2}, \tag{23}$$

it is straightforward to write

$$\rho_I(r) = A[1 - 2Zr + (2C + Z^2)r^2 + \tfrac{1}{3}(Z^2 - 10ZC + V_1)], \tag{24}$$

which, if we determine the values of A and C, allows us to take into account implicitly the contribution of all n orbitals to the electron density. This is a consequence of the linear dependence of $|\psi_n|^2$ on the parameters a_n^2 and c_n.

The above expression for ρ_I and its first derivative will be matched to the TFD values at $r = r_0$. This allows us to obtain the values of A and C, provided r_0 and V_1 are known, by means of the expressions

$$C = \frac{1 + 2Z(R_0 - r_0) - 2Z^2 R_0 r_0 + (Z^2 - Z^3 R_0 - V_1 R_0)r_0^2 + (Z^3 + V_1)r_0^3/3}{4R_0 r_0 - 2(1 + 5ZR_0)r_0^2 + 10Zr_0^3/3}, \tag{25}$$

where $R_0 = \rho_{TFD}(r_0)/\rho'_{TFD}(r_0)$, and

$$A = \frac{\rho_{TFD}(r_0)}{1 - 2Zr_0 + (2C + Z^2)r_0^2 + \frac{1}{3}(Z^2 - 10ZC + V_1)r_0^3}. \tag{26}$$

The matching point r_0 will be determined by imposing continuity of the energy density, i.e., by matching the TFD expression with the inner one, which is given by

$$\epsilon_I(r) = \sum_n \epsilon_n |\psi_n|^2$$

$$= \sum_n a_n^2 (Z^2 + V_0 - 3c_n) \left[1 - 2Zr + (2c_n + Z^2)r^2 \right.$$

$$\left. + \frac{1}{3}(Z^3 - 10Zc_n + V_1)r^3 \right]. \tag{27}$$

We have to express the sum in terms of the total parameters A and C. Due to the presence of c_n^2 in the r^2 and r^3 terms, we make the following approximation for those terms:

$$\sum_n a_n^2 c_n^2 \approx \frac{\left(\sum_n a_n^2 c_n \right)^2}{\sum_n a_n^2}, \tag{28}$$

which is justified when the sum is mainly dominated by a single term (the $1s$ orbital). We can estimate the error of this approximation by considering the two most contributing hydrogenic orbitals ($1s$ and $2s$), for which $a_2 = a_1/\sqrt{8}$ and $c_2 = 3c_1/4$. The left-hand side of Eq. (28) would be equal to $1.070 a_1^2 c_1^2$, while the right-hand one would be $1.063 a_1^2 c_1^2$, an error less than 1%. Moreover, this approximation has to be done just in the third and fourth terms of the energy density for small distances. Therefore, with this approximation we obtain

$$\epsilon_I(r) = A(Z^2 + V_0 - 3C)[1 - 2Zr + (2C + Z^2)r^2$$

$$+ \frac{1}{3}(Z^3 - 10ZC + V_1)r^3]. \tag{29}$$

III. PROCEDURE

The specific procedure for the application of the present method is quite self-consistent: For a given value of x_l we solve numerically the TFD differential equation inward from the initial condition $\phi(x_l) = x_l \beta^2/16$, giving different values of $\phi'(x_l)$ until $\phi(0) = 1$ is reached at the end of the integration. Then all the values of $\phi(x)$ and $\phi'(x)$ are stored. The values of the potential $V(r)$ are obtained from $\phi(x)$ for $r = 0$ up to a value guessed for $r = r_0$ and fitted by the right-hand side of Eq. (15) [actually, $rV(r)$ is fitted in order to avoid singularity problems at $r = 0$]. This provides us with a

first estimate of V_0 and V_1. Then we recall the $\phi(x)$ and $\phi'(x)$ values and for any x we impose the continuity of ρ and ρ' at $r = bx$. The parameters A and C for any x are determined through Eqs. (25) and (26) with the V_1 value obtained from the previous fit. We then evaluate the energy density with Eq. (29) and compare to the TFD values [Eq. (3)]. For the x where both coincide, we identify the corresponding r as a new r_0 and start again the above procedure from the fitting of $V(r)$. This is done until the same value of r_0 is reached from one iteration to the next. Then the number of electrons is calculated. The fraction of inner electrons ($r \leq r_0$) is given by

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

$$= \frac{4}{3}\pi A^3 r_0^3 \left[1 - \frac{3}{2}Zr_0 + \frac{3}{5}(2C + Z^2)r_0^2 \right.$$

$$\left. + \frac{1}{6}(Z^3 - 10ZC + V_1)r_0^3 \right], \tag{30}$$

which has to be summed to the fraction of statistical ones N_2, given by Eq. (13). Then the whole procedure is repeated for different initial guesses of x_l until $N = N_1 + N_2$ is equal to the number of electrons of the atom under consideration.

