

Solution of the relativistic Thomas-Fermi-Dirac-Weizsäcker model for the case of neutral atoms and positive ions

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We present an accurate numerical solution of the relativistic Thomas-Fermi-Dirac-Weizsäcker variational equation for the case of neutral atoms and positive ions.

I. INTRODUCTION

In a previous paper¹ we presented a relativistic extension of the well-known Thomas-Fermi-Dirac-Weizsäcker (TFDW) model.²⁻⁵ Starting from the Hartree Fock (HF) limit of quantum electrodynamics (QED) we derived, after renormalization, an energy density functional in the spirit of Hohenberg and Kohn⁶ on the basis of gradient expansion techniques.⁷ The functional suggested includes second-order gradient terms for the kinetic energy density, whereas the exchange contribution is treated on the level of the local density approximation.

In this contribution we discuss an accurate numerical solution of the resulting relativistic TFDW variational equation for the case of neutral atoms and positive ions employing methods similar to those used to solve the nonrelativistic TFDW variational equation.⁸⁻¹¹ The numerical scheme is set up in Sec. II, the boundary conditions at the origin and at infinity are obtained in Sec. III via an explicit discussion of the corresponding nonlinear differential equations in the high- and low-density regime. After a brief comment on numerical aspects in Sec. IV, we present results for ground-state energies and densities in comparison with Dirac-Fock data in Sec. V.

In the nonrelativistic case, some emphasis has been placed on the question of an appropriate choice of the coefficient λ of the gradient correction to the kinetic energy. One obtains favorable results for the ground-state energy of atoms and ions⁹ with $\lambda = \frac{1}{3}$, whereas the semiclassical expansion yields $\lambda = \frac{1}{9}$. Furthermore, it has been

demonstrated¹² with the aid of a $1/Z$ expansion that the ground-state energy of the TF(D)W model corresponds to the exact ground-state energy in the limit $Z \rightarrow \infty$ to order Z^2 if $\lambda = 0.185909\dots$ is used. We show that a corresponding statement cannot be expected in relativistic density functional theory.

We use the relativistic convention $\hbar = c = 1$ throughout; in addition, we set $m = 1$ in the discussion of the variational equation for the sake of brevity. The numerical values for the energies are, however, given in atomic units in order to facilitate comparison with nonrelativistic results.

II. RELATIVISTIC TFDW VARIATIONAL EQUATION

In Ref. 1 we derived a relativistic extension of the TFDW energy density functional in terms of the local Fermi momentum and energy [note that in Ref. 1 the charge density $\rho_c(\mathbf{x}) = -e\rho(\mathbf{x})$ is employed rather than the probability density $\rho(\mathbf{x})$],

$$\begin{aligned} p(\mathbf{x}) &= [3\pi^2\rho(\mathbf{x})]^{1/3}, \\ E(\mathbf{x}) &= [1 + p^2(\mathbf{x})]^{1/2}. \end{aligned} \tag{1}$$

Introducing, in analogy to the nonrelativistic case, a parameter λ in the gradient term of the kinetic energy density in order to account for higher-order gradient terms, the relativistic ground-state-energy density functional is

$$\begin{aligned} \epsilon_{\text{RTFDW}}[p(\mathbf{x})] &= \frac{1}{8\pi^2} \left[p(\mathbf{x})E^3(\mathbf{x}) + p^3(\mathbf{x})E(\mathbf{x}) - \text{arcsinh}[p(\mathbf{x})] - \frac{8}{3}p^3(\mathbf{x}) \right. \\ &\quad \left. + 3\lambda[\nabla p(\mathbf{x})]^2 \frac{p(\mathbf{x})}{E(\mathbf{x})} \left(1 + 2\frac{p(\mathbf{x})}{E(\mathbf{x})} \text{arcsinh}[p(\mathbf{x})] \right) + \frac{8}{3}V_{\text{ext}}(\mathbf{x})p^3(\mathbf{x}) \right. \\ &\quad \left. + \frac{4\alpha}{9\pi^2} \int d^3y \frac{p^3(\mathbf{x})p^3(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} + \frac{\alpha}{\pi} (-2p^4(\mathbf{x}) + 3\{p(\mathbf{x})E(\mathbf{x}) - \text{arcsinh}[p(\mathbf{x})]\}^2) \right]. \end{aligned} \tag{2}$$

The external potential $V_{\text{ext}}(\mathbf{x})$ represents the potential of the nucleus in the present investigation, and α the fine-structure constant. The functional (2) corresponds to the spin unpolarized version of nonrelativistic density functional theory. It contains, however (as can be seen by a $1/m$ expansion), all spin contributions appropriate in this limit.

The energy density functional (2) should be used, as emphasized in Ref. 1, to calculate the ground-state binding energy of a many-electron system as the difference of the ground-state and the vacuum-state contributions. However, for the discussion of properties of neutral atoms and ions with nuclear charge less than 120, vacuum corrections can be neglected.

