

## New quadratic nondifferential Thomas-Fermi-Dirac-type equation for atoms

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This paper reports the first quadratic, nondifferential, and self-consistent solution to a Thomas-Fermi-Dirac(TFD)-type equation for many-electron atoms. The essential feature in the Euler-Lagrange equation is the inclusion of a "first-gradient" correction to the TF kinetic energy, which leads to chemical binding in molecules and solids. The calculations are easier to perform than other TFD-type calculations, while the radial density and energy obtained compare very well with similar calculations.

The Thomas-Fermi-Dirac (TFD) method<sup>1</sup> is the early precursor of powerful density-functional methods<sup>1-5</sup> for studying structure and dynamics of many-particle systems (nuclei, atoms, molecules, and solids). It has also raised the possibility of *direct ab initio* calculation of the single-particle density through a *single* equation, bypassing the wave function in both time-independent<sup>7-9</sup> and time-dependent<sup>10-13</sup> situations. Here, starting from a new kinetic-energy-density (KED) functional,<sup>14</sup> we propose a TFD-type equation for many-electron atoms which is easier to solve than other similar equations and may therefore be more advantageous in relatively complicated situations.

We start from the usual<sup>1</sup> basic density-functional equations ( $\rho$  is the electron density)

$$E[\rho] = T[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho], \quad (1)$$

$$\frac{\delta E[\rho]}{\delta \rho} = \mu, \quad (2)$$

and replace  $E_{xc}$  by the Dirac exchange term  $E_x$ . The terms in Eq. (1) are written as (atomic units employed)

$$T[\rho] = C_k \int \rho^{5/3} d\mathbf{r} - \frac{1}{40} \int \frac{\mathbf{r} \cdot \nabla \rho}{r^2} d\mathbf{r}, \quad (3)$$

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

$$v(\mathbf{r}) = -Z/r \text{ for an atom}, \quad (4)$$

$$E_x[\rho] = -C_x \int \rho^{4/3} d\mathbf{r}, \quad C_x = \frac{3}{4\pi} (3\pi^2)^{1/3}. \quad (5)$$

Equation (3) contains the "first-gradient" correction<sup>14</sup> to the TF KED and, with near-Hartree-Fock (HF) atomic densities,<sup>15</sup> gives significantly better values<sup>14,16</sup> for the global KE and the local KED (for  $0 \leq r \leq \infty$ ) for spherically symmetric systems than any other prescription. In particular, the atomic KED in Eq. (3) goes to  $+\infty$  as  $r \rightarrow 0$ . Although this is essential for the stability of matter,<sup>17</sup> other KED functionals<sup>18,19</sup> generally either tend to a finite value or to  $(-\infty)$  as  $r \rightarrow 0$ . The  $(\frac{1}{40})$  factor in Eq. (3) was discovered by trial with the Ne atom, al-

though it works even better with certain other atoms.<sup>14</sup> This factor may be understood in two ways: For spherically symmetric densities,<sup>20</sup>

$$-\int \frac{\mathbf{r} \cdot \nabla \rho}{r^2} d\mathbf{r} = \int \frac{\rho}{r^2} d\mathbf{r}. \quad (6)$$

The Weizsäcker correction  $T_W$  is bounded from below as<sup>21,22,20,23</sup>

$$T_W > \frac{1}{8} \int \frac{\rho}{r^2} d\mathbf{r}. \quad (7)$$

Therefore,  $T_2 (= T_W/9)$  becomes<sup>22</sup>

$$T_2 \approx \frac{C}{72} \int \frac{\rho}{r^2} d\mathbf{r} = -K \int \frac{\mathbf{r} \cdot \nabla \rho}{r^2} d\mathbf{r}, \quad (8)$$

where  $K = C/72$ . Taking  $C = 1.840$  for first-row atoms<sup>22</sup>  $K \approx \frac{1}{39}$ . Alternatively, instead of  $T_W/9$  one may take  $T_W/5$  as the KE correction because (i) the TFD- $T_W/5$  method best reproduces the total energy and binding energy of  $N_2$  molecule by solving the Euler equation;<sup>24</sup> (ii) the Scott conjecture<sup>1</sup> can be derived by using  $0.186T_W$  ( $\approx T_W/5$ ) which also gives very good total energy.<sup>25</sup> Thus, using (6) and (7) one obtains the lower-bound relation

$$\frac{1}{5} T_W > -\frac{1}{40} \int \frac{\mathbf{r} \cdot \nabla \rho}{r^2} d\mathbf{r}. \quad (9)$$

Now, the "first-gradient" KE correction differs significantly from  $T_2$  globally, locally (especially at  $r=0$ ) and in the functional derivative. Also, the HF density is *not* a solution of the Euler-Lagrange (EL) equation resulting from (3). Therefore, we now proceed to derive and solve this EL equation. For atoms, substituting Eqs. (3)-(5) into Eq. (1), the EL equation (2) simplifies to the quadratic form

$$a\theta^2 + b\theta + c = 0, \quad (10)$$

where

$$\theta = \rho^{1/3}, \quad a = -(\frac{5}{3})C_k r,$$

$$b = (\frac{4}{3})C_x r, \quad c = -(\frac{1}{40})(1/r) + Q(\mathbf{r}) + \mu r,$$

and

$$Q(r) = Z - r \int \rho(r') (|r - r'|)^{-1} dr'$$

is a screened nuclear charge of the atom.