The self-consistent procedure for the determination of r_0 for any x_l is extremely fast (less than five iterations in any case). It does not depend upon the initial guess of r_0 and allows us to complete the calculations in a very short time.

We want to point out that with the present scheme we include the first terms of the exact wave function for the potential given by Eq. (15), without taking into account any property outside the sphere of radius r, in contrast to previous work [2], where the integrability of the wave function at $r \rightarrow \infty$ is implicitly taken into account.

IV. RESULTS

The present procedure provides then the values of the electron density

$$\rho(r) = \begin{cases} \rho_I(r) & \text{if } r < r_0 \\ \rho_{TFD} & \text{if } r \geq r_0 \end{cases} \tag{31}$$

and the total energy, which is calculated by

TABLE I. Energies of single charged positive ions (in keV) evaluated by the method of the present work (PW) compared to previous work and Hartree-Fock values (HF) [9].

Z	$-E$ (TF)	$-E$ (HF)	$-E$ (Ref. [2])	$-E$ (PW)
11	5.62	4.40	3.59	4.27
37	95.4	80.0	72.3	79.0
55	240.6	205.6	189.5	204.6
79	560.3	486.0	454.7	484.3
87	701.9	611.4	573.6	611.3

TABLE II. Energies of some neutral atoms evaluated in the present work (PW) compared to Thomas-Fermi-Dirac-Weizsäcker values [10] using prefactors $\lambda = 1/9$ [TFDW(1/9)] and $\lambda = 1/5$ [TFDW(1/5)] in the gradient correction. Also, Hartree-Fock values (HF) from Ref. [11] are displayed for comparison.

Z	$-E$ (TF)	$-E$ [TFDW(1/9)]	$-E$ [TFDW(1/5)]	$-E$ (PW)	$-E$ (HF)
10	165.619	139.886	128.755	125.893	128.547
20	834.667	720.871	674.851	666.688	676.758
30	2149.78	1881.99	1776.55	1762.61	1777.85
40	4206.46	3717.24	3527.58	3492.34	3538.97
50	7080.11	6301.06	6002.23	5963.79	6022.92
60	10 834.2	9696.28	9263.21	9295.73	9283.70
70	15 524.1	13 957.8	13 365.3	13 406.3	13 391.5
80	21 194.2	19 134.6	18 357.5	18 406.5	18 409.0
90	27 904.6	25 271.4	24 284.4	24 134.6	24 359.6

$$E = 4\pi \left[\int_0^{r_0} r^2 \epsilon_I(r)dr + \int_{r_0}^{r_l} r^2 \epsilon_{TFD}(r)dr \right]. \quad (32)$$

Also we will evaluate some radial expectation values

$$\langle r^k \rangle = 4\pi \int_0^{r_l} r^{k+2}\rho(r)dr \quad (33)$$

in order to compare the quality of the density obtained with respect to HF values.

The numerical results for the energy of some positive ions are shown in Table I and are compared to the results of Ashby and Holzman [2] as well as HF values [9]. The improvement is quite noticeable and it is attributed not only to the inclusion of exchange but also to the different treatment of the inner electron and energy densities, which provides a larger correction. As an illustration of this, notice that the sole introduction of exchange in the original procedure of Ref. [2], e.g., for $Z = 87$, modifies the energy result from -574 to -586 keV.

In the case of neutral atoms, the two constraints [$\phi(0) = 1$ for a proper small-r behavior of the potential and $N = Z$ for a proper normalization] cannot be held simultaneously as precisely as we wish due to numerical precision problems [values of $\phi'(x_l)$ extremely small]. This problem is avoided by performing a two-step procedure. With a first run, we determine the parameters in the potential, letting the first constraint accurately hold but relaxing slightly the normalization one (a few percent, which does not affect the potential at short distances). Then a second run follows, where the density and energy are evaluated keeping the parameters of the potential fixed from the previous step and imposing now the proper normalization.

This leads to the energy values displayed in Table II, where comparisons to the TF and Thomas-Fermi-Dirac-Weizsäcker (TFDW) estimates with coefficients 1/9 [TFDW(1/9)] [10] and 1/5 [TFDW(1/5)] [10] and HF [11] calculations are included. We observe how the present work provides accurate estimations of the energy if we take into account the simplicity of the method and its statistical nature.