In this case, the variation of the energy functional,

$$\frac{\delta}{\delta p} \int d^3x \left[\varepsilon_{\text{RTFDW}}[p(\mathbf{x})] + \frac{\mu}{3\pi^2} p^3(\mathbf{x}) \right] = 0, \quad (3)$$

under the condition of fixed electron number,

$$N_e = \frac{1}{3\pi^2} \int d^3x p^3(\mathbf{x}), \quad (4)$$

yields the nonlinear integrodifferential equation

$$\begin{aligned} 0 = & 24E(\mathbf{x}) \left[E(\mathbf{x}) + V_{\text{ext}}(\mathbf{x}) + \frac{\alpha}{3\pi^2} \int d^3y \frac{p^3(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} + \mu - 1 \right] \\ & - 9\lambda \frac{[\nabla p(\mathbf{x})]^2}{p^2(\mathbf{x})} \left[1 + \frac{p^2(\mathbf{x})}{E^2(\mathbf{x})} + 4 \frac{p(\mathbf{x})}{E^3(\mathbf{x})} \operatorname{arcsinh}[p(\mathbf{x})] \right] \\ & - 18\lambda \frac{\Delta p(\mathbf{x})}{p(\mathbf{x})} \left[1 + 2 \frac{p(\mathbf{x})}{E(\mathbf{x})} \operatorname{arcsinh}[p(\mathbf{x})] \right] + \frac{12\alpha}{\pi} \{p(\mathbf{x})E(\mathbf{x}) - 3 \operatorname{arcsinh}[p(\mathbf{x})]\}. \end{aligned} \quad (5)$$

Introducing the total electrostatic potential $U(\mathbf{x})$,

$$U(\mathbf{x}) := V_{\text{ext}}(\mathbf{x}) + \frac{\alpha}{3\pi^2} \int d^3y \frac{p^3(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}, \quad (6)$$

Eq. (5) can be separated into two coupled differential equations:

$$\begin{aligned} 24E(\mathbf{x})[E(\mathbf{x}) + U(\mathbf{x}) + \mu - 1] - 9\lambda \frac{[\nabla p(\mathbf{x})]^2}{p^2(\mathbf{x})} \left[1 + \frac{p^2(\mathbf{x})}{E^2(\mathbf{x})} + 4 \frac{p(\mathbf{x})}{E^3(\mathbf{x})} \operatorname{arcsinh}[p(\mathbf{x})] \right] \\ - 18\lambda \frac{\Delta p(\mathbf{x})}{p(\mathbf{x})} \left[1 + 2 \frac{p(\mathbf{x})}{E(\mathbf{x})} \operatorname{arcsinh}[p(\mathbf{x})] \right] + \frac{12\alpha}{\pi} \{p(\mathbf{x})E(\mathbf{x}) - 3 \operatorname{arcsinh}[p(\mathbf{x})]\} = 0 \end{aligned}$$

and

$$\Delta U(\mathbf{x}) = -4\pi\alpha\rho_{\text{ext}}(\mathbf{x}) - \frac{4\alpha}{3\pi} p^3(\mathbf{x}). \quad (8)$$

The nuclear charge density is positive, thus $\rho_{\text{ext}}(\mathbf{x})$ has to be negative in accordance with the definition of $\rho(\mathbf{x})$, e.g., for a point nucleus

$$\rho_{\text{ext}}(\mathbf{x}) = -Z\delta^{(3)}(\mathbf{x}).$$

Assuming radial symmetry of the charge distribution of neutral atoms and ions, the differential equations simplify further,

$$\begin{aligned} p''(r) = & -2 \frac{p'(r)}{r} + \frac{4p(r)}{1 + 2[p(r)/E(r)] \operatorname{arcsinh}[p(r)]} \\ & \times \left[\frac{E(r)}{3\lambda} [E(r) + U(r) + \mu - 1] - \frac{p'(r)^2}{8p^2(r)} \left[1 + \frac{p^2(r)}{E^2(r)} + 4 \frac{p(r)}{E^3(r)} \operatorname{arcsinh}[p(r)] \right] \right. \\ & \left. + \frac{\alpha}{6\pi\lambda} \{p(r)E(r) - 3 \operatorname{arcsinh}[p(r)]\} \right], \end{aligned} \quad (9)$$

$$U''(r) = -2 \frac{U'(r)}{r} - 4\pi\alpha\rho_{\text{ext}}(r) - \frac{4\alpha}{3\pi} p^3(r). \quad (10)$$

As the Lagrangian multiplier μ , the chemical potential, is unknown we use as a third differential equation

$$\mu'(r) = 0. \quad (11)$$

In analogy to Ref. 11 we furthermore introduce the differential version of Eq. (4) (with radial symmetry),

$$N'(r) = \frac{4}{3\pi} r^2 p^3(r), \quad (12)$$

with the boundary conditions

$$N(0) = 0,$$

$$N(\infty) = N_e.$$

The system of coupled equations (9)–(12) has to be solved under appropriate boundary conditions which are consistent with the differential equations. We extract these by a detailed discussion of the asymptotic region $r \rightarrow \infty$ and the structure of the equations for $r \rightarrow 0$.

