

Extension of the Thomas–Fermi–Dirac–Weizsäcker model: fourth-order gradient corrections to the kinetic energy†

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Abstract. We present an accurate numerical solution of the variational equation resulting from the standard Thomas–Fermi–Dirac–Weizsäcker energy functional plus fourth-order gradient terms of the kinetic energy. We show that the solution of the variational equation leads to kinetic energies that differ from estimates obtained by evaluation of the kinetic energy functional to fourth order with Hartree–Fock densities.

1. Introduction

Among the simpler density functional models used for the investigation of atomic and molecular ground-state properties via direct application of the Hohenberg–Kohn variational principle (Hohenberg and Kohn 1964), the T_{FDW} model has enjoyed some success (see, e.g., Gross and Dreizler 1985). For spin-saturated atomic systems the ground-state energy functional of this model (see Oliver and Perdew (1979) for the spin polarised case)

$$E_{\text{T}_{\text{FDW}}}[\rho] = \int d^3x \left(\frac{3}{10} (3\pi^2)^{2/3} \rho(x)^{5/3} + \frac{\lambda}{8} \frac{(\nabla\rho(x))^2}{\rho(x)} \right) + V_{\text{ext}}(x)\rho(x) + \frac{\alpha}{2} \int d^3y \frac{\rho(x)\rho(y)}{|x-y|} - \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \alpha \rho(x)^{4/3} \quad (1)$$

features the gradient expansion of the non-interacting kinetic energy T_s to second order, the standard potential terms and the local approximation for the exchange contribution. Correlation effects are neglected, thus the model can at best constitute an approximation at the level of the Hartree–Fock approximation. We discuss the model and the question of a density functional representation of T_s in more detail in § 2.

The gradient expansion of T_s (Kompaneets and Pavlovskii 1957, Kirzhnits 1957, Kohn and Sham 1965, Kirzhnits 1967) yields $\lambda = \frac{1}{5}$ for the coefficient of the second-order gradient term. The solution of the Hohenberg–Kohn variational equations leads, in this case, to ground-state energies for neutral atoms with $Z \geq 20$ that agree to within about 7% with non-relativistic Hartree–Fock results. Optimal results (with a deviation of less than 0.5% for neutral (non-relativistic) atoms with $Z \geq 10$ in comparison with HF data) are obtained for the choice $\lambda = \frac{1}{5}$ (Yonei and Tomishima 1965, Tomishima and Yonei 1966, Gross and Dreizler 1979, Stich *et al* 1982).

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As the gradient expansion of T_s has been evaluated in fourth (Hodges 1973) and sixth order (Murphy 1981), the question of the 'convergence' of this expansion has been addressed. Evaluation of the terms to fourth order (Wang *et al* 1976, Murphy and Wang 1980) using Hartree-Fock densities for neutral atoms, indicates an accuracy of the kinetic energy values between 0.96% for Ne and 0.071% for Xe decreasing with Z (again in comparison with HF data). Sixth-order contributions are, however, exponentially divergent if evaluated with Hartree-Fock densities, emphasising the asymptotic nature of this expansion, first indicated by Hohenberg and Kohn (1964). Pearson and Gordon (1985) have demonstrated that this difficulty can be remedied by applying the standard truncation prescription for asymptotic series locally at each point in space.

On the other hand, the solution of the Hohenberg-Kohn variational equations for an extended TFDW model, which includes the gradient terms in T_s to fourth order, leads to densities which fall off according to a power law (rather than the expected exponential fall off) for $r \rightarrow \infty$. This then raises the question of how the solution of this model compares with the estimates obtained by using 'good densities'. In order to answer this question we present, in this paper, an accurate numerical solution of the non-linear variational equation of this extended TFDW model. After some comments on technical details for the solution of the variational equation in § 3, we will present and discuss the results in § 4.

We use the convention $\hbar = c = m = 1$ throughout. The numerical values for the energies are given in atomic units.

2. Background material

The ground-state energy functional of a many-fermion system is most conveniently partitioned (Kohn and Sham 1965) in the form

$$E_0[\rho] = T_s[\rho] + E_{\text{ext}}[\rho] + E_d[\rho] + E_{\text{xc}}[\rho]. \quad (2)$$

E_{ext} and E_d are the energy contributions due to the external potential and the direct part of the two-particle interaction (in our case Coulomb forces). T_s represents the kinetic energy of an equivalent non-interacting system with the same density as the interacting system under consideration. E_{xc} contains the exchange and correlation contributions, including the difference $T[\rho] - T_s[\rho]$. Neither $T_s[\rho]$ nor $E_{\text{xc}}[\rho]$, is known exactly.