As an illustration of the values of the parameters involved, the self-consistent procedure for krypton ($Z = 36$) gives $x_l = 16.79$, $r_0 = 0.0139$, $\phi(x_0) = 0.931\,553\,809\,44$, $\phi'(x_0) = -1.175\,703\,489$, $V_0 = 201.438\,114\,3$, $V_1 = -1\,793.867\,075$, $A = 33\,358.58$, $C = 869.1039$, and $D = -13\,381.47$, which provides an energy of -2719.37 a.u. to be compared to the HF result of -2752. a.u. In Table III the most important parameters for some atoms are presented.

With respect to the electron density, illustrated in Figs. 1 [$r^2\rho(r)$] and 2 [$\rho(r)$] for the case of krypton ($Z = 36$), this procedure corrects the main deficiency of the TFD method and gives values very close to the HF density at short distances from the nuclei. At larger distances, our density values join the curve of the TFD method in the region where a fair average of the different shell contributions is given. These facts are also reflected in the radial expectation values and the density at the nucleus, which are displayed in Table IV. The values of $\rho(0)$, $\langle r^{-2} \rangle$, and $\langle r^{-1} \rangle$ are very close to

TABLE III. Parameters of the present model (a.u.) for different neutral atoms.

| Z	r_0	V_0	V_1	A	B	C	x_l	r_l
10	5.03[-2]	35.86	-133.1	6.535[2]	74.17	-3.500[2]	9.787	4.02
20	2.51[-2]	91.18	-543.3	5.513[3]	280.3	-2.494[3]	13.17	4.30
30	1.67[-2]	157.6	-1242	1.907[4]	617.3	-8.054[3]	15.58	4.44
40	1.25[-2]	232.2	-2221	4.609[4]	1055	-1.784[4]	17.53	4.53
50	1.00[-2]	313.6	-3486	9.074[4]	1659	-3.505[4]	19.18	4.60
60	8.30[-3]	400.6	-5016	1.565[5]	2522	-6.573[4]	20.63	4.66
70	7.11[-3]	493.0	-6842	2.501[5]	3408	-1.030[5]	21.93	4.72
80	6.22[-3]	590.0	-8944	3.753[5]	4416	-1.517[5]	23.12	4.75
90	5.55[-3]	691.3	-11332	5.432[5]	5158	-1.899[5]	24.21	4.78
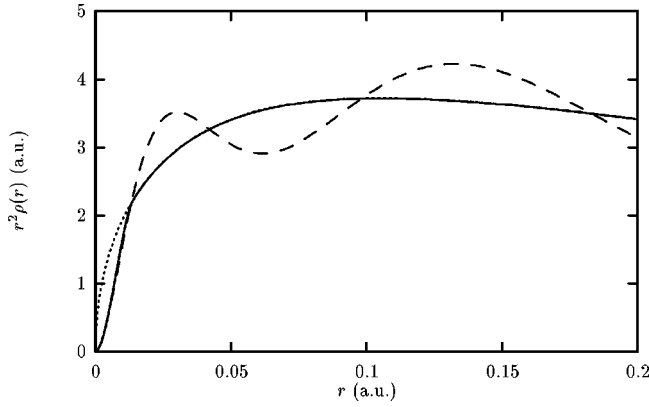
FIG. 1. Radial electron density of krypton of the present work (solid line) compared to HF values [16] (dashed line) and TFD values (dotted line). The solid line has a continuous derivative at any point, although it may not seem so in the graph.
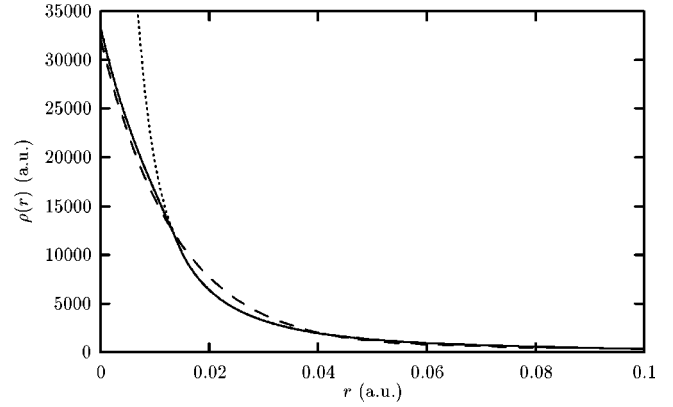

FIG. 2. Electron density of krypton evaluated with the method of the present work (solid line) compared to HF values (dashed line) and TFD values (dotted line).

the HF ones, which reflects the appropriate small-r behavior [note in addition that the cusp relation $\rho'(0) = -2Z\rho(0)$ is exactly incorporated] and improves greatly the values obtained from a gradient expansion calculation including even fourth-order terms [e.g., for krypton, the TFDW(1/9) value of $\rho(0)$ is 3.1217×10^5, while the TFDW(1/5) value is 1.2662×10^5 and the TFDW+Hodges term gives 68 199 [7]]. With the present method we obtain 33 358, which compares fairly to the HF result of 32 228 a.u.