III. SOLUTIONS OF THE RTFDW EQUATION IN THE LOW- AND HIGH-DENSITY REGIME AND BOUNDARY CONDITIONS

A. $r \rightarrow \infty$

For large r one expects the density $\rho(r)$ and consequently the local Fermi momentum $p(r)$ as well as the potential $U(r)$ to become small, which means in our system of units $\rho(r), p(r), U(r) \ll 1$. As this limit is exactly the nonrelativistic limit an expansion of $E(r)$ and $\text{arcsinh}[p(r)]$ in Eq. (9) leads to the nonrelativistic TFDW variational equation,

$$p''_{\text{as}}(r) = -2 \frac{p'_{\text{as}}(r)}{r} + 12p_{\text{as}}(r) \left[\frac{1}{9\lambda} \left[U(r) + \mu + \frac{p_{\text{as}}(r)^2}{2} \right] - \frac{p'_{\text{as}}(r)^2}{24p_{\text{as}}(r)^2} - \frac{\alpha}{9\pi\lambda} p_{\text{as}}(r) \right]. \quad (13)$$

Using

$$\frac{p'(r)}{p(r)} = \frac{\rho'(r)}{3\rho(r)},$$

$$\frac{p''(r)}{p(r)} = \frac{1}{3} \left[\frac{\rho''(r)}{\rho(r)} - \frac{2\rho'(r)^2}{3\rho(r)^2} \right],$$

one immediately obtains the usual nonrelativistic TFDW equation,

$$\frac{\lambda}{8} \left[2 \frac{\rho''(r)}{\rho(r)} + 4 \frac{\rho'(r)}{r\rho(r)} - \frac{\rho'(r)^2}{\rho(r)^2} \right] = \frac{(3\pi^2)^{2/3}}{2} \rho^{2/3}(r) + U(r) + \mu - \alpha \left[\frac{3}{\pi} \right]^{1/3} \rho^{1/3}(r).$$

The asymptotic solutions of the coupled system of equations (13), (10), and (12) are well known:¹⁰

$$p_{\text{as}}(r) = d \frac{\exp[-\frac{2}{3}\sqrt{2(\mu/\lambda)}r]}{r^{(2/3)-(2\alpha/3\sqrt{2\mu\lambda})(Z-N_e)}}, \quad (14)$$

$$U_{\text{as}}(r) = -\frac{(Z-N_e)\alpha}{r} - \frac{\alpha\lambda d^3}{6\pi\mu} \frac{\exp[-2\sqrt{2(\mu/\lambda)}r]}{r^{2-(2\alpha/\sqrt{2\mu\lambda})(Z-N_e)}}, \quad (15)$$

$$N_{\text{as}}(r) = N_e - \frac{\sqrt{2\lambda}d^3}{3\pi\sqrt{\mu}} r^{(2\alpha/\sqrt{2\mu\lambda})(Z-N_e)} \times \exp[-2\sqrt{2(\mu/\lambda)}r]. \quad (16)$$

In order to use Eqs. (14)–(16) as boundary conditions we eliminate the unknown factor d in favor of a relation between $p_{\text{as}}(r)$ and $p'_{\text{as}}(r)$,

$$p'_{\text{as}}(r) = d \left[-\frac{2}{3} + \frac{2\alpha}{3\sqrt{2\mu\lambda}}(Z-N_e) - \frac{2}{3} \left[2\frac{\mu}{\lambda} \right]^{1/2} r \right] \times \frac{\exp[-(2/3)\sqrt{2(\mu/\lambda)}r]}{r^{(5/3)-(2\alpha/3\sqrt{2\mu\lambda})(Z-N_e)}} = \left[-\frac{2}{3} + \frac{2\alpha}{3\sqrt{2\mu\lambda}}(Z-N_e) - \frac{2}{3} \left[2\frac{\mu}{\lambda} \right]^{1/2} r \right] \times \frac{p_{\text{as}}(r)}{r}, \quad (17)$$

$$U_{\text{as}}(r) = -\frac{(Z-N_e)\alpha}{r} - \frac{\alpha\lambda}{6\pi\mu} p_{\text{as}}^3(r), \quad (18)$$

$$N_{\text{as}}(r) = N_e - \frac{\sqrt{2\lambda}}{3\pi\sqrt{\mu}} r^2 p_{\text{as}}^3(r). \quad (19)$$

B. $r \rightarrow 0$

In this region we explicitly discuss only the more critical case of a point nucleus. In principle one could have solutions with either

$$p_0(r) \xrightarrow[r \rightarrow 0]{} \infty,$$

or

$$p_0(r) \xrightarrow[r \rightarrow 0]{} \text{const}.$$

Both possibilities are examined separately.

1. $p_0(r) \xrightarrow[r \rightarrow 0]{} \infty$

In this case we expand all expressions in the RTFDW equation in powers of p^{-1} and obtain the ultrarelativistic RTFDW equation

$$p''_0(r) = -2 \frac{p'_0(r)}{r} + \frac{6p_0(r)}{\ln[2p_0(r)]} \left[\left[1 + \frac{\alpha}{2\pi} \right] p_0^2(r) + p_0(r)[U_0(r) + \mu - 1] - \frac{p'_0(r)^2}{12p_0^2(r)} \right],$$

where we used $\lambda = \frac{1}{9}$ for brevity. The most simple ansatz one could make for the solution of this differential equation is a power law,

$$p_0(r) = \frac{c}{r^\gamma}, \quad \gamma > 0. \quad (21)$$

The corresponding solution of the Poisson equation,

$$\partial_r^2 [rU_0(r)] = -\frac{4\alpha}{3\pi} r p_0^3(r)$$

for all $\gamma \neq 1, \frac{2}{3}$ is

$$U_0(r) = -\frac{Z\alpha + c_1}{r} + c_2 - \frac{4\alpha}{3\pi} \frac{c^3 r^{2-3\gamma}}{(3-3\gamma)(2-3\gamma)}. \quad (22)$$