In numerically and self-consistently solving Eq. (10),  $Q(r)$  is evaluated by using results of the previous iteration. For a particular mesh point  $x_j$  ( $x_j^2 = r_j$ ;  $x_j = x_{j-1} + h$ ), the solution is

$$\theta_j = \rho_j^{1/3} = (-b_j - \Delta_j^{1/2}) / 2a_j, \quad (11)$$

where  $\Delta_j = b_j^2 - 4a_j c_j$ . In (11), the other solution is not considered since it becomes negative at certain mesh points. The unknown  $\mu$  is fixed by a Newton-Raphson technique ( $N$  is the number of electrons), viz.,

$$\mu_{\text{new}} = \mu_{\text{trial}} - f(\mu) / f'(\mu), \quad (12)$$

where

$$f(\mu) = I - N, \quad I = 4\pi \int_0^\infty \rho r^2 dr, \quad (13)$$

$$f'(\mu) = 4\pi \int_0^\infty (\partial \rho / \partial \mu) r^2 dr. \quad (14)$$

The solution begins with a trial input  $\{\rho_j\}$  and  $\mu$ . After calculating  $Q(r)$ , Eq. (10) is solved for new  $\{\bar{\rho}_j\}$  using  $\mu_{\text{new}}$ , fixed by Eq. (12). This process (inner iteration) is repeated until the prescribed accuracy

$$|\mu_{\text{old}} - \mu_{\text{new}}| / |\mu_{\text{new}}| \leq 0.001$$

is satisfied. We then construct

$$\rho_j^{\text{new}} = 0.5\rho_j + 0.5\bar{\rho}_j, \quad \forall j,$$

for ensuring stability and convergence. The next iteration begins by recalculating  $Q(r)$  using  $\{\rho_j^{\text{new}}\}$ . The process is continued until the self-consistency criteria for both  $\mu$  (see above) and  $\rho$

$$|\rho_j^{\text{old}} - \rho_j^{\text{new}}| / \rho_j^{\text{new}} \leq 0.01, \quad \forall j$$

are satisfied. The following trial input densities were employed ( $y = r\rho^{1/2}$ ):

$$(1) \quad y = 19.19r \exp(-7.279r),$$

$$(2) \quad y = 10r \exp(-10r),$$

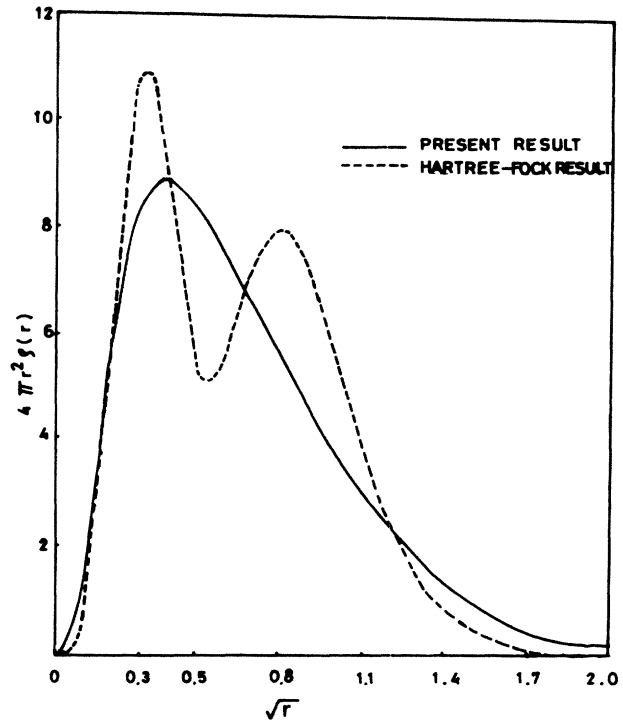


FIG. 1. Radial-density plot (a.u.) for the ground state of the Ne atom, with initial density input Ref. (1).

$$(3) \quad y = 19r \exp(-7r^2),$$

$$(4) \quad y = 10r \exp(-10r^2),$$

and near-Hartree-Fock (HF).<sup>15</sup> The final results (Table I, Fig. 1) do not depend significantly on the initial input. A local correlation term  $E_C$  can readily be incorporated in  $Q(r)$ . However, Eq. (10) yields negative  $\Delta_j$  for  $r \leq 0.0005$  and  $r \rightarrow \infty$ , due to the wrong nuclear cusp<sup>26</sup> and improper asymptotic behavior,<sup>27</sup> respectively, of the TFD solution. Therefore, we have imposed the cusp constraint to obtain  $\rho(0)$ , the density at nuclear site, as

$$-2Z\rho(0) = \rho'(0) = \frac{\rho(1) - \rho(0)}{\Delta r}, \quad (15)$$

TABLE I. Results (a.u.) from Eqs. (10), (1), and (3) for the ground state of the Ne atom (HF  $\equiv$  Hartree-Fock,  $T_r \equiv$  first-gradient correction,  $T_0 \equiv$  Thomas-Fermi).