We have also compared our results with other modified TF models of the literature, e.g., those of Parr and Ghosh [12,13] as cited by Parr and Yang [1], those of Csavinsky [14], and those of Wang and Parr [15]. With respect to the first of these approaches, which utilize additional conditions for the finiteness of the electron density at the nucleus and does not include exchange, our method improves slightly the energy value of small-Z atoms (for Ne, -125.89 versus -124.16, to be compared to the HF value of -128.55 a.u. [16]) and both give similar results for large-Z atoms (for Rn, $-22\,018.1$ versus $-22\,019.7$). The improvement is more noticeable for the density at the nucleus; the above-mentioned Parr-Ghosh method provides a value for krypton of 20 178 a.u. [13] (there are other variants of this method that provide better values, the best one being 29 990.4, but this choice gives less accurate energies).

With respect to the approaches of Csavinsky [14] and Wang and Parr [15], both including exchange, we can com-

pare the value reported for the energy of Na, the first giving values of -182.12 (without the Weizsäcker term) and -171.56 (with the Weizsäcker term) and the second giving a best value of -164.5. The present approach provides a value of -158.04, to be compared to the HF value of -161.8. Finally, the corrections for strongly bound electrons of Englert and Schwinger [3] predict an energy value for $Z=N$ $=80$ of $-18\,340$ a.u., to be compared to the present estimation of $-18\,406.5$ and the HF value of $-18\,409.0$.

As the present approach compares rather well with HF results, we remember the remaining gap to the *exact* nonrelativistic result, i.e., the correlation energy. A configuration interaction [17] for the case of neon [17] provides an estimated energy of $-128.937\,0$, the HF value being -128.55 a.u. and the present work estimation -125.89 (we have taken a light atom as an example because the percentage of correlation energy with respect to the total value decreases with Z). Therefore, most of the remaining gap between the modified TFD value and the exact one appears to be the limitations of the TFD procedure rather than the effects of correlation.

V. CONCLUSION

In summary, we find that by means of a simple but consistent approach for correcting the short distance treatment of

TABLE IV. Results for the electron density at the nucleus and some radial expectation values for neutral atoms with the present modified TFD method (PW) compared to Hartree-Fock values (HF) [16].

Z	$\rho(0)_{PW}$	$\rho(0)_{HF}$	$\langle r^{-2} \rangle_{PW}$	$\langle r^{-2} \rangle_{HF}$	$\langle r^{-1} \rangle_{PW}$	$\langle r^{-1} \rangle_{HF}$	$\langle r \rangle_{PW}$	$\langle r \rangle_{HF}$
10	653.47	620.15	414.59	414.90	30.05	31.11	9.96	7.89
20	5513.45	5319.92	1815.1	1834.4	79.37	80.16	17.44	21.25
30	19 071.92	18 448.59	4272.6	4312.0	139.59	142.06	23.94	22.00
40	46 092.11	44 466.83	7830.5	7901.0	208.10	210.79	29.87	32.68
50	90 745.07	87 899.02	12 473	12 612	283.25	286.51	35.38	36.47
60	1.564[5]	1.533[5]	18 200	18 463	364.31	366.87	40.58	45.40
70	2.500[5]	2.449[5]	25 071	25 435	450.42	455.83	45.53	45.35
80	3.753[5]	3.674[5]	33 095	33 576	541.30	548.13	50.27	48.00
90	5.432[5]	5.256[5]	42 472	42 895	636.91	642.23	54.84	61.12

the Thomas-Fermi-Dirac method, fair comparisons to Hartree-Fock results can be found not only for the energy values but also for the density near the nucleus, where the TF method and its extensions describe it worst. This success appears to be related to the exact asymptotic nature of the expressions utilized and the present results are very promising for further applications such as the inclusion of relativistic effects, which depends crucially on the near-nuclear region.

[1] Among the number of textbooks in which the TF and related theories are described see, for example, N.H. March, *Self-Consistent Fields in Atoms* (Pergamon, Oxford, 1975), and R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989). See also references therein.

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