For the special cases $\gamma = 1, \frac{1}{2}$ one has

$$\begin{aligned} \frac{2}{r^2} &= \frac{2}{r^2} - \frac{6}{\ln(r)} \left[\left[1 + \frac{\alpha}{2\pi} \right] \frac{c^2}{r^2} + \frac{c}{r} \left[-\frac{Z\alpha + c_1}{r} + c_2 + \frac{4\alpha}{3\pi} c^3 \frac{\ln(r)}{r} + \mu - 1 \right] - \frac{1}{12r^2} \right] \\ &= \frac{2}{r^2} - \frac{8\alpha c^4}{\pi r^2} - \frac{6}{\ln(r)} \left\{ \left[\left[1 - \frac{\alpha}{2\pi} \right] c^2 - \frac{1}{12} - (Z\alpha + c_1)c \right] \frac{1}{r^2} + O(r^{-1}) \right\}. \end{aligned}$$

The most divergent terms are proportional to r^{-2} . The equation cannot, however, be satisfied in this dominant order for any choice of c and c_1 . In consequence, the electron density cannot be proportional to r^{-3} in the region $r \rightarrow 0$ as proposed in the literature.¹³

In the same fashion one can exclude the possibility of solutions with

$$p_0(r) = \frac{c}{r^\gamma}, \quad \gamma \neq 1, \quad \gamma > 0$$

as well as solutions of the type

$$p_0(r) = \frac{c(\ln r)^\delta}{r^\gamma}, \quad \gamma > 0 \quad (25)$$

and

$$p_0(r) = c(\ln r)^\delta, \quad \delta > 0. \quad (26)$$

Therefore at least the most plausible types of functions which diverge in the limit $r \rightarrow 0$ cannot be solutions of the relativistic TFDW equation.

$$2. \quad p_0(r) \xrightarrow{r \rightarrow 0} \text{const}$$

The most general ansatz one can employ in this case is a generalized power series in r :

$$\begin{aligned} p_0(r) &= a_0 r^\gamma + a_1 r^\delta + a_2 r^\epsilon + \dots, \\ \gamma &\geq 0, \quad \gamma < \delta < \epsilon < \dots \end{aligned} \quad (27)$$

The corresponding potential,

$$U_0(r) = -\frac{Z\alpha + c_1}{r} + c_2 + \frac{4\alpha}{3\pi} c^3 \frac{\ln(r)}{r} \quad \text{for } \gamma = 1 \quad (23)$$

$$U_0(r) = -\frac{Z\alpha + c_1}{r} + c_2 + \frac{4\alpha}{3\pi} c^3 [1 - \ln(r)] \quad \text{for } \gamma = \frac{2}{3}. \quad (24)$$

If one inserts the ansatz for p_0 , Eq. (21), together with the corresponding potential, Eqs. (22)–(24), into the ultra-relativistic RTFDW equation one can investigate whether there exist combinations of the constants c and γ which solve the equation at least in the most dominant order for $r \rightarrow 0$.

As an example for this procedure we indicate the case $\gamma = 1$.

$$\begin{aligned} U_0(r) &= -\frac{Z\alpha + c_1}{r} + c_2 \\ &\quad - \frac{4\alpha}{3\pi} \left[\frac{a_0^3 r^{3\gamma+2}}{(3\gamma+2)(3\gamma+3)} \right. \\ &\quad \left. + \frac{3a_0^2 a_1 r^{2\gamma+\delta+2}}{(2\gamma+\delta+2)(2\gamma+\delta+3)} + \dots \right], \end{aligned} \quad (28)$$

is dominated by its point charge part. The electron-electron interaction gives only a constant contribution for $r \rightarrow 0$.

As long as $\gamma > 0$ the density $p_0(r)$ vanishes at $r = 0$. One thus can use the RTFDW equation in its limit of low density, Eq. (13), which gives to dominant order

$$\frac{\gamma(\gamma-1)}{r^2} = -2\frac{\gamma}{r^2} + 12 \left[-\frac{1}{9\lambda} \left[\frac{Z\alpha + c_1}{r} \right] - \frac{\gamma^2}{24r^2} \right].$$

This equation could only be satisfied with

$$\gamma\left(\frac{3}{2}\gamma + 1\right) = 0,$$

leading to $\gamma = 0$ or $\gamma = -\frac{2}{3}$, in contradiction to our assumption $\gamma > 0$. No solution of the type (27) with $\gamma > 0$ is possible.

In the case $\gamma = 0$ one has to consider the full RTFDW equation. With the abbreviation

$$E_0 = (1 + a_0^2)^{1/2}$$

one obtains by insertion of Eq. (27) into Eq. (9)

$$\begin{aligned}
a_1 \delta(\delta-1)r^{\delta-2} = & -2a_1 \delta r^{\delta-2} + \frac{12a_0}{1+2(a_0/E_0) \operatorname{arcsinh}(a_0)} \left[\frac{E_0}{9\lambda} \left[E_0 - \frac{Z\alpha + c_1}{r} + c_2 + \mu - 1 \right] \right. \\
& - \frac{a_1^2 \delta^2 r^{2\delta-2}}{24a_0^2} \left[1 + \frac{a_0^2}{E_0^2} + 4 \frac{a_0}{E_0^3} \operatorname{arcsinh}(a_0) \right] \\
& \left. + \frac{\alpha}{18\pi\lambda} [a_0 E_0 - 3 \operatorname{arcsinh}(a_0)] \right]. \quad (29)
\end{aligned}$$