For T_s essentially two approximations (with variants) have been discussed. Expansion around the homogeneous limit (formally valid for slowly varying densities) leads to the gradient expansion indicated in the introduction (see, e.g., Gross and Dreizler 1985 for details). The fourth-order kinetic energy density has been given by Hodges (1973), as

$$t^{[4]}[\rho] = \frac{\rho^{1/3}}{540(3\pi^2)^{2/3}} \left[\left(\frac{\Delta\rho}{\rho} \right)^2 - \frac{9}{8} \left(\frac{\Delta\rho}{\rho} \right) \left(\frac{\nabla\rho}{\rho} \right)^2 + \frac{1}{3} \left(\frac{\nabla\rho}{\rho} \right)^4 \right] \quad (3)$$

(correcting an error in the original derivation of Kirzhnits (1957)) starting from the Dirac density matrix based on the Kohn-Sham density operator

$$\hat{\rho}_{\text{KS}} = \Theta(\epsilon_{\text{F}} - \hat{t} - \hat{v}_{\text{KS}})$$

and by Jennings (Jennings 1973, Brack *et al* 1976) as

$$t^{[4]}[\rho] = \frac{\rho^{1/3}}{4320(3\pi^2)^{2/3}} \left(12 \frac{\Delta^2 \rho}{\rho} - 30 \frac{\nabla \rho \cdot \nabla \Delta \rho}{\rho^2} - 14 \frac{(\Delta \rho)^2}{\rho^2} - 7 \frac{\Delta(\nabla \rho)^2}{\rho^2} \right. \\ \left. + \frac{140}{3} \frac{(\nabla \rho)^2 \Delta \rho}{\rho^3} + \frac{92}{3} \frac{\nabla \rho \cdot \nabla(\nabla \rho)^2}{\rho^3} - 48 \frac{(\nabla \rho)^4}{\rho^4} \right) \quad (4)$$

on the basis of the corresponding Bloch density matrix.

The form given in equation (3) incorporates the usual simplification with the aid of the Green theorem neglecting surface terms. The full form (4) would be relevant for infinite systems or for a piecewise analytic representation of the density (Perdew *et al* 1986). In addition it has been argued (Perdew *et al* 1986) that the term proportional to $\Delta^2 \rho / \rho^{2/3}$ occurring in the form given by Jennings leads to a cusp correction at the origin for the case of atoms,

$$E_{\text{cusp}} = \frac{1}{45} \pi (3\pi^2 \rho(0))^{-2/3} d\rho(r=0)/dr.$$

This statement has since been modified (Perdew *et al* 1988). The functionals (3) and (4) are mathematically equivalent for densities which decrease for $r \rightarrow \infty$. The point to be noted is the following. Using the Green theorem to reduce the term in question to its standard form, one finds

$$\int d^3x \frac{\Delta^2 \rho}{\rho^{2/3}} = \int d^3x \Delta \rho \left(\frac{10}{9} \frac{(\nabla \rho)^2}{\rho^{8/3}} - \frac{2}{3} \frac{\Delta \rho}{\rho^{5/3}} \right) \quad (5)$$

plus surface terms which vanish for the situation considered.

The statement arose from the evaluation of the integral in question with the assumption of spherically symmetric densities. For a density which is finite at the origin one obtains

$$\Delta^2 \rho(r) = \Delta \left(\frac{1}{r} \frac{d^2}{dr^2} r\rho(r) \right) = \Delta \left(\rho''(r) + \frac{2}{r} \rho'(r) \right) \\ = \frac{1}{r} \frac{d^4}{dr^4} (r\rho(r)) - 8\pi \rho'(0) \delta^{(3)}(x).$$

The second term of the last equation cancels the cusp correction (obtained by double partial integration of the first term) exactly and equation (5) also holds in this case.

The variational equation that one obtains from either the functionals (3) or (4) also features a δ -type contribution resulting from the $\Delta^2 \rho$ term for spherically symmetric densities. However, a solution containing a δ -function contribution is not compatible with the differential equation. Furthermore, the differential equation demands, as we indicate below, that the derivative of the density vanishes at the origin for the case of a point-like nucleus at this position. Thus the $\rho'(r)\delta(r)$ term affects neither the solution of the differential equation nor the boundary conditions: it is an artefact due to the geometry assumed.