Trial density	Radial density			$T_0$	$T_r$	$T = T_0 + T_r$	$-V$	$-(V/T)$	$-E$
	$-\mu$	Peak position ( $r^{1/2}$ )	Peak height						
(1)	0.066	0.39	8.9	123	18	141	277	1.96	136
(2)	0.053	0.38	8.7	124	18	142	278	1.96	136
(3)	0.065	0.44	8.9	119	18	137	273	1.99	136
(4)	0.11	0.46	9.1	118	17	135	271	2.01	136
HF	0.065	0.40	8.6	120	17	137	273	1.99	136
HF result		0.32 (first peak)	10.90 (first peak)	117.76	10.37	128.13	256.02	1.998	127.89

where  $\rho(1)$  is the density at the first mesh point near the nucleus where  $\Delta_j \geq 0$ . In addition, the long-range behavior of  $\rho$  is improved by using the relation

$$\rho(r) \sim \exp[-2(-2\mu)^{1/2}r], \quad r \rightarrow \infty. \quad (16)$$

Results are reported in Table I and Fig. 1. Note that the TF equation in the form of Eq. (10) cannot be solved because  $\Delta_j$  becomes negative for all mesh points and  $\mu$  diverges rapidly, whereas  $\mu=0$  for a neutral TF atom.

In Fig. 1 the "average smeared out" radial density, without the peaks characterizing shell structure, is a feature of all TF-type calculations unless shell structure is forced directly<sup>28</sup> or indirectly<sup>7</sup> into the calculation. The shell structure can enter through the  $(-\nabla^2\rho)$  term<sup>29</sup> in the KED. Since the first-gradient correction in Eq. (3) is just one part of the  $(-\nabla^2\rho)$  term, one does not expect shell structure in this case. However, the small negative value of  $\mu$  (Table I) is as expected in this TFD-type calculation since  $\mu_{TF}=0$ .

For all trial densities studied by us (see above) in Table I, the total energy is the same within the error limits of this calculation, although its kinetic and potential components vary somewhat from function to function. Such variations take place primarily because of  $\rho(0)$  and our prescription (see above) to deal with it. However, in all cases the errors in the energy components tend to cancel one another to produce the same total energy. As the ninth column of Table I shows, the virial satisfaction is quite good, close to the ideal value of 2. The present energy value (136) compares favorably with the TF value (166), the TFD- $T_W$  value (86.46), the TFD- $T_W/5$  value (128.83),<sup>24</sup> and the nonlocal value (129.05) of Alvarelos, Tarazona, and Chacon.<sup>30</sup> Our results also compare very well with Yang's<sup>25</sup> recent results, both locally and globally. In particular, our global energy is better than those from TF, TFD, TFD- $T_W$ , TFD- $T_W/3$ , and TFD- $T_W/9$  methods.<sup>25</sup> With an increase in the number of electrons, the first-gradient KE correction should give better energy values. However, although this correction gives rise to chemical binding in molecules and solids,<sup>14</sup> neither this

correction nor  $T_2 (=T_W/9)$  has a linear correlation with binding energies of diatomic molecules.<sup>31</sup> Since in the TF- $T_W$  theory chemical binding and the existence of negative ions are closely related, it is clear that negative ions also exist with the first-gradient correction.

As an additional numerical check, we have also performed these calculations with a near-HF input density for the Ne atom, by employing a logarithmic mesh,

$$r = -\ln(1-\lambda), \quad 0 \leq \lambda \leq 1 \text{ implies } 0 \leq r \leq \infty. \quad (17)$$

The self-consistent results (a.u.) are  $\mu = -0.11$ , kinetic energy = 136, potential energy = -264; the radial density has a single peak at  $r^{1/2} = 0.38$  with peak height 8.7 (cf. Table I). Although the total energy (-128 a.u.) is excellent, the virial satisfaction (1.94) is not as good as with the  $r = x^2$  mesh which was preferred.

In conclusion, the energy and density in the present calculations are quite satisfactory as far as TFD-type models are concerned. In the context of general density-functional theory such an approach has quite interesting possibilities. Indeed, from the considerations of simplicity, ease in calculation, accuracy, local, and global behavior as well as the behavior of the functional derivative, it is reasonable to say that *the first-gradient correction in Eq. (3) offers the best practical compromise for a suitable KED functional for many-electron systems.* We have already employed this KED functional for studying the dynamics of high-energy ion-atom collisions with quite interesting results.<sup>10</sup> The proposed quadratic equation has many potential uses in the structures and dynamics of many-fermion systems. The method of solution adopted here may be more advantageous than certain recent methods such as the imaginary time-step method.<sup>32</sup>

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