Only the choice $\delta=1$ allows compensation of the terms proportional to $r^{\delta-2}$ with the point charge part. Thus one extracts the condition

$$a_1 = - \frac{2a_0 E_0}{1+2(a_0/E_0) \operatorname{arcsinh}(a_0)} \frac{(Z\alpha + c_1)}{3\lambda}. \quad (30)$$

In the same way one finds $\varepsilon=2$ and

$$\begin{aligned}
a_2 = & \frac{2a_0}{1+2(a_0/E_0) \operatorname{arcsinh}(a_0)} \left[\frac{E_0}{9\lambda} (E_0 + c_2 + \mu - 1) - \frac{a_1^2}{24a_0^2} \left[1 + \frac{a_0^2}{E_0^2} + 4 \frac{a_0}{E_0^3} \operatorname{arcsinh}(a_0) \right] \right. \\
& \left. + \frac{\alpha}{18\pi\lambda} [a_0 E_0 - 3 \operatorname{arcsinh}(a_0)] \right].
\end{aligned}$$

As nowhere in the differential equation occur fractional powers of r , $p_0(r)$ has to be a standard power series

$$p_0(r) = \sum_{n=0}^{\infty} a_n r^n. \quad (31)$$

Therefore we are led to the same structure of the solution near the origin as in the nonrelativistic TFDW model. Taking the nonrelativistic limit,

$$a_0 \ll 1, \quad c_1 = 0,$$

one finds

$$a_1 = -2a_0 \frac{Z\alpha}{3\lambda}, \quad (32)$$

which is exactly the relation the nonrelativistic TFDW equation demands.¹¹

We note that one can also exclude a solution of the type

$$\begin{aligned}
p_0(r) = & c(\ln r)^\gamma (a_0 r^\gamma + a_1 r^\delta + \dots), \\
\gamma > 0, \gamma < \delta < \dots. \quad (33)
\end{aligned}$$

We are now able to formulate three boundary conditions at the origin. First of all, c_1 has to vanish as there should be no additional charge at the origin except the nucleus. From Eqs. (28) and (30) we then derive (adding the norm condition)

$$N(0) = 0, \quad (34)$$

$$\lim_{r \rightarrow 0} [rU(r)] = -Z\alpha, \quad (35)$$

$$p'(0) = - \frac{2p(0)[1+p^2(0)]^{1/2}}{1+2 \frac{p(0)}{[1+p^2(0)]^{1/2}} \operatorname{arcsinh}[p(0)]} \frac{Z\alpha}{3\lambda}. \quad (36)$$

The analogous boundary conditions for an extended nucleus are

$$N(0) = 0, \quad (37)$$

$$\lim_{r \rightarrow 0} [rU(r)] = 0, \quad (38)$$

$$p'(0) = 0 \quad (39)$$

as, due to Eq. (29), the coefficient a_1 in the series (31) has to vanish if the potential is not proportional to r^{-1} but a constant at the origin.

IV. REMARKS ON THE NUMERICAL SOLUTION

In order to incorporate the condition (35) more directly we introduce the potential

$$W(r) := rU(r). \quad (40)$$

The most sensitive region for the solution of equations (9)–(12) is then the region of the origin. We therefore

used the transformation

$$y = \sqrt{r} \quad (41)$$

to spread this region. As upper boundary y_R for the numerical integration we chose a value such that stability of

the solution was ensured if one enlarged y_R further. For neutral uranium stability was reached at about 30 in our system of units. In the computations we used $y_R = 74.16$ for neutral systems corresponding to 40.15 a.u.

The transformed equations

$$\mu'(y) = 0, \quad (42)$$

$$N'(y) = \frac{8}{3\pi} y^5 p^3(y), \quad (43)$$

$$W''(y) = \frac{W'(y)}{y} - 16\pi\alpha y^4 \rho_{\text{ext}}(y^2) - \frac{16\alpha}{3\pi} y^4 p^3(y), \quad (44)$$

$$p''(y) = -3 \frac{p'(y)}{y} + \frac{16y^2 p(y)}{1 + 2[p(y)/E(y)] \operatorname{arcsinh}[p(y)]} \times \left[\frac{E(y)}{3\lambda} \left[E(y) + \frac{W(y)}{y^2} + \mu - 1 \right] - \frac{p'(y)^2}{32y^2 p^2(y)} \left[1 + \frac{p^2(y)}{E^2(y)} + 4 \frac{p(y)}{E^3(y)} \operatorname{arcsinh}[p(y)] \right] + \frac{\alpha}{6\pi\lambda} \left[p(y)E(y) - 3 \operatorname{arcsinh}[p(y)] \right] \right] \quad (45)$$

were solved with the following boundary conditions. At the origin one has in the case of a point nucleus,

$$N(0) = 0, \quad (46)$$

$$W(0) = -Z\alpha, \quad (47)$$

$$p'(0) = 0, \quad (48)$$

and for an extended nucleus,

$$N(0) = 0, \quad (49)$$

$$W(0) = 0, \quad (50)$$

$$p'(0) = 0, \quad (51)$$

and at y_R ,

$$N_{\text{as}}(y_R) = N_e - \frac{\sqrt{2\lambda}}{3\pi\sqrt{\mu}} y_R^4 p_{\text{as}}^3(y_R), \quad (52)$$

$$W_{\text{as}}(y_R) = -(Z - N_e)\alpha - \frac{\alpha\lambda}{6\pi\mu} y_R^2 p_{\text{as}}^3(y_R), \quad (53)$$

$$p'_{\text{as}}(y_R) = \left[-\frac{4}{3y_R} + \frac{4\alpha}{3\sqrt{2\mu\lambda}y_R} (Z - N_e) - \frac{4}{3} \left[2 \frac{\mu}{\lambda} \right]^{1/2} y_R \right] p_{\text{as}}(y_R). \quad (54)$$

For the solution of the system of coupled nonlinear differential equations in one dimension we used the program package COLSYS.¹⁴⁻¹⁶

TABLE I. Comparison of the binding energy of atomic systems with data of HF computations.

Z	E_{HF}	$E_{\text{TFDW}}^{\lambda=\frac{1}{9}}$	$E_{\text{TFDW}}^{\lambda=\frac{1}{5}}$	E_{DF}	$E_{\text{RTFDW}}^{\lambda=\frac{1}{9}}$	$E_{\text{RTFDW}}^{\lambda=\frac{1}{5}}$
10	128.547	139.858	128.755	128.674	139.533	128.482
20	676.758	720.871	674.851	679.502	718.590	671.805
30	1777.85	1881.99	1776.55	1793.78	1881.09	1768.13
40	3538.97	3717.24	3527.58	3594.81	3738.16	3518.41
50	6022.92	6301.06	6002.23	6171.21	6395.43	6012.97
60	9283.70	9696.28	9263.21	9615.86	9963.58	9340.26
70	13 391.5	13 957.8	13 365.3	14 051.9	14 566.5	13 591.7
80	18 409.0	19 134.6	18 357.5	19 623.5	20 350.8	18 865.9
90	24 359.6	25 271.4	24 284.4	26 471.9	27 498.6	25 272.3
100	31 282.7	32 409.2	31 187.0	34 806.3	36 247.4	32 936.7
110	39 225.0	40 586.2	39 103.4	44 950.0	46 921.9	42 006.6
120	48 202.9	49 837.9	48 069.1	57 386.9	59 988.5	52 660.2

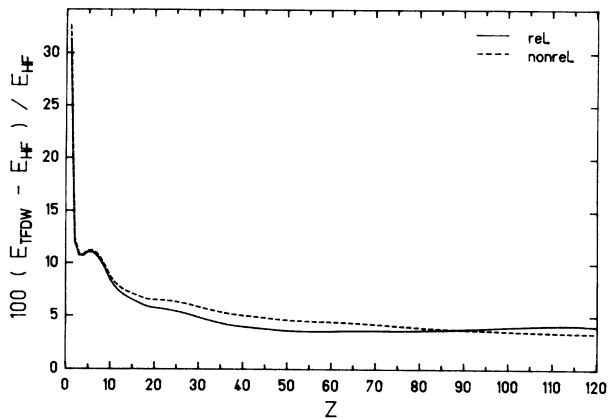


FIG. 1. Percentage deviation of (R)TFDW energies from (Dirac-) Hartree-Fock results.

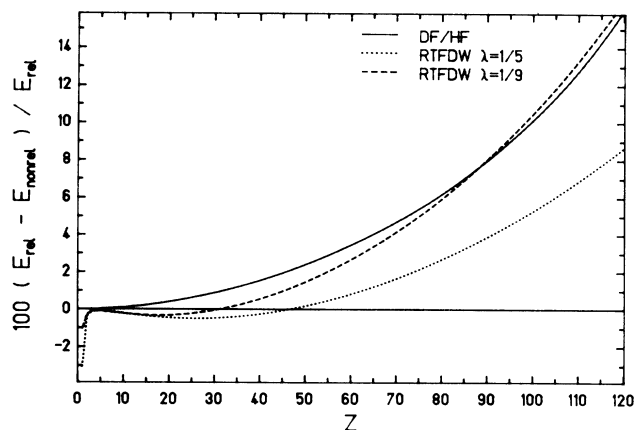


FIG. 4. Relativistic contributions to the binding energy of neutral atoms in different approximations.

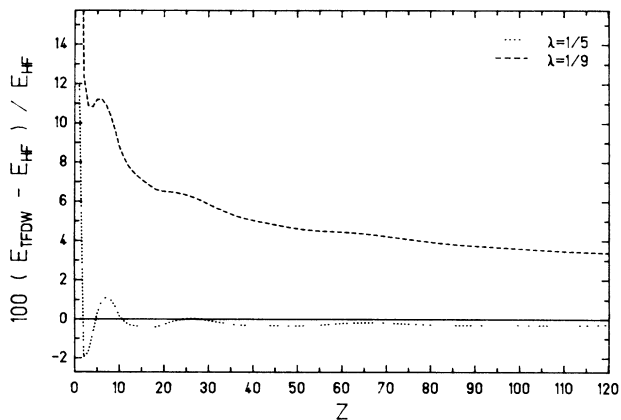


FIG. 2. Percentage deviation of TFDW energies from Hartree-Fock data for different values of λ .

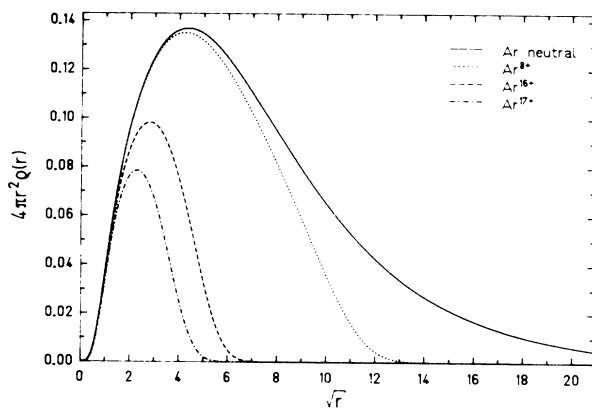


FIG. 5. Radial density of argon for several degrees of ionization.

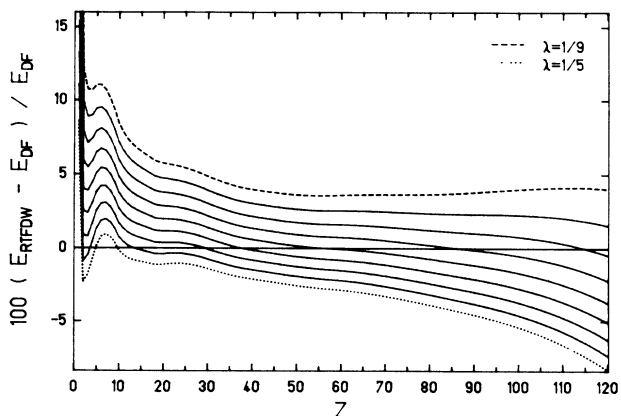


FIG. 3. Percentage deviation of RTFDW energies from Dirac-Fock data for different values of λ ($\Delta\lambda = \frac{1}{90}$).

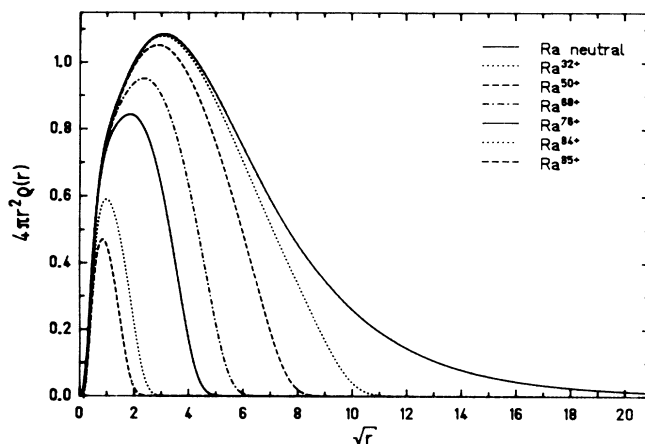


FIG. 6. Radial density of radon for several degrees of ionization.

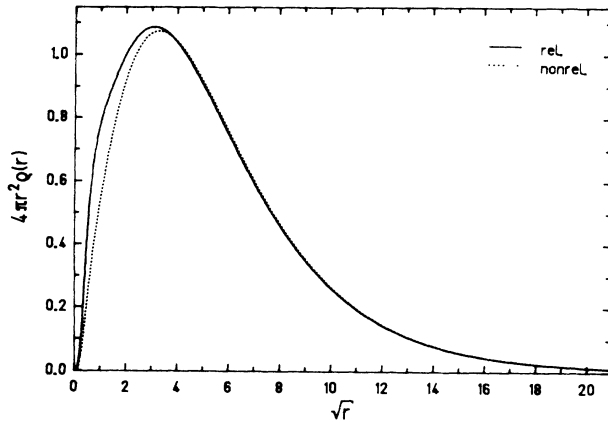


FIG. 7. Radial density of radon; RTFDW model vs TFDW model.

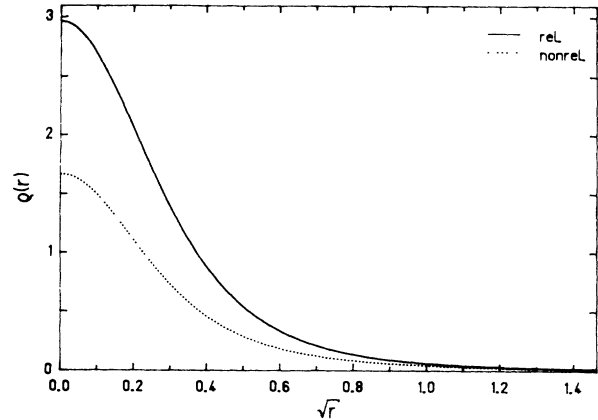


FIG. 8. Density of radon; RTFDW model vs TFDW model.

The numerical precision of the solutions μ , $N(r)$, $p(r)$, and $U(r)$ was better than 10^{-9} for large nuclear charge Z ($Z > 80$) and 3×10^{-11} for very small Z . The resulting energy values have an accuracy of 10^{-7} for large Z and at least 10^{-4} for $Z = 1, 2$. The large difference is due to the fact that we have to subtract the rest mass of the bound electrons which represents a much larger part of the total energy for light atoms than for heavier ones.

V. RESULTS

In this section we present results for neutral atoms and positive ions with nuclear charge $Z \leq 120$. We first discuss the accuracy of the RTFDW model. As the RTFDW model can be viewed as an approximation to the Hartree-Fock limit we compare the binding energy of atomic systems ($E_0 = -E_b$) with data¹⁷ of relativistic HF

TABLE II. Various contributions to the binding energy with the corresponding chemical potentials for some noble gases with closed shells.

Z	N_e	E_{kin}^0	E_{kin}^2	E_{pot}	E_{exc}^0	E_b	μ
2	2	2.607 14	0.627 23	-5.678 63	-0.763 09	-3.207 35	0.061 361 5
2	1	2.236 61	0.640 68	-5.204 63	-0.548 66	-2.876 00	0.793 579
10	10	122.264	16.7570	-268.133	-10.4299	-139.542	0.064 995 2
10	2	83.1721	16.9316	-196.101	-4.688 83	-100.686	18.0022
10	1	59.3165	16.3897	-149.184	-2.859 99	-76.3382	33.3994
18	18	501.714	56.9409	-1091.22	-27.3725	-559.934	0.065 863 4
18	10	477.541	57.4298	-1048.47	-22.8153	-536.317	8.062 79
18	2	274.538	56.5561	-656.173	-8.46 267	-333.541	66.4597
18	1	190.301	54.0731	-486.941	-5.04 895	-247.616	113.844
36	36	2693.97	269.569	-5783.50	-85.2848	-2905.24	0.066 677 1
36	18	2537.14	271.395	-5491.46	-68.2702	-2751.19	161.305
36	10	2198.71	272.107	-4838.89	-49.3897	-2417.46	65.3044
36	2	1123.11	258.868	-2723.52	-16.1742	-1357.71	290.902
36	1	754.537	242.869	-1978.47	-9.35 060	-990.416	477.480
54	54	7427.55	775.354	-15 744.8	-164.976	-7706.83	0.067 068 3
54	36	7300.13	777.196	-15 509.8	-149.771	-7582.25	18.5310
54	18	6465.00	779.951	-13 903.1	-106.537	-6764.72	86.8493
54	10	5433.27	776.923	-11 899.1	-73.7675	-5762.73	178.121
54	2	2673.55	721.746	-6503.95	-22.4466	-3131.09	690.090
54	1	1759.81	664.198	-4675.06	-12.5803	-2263.63	1123.97
86	86	26 051.8	3564.37	-53734.1	-345.952	-24 463.9	0.067 453 0
86	54	25 555.9	3568.81	-52 797.8	-306.539	-23 979.7	41.7005
86	36	24 217.1	3571.51	-50 223.7	-251.951	-22 687.0	111.056
86	18	20 697.4	3558.11	-43 450.9	-163.962	-19 359.4	293.982
86	10	17 262.2	3517.38	-36 885.0	-107.503	-16 212.9	530.750
86	2	8461.80	3142.02	-20 270.3	-27.7157	-8694.17	1956.23
86	1	5406.19	2769.64	-14 381.0	-14.3363	-6219.50	3227.20

(Dirac-Fock) computations. Exactly as in the nonrelativistic theory the RTFDW model overestimates the binding energy of atomic systems if $\lambda = \frac{1}{9}$ (obtained via the gradient expansion) is taken (see Table I). Figure 1 shows the percentage deviation of the ground-state energies of neutral atoms of the RTFDW model (with $\lambda = \frac{1}{9}$) from Dirac-Fock results. Both computations used an extended nucleus with a Fermi (RTFDW) or a homogeneous (DF) profile. For comparison we also show the corresponding deviation of the nonrelativistic TFDW model with $\lambda = \frac{1}{9}$ from nonrelativistic HF data. The accuracy of the RTFDW model is of the same order of magnitude as that of its nonrelativistic counterpart.

The nonrelativistic gradient correction to the kinetic energy density,

$$\lambda \frac{[\nabla\rho(\mathbf{x})]^2}{8\rho(\mathbf{x})},$$

was initially derived by von Weizsäcker⁵ with a value $\lambda=1$ whereas the systematic gradient expansion by Kirznits⁷ leads to $\lambda = \frac{1}{9}$. For the nonrelativistic TFDW model one has the possibility to improve the agreement with HF data by adjusting λ . It has been shown⁹ that a value of $\lambda = \frac{1}{5}$ gives best results. The quality of this choice is depicted in Fig. 2. In nonrelativistic density functional theory one furthermore can prove¹² that for nuclear charge $Z \rightarrow \infty$ the TFW energy functional with λ close to $\frac{1}{5}$ leads to the correct binding energies up to the order Z^2 . We tested the effect of variable λ in the

relevant region for the relativistic theory. The results are shown in Fig. 3. Obviously $\lambda = \frac{1}{5}$ does not give a drastically higher accuracy. It still improves the agreement with DF results for the nonrelativistic region of small Z but it misrepresents the relativistic corrections by about a factor of 2. This is explicitly demonstrated in Fig. 4, where the relativistic contributions are shown as a function of Z for the different models. Thus one cannot expect an equivalent theorem on the large- Z behavior of the binding energy in the relativistic domain.

In Figs. 5 and 6 we present, as an example, the radial densities $4\pi r^2 \rho(r)$ (for a point nucleus) of argon and radon for several degrees of ionization. As is well known, the TFDW model averages over the shell structure of the systems. The relativistic effect on the density of radon is indicated in Figs. 7 and 8. As expected, the density is more concentrated in the vicinity of the nucleus in the relativistic case. Finally in Table II we list the various contributions to the binding energy together with the corresponding chemical potentials for some noble gases with closed shells.

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