The asymptotic nature of this expansion can be seen to arise directly from the interchange of summation and Laplace integration in the evaluation of the appropriate matrix elements of the density operator in equation (4). Besides the practical cure suggested by Pearson and Gordon (1985), a number of partial resummation schemes of the gradient series have been advanced (e.g. Baltin 1972, Durand *et al* 1978, 1980, Plumer and Geldart 1983, Ghosh and Balbas 1985, Plumer and Stott 1985).

Alternatively one can envisage that the original von Weizsäcker term (von Weizsäcker 1935),

$$T_w[\rho] = \frac{1}{8} \int d^3x [(\nabla\rho)^2/\rho] \quad (6)$$

is the leading term of the representation of T_s . This term (i) constitutes a rigorous lower bound for the exact kinetic energy (Harriman 1987), (ii) seems to be the correct limit for the case of small but rapid density variations (Jones 1971, Jones and Young 1971), (iii) reproduces the nuclear cusp at the position of nuclei for Coulomb systems (Bader and Bedall 1972), (iv) is exact in the asymptotic ($r \rightarrow \infty$) region (March 1982, Alonso and March 1983) and (v) is exact for a many-boson system (von Weizsäcker 1935). In view of these features one can imagine the expansion

$$T_s[\rho] = T_w[\rho] + T_f[\rho] \quad (7)$$

where T_f may be interpreted (Herring 1986) as the additional energy necessitated by the exclusion principle. We will not pursue the attempts to model T_f , but only note that the crudest estimate of T_f leads to the Thomas-Fermi functional included in equation (1).

The parameter λ of the TFDW model may be viewed as an interpolation between the rapidly and slowly varying density regimes. The optimal value $\lambda = \frac{1}{3}$ corresponds quite closely to the linear response result of Meyer *et al* (1976) ($\lambda = 0.205$) and the value $\lambda = 0.1859$ obtained by Lieb (1981) from analysis of the $1/Z$ expansion of the TFW model.

We will not consider the development of the exchange correlation contribution, but only offer an additional remark on the pure exchange limit. The gradient expansion of the exchange term is available to second order. The second-order exchange energy density (to first order in the fine-structure constant) is (Herman *et al* 1969, Sham 1971, Gross and Dreizler 1981)

$$\varepsilon_x^{[2]}[\rho] = -\frac{\gamma_x \alpha}{\pi(3\pi^2)^{1/3}} \frac{(\nabla\rho)^2}{\rho^{4/3}}. \quad (8)$$

The standard prefactor $\gamma_x = \frac{7}{432}$, which was first evaluated by Sham (1971), has recently been corrected following the suggestion of Kleinman (Kleinman and Lee 1987, Chevary and Vosko 1988) to $\gamma_x \approx \frac{10}{432}$. We will include this term (with Sham's factor) in the calculation only to demonstrate that it is definitely less important than the fourth-order kinetic-energy contribution.

The final functional is thus composed of the terms given in equation (1) with the gradient expansion value $\lambda = \frac{1}{9}$, the fourth-order kinetic-energy contribution, equation (3), and, in some of the results quoted, the second-order exchange term.

The variation of the energy functional,

$$\frac{\delta}{\delta\rho} \left(E[\rho] + \mu \int d^3x \rho(x) \right) = 0$$

under the condition of fixed electron number,

$$N_e = \int d^3x \rho(x) \quad (9)$$

yields a fourth-order non-linear integro-differential equation. Introducing the total electrostatic potential $U(x)$,

$$U(x) \equiv V_{\text{ext}}(x) + \alpha \int d^3y \frac{\rho(y)}{|x-y|} \quad (10)$$

this equation can be separated into two coupled differential equations. Assuming radial symmetry of the charge distribution of neutral atoms and ions and introducing the quantity $p(r)$,

$$p(r) \equiv (3\pi^2\rho(r))^{1/3} \quad (11)$$

to simplify the forthcoming discussion (and the numerical solution), the differential equations can be written as

$$\begin{aligned} 0 = & \frac{p''''(r)}{p(r)} + \frac{4}{r} \frac{p'''(r)}{p(r)} - 2 \frac{p'''(r)p'(r)}{p(r)^2} - \frac{3}{2} \frac{p''(r)^2}{p(r)^2} - 2 \frac{p''(r)p'(r)^2}{p(r)^3} \\ & - \frac{25}{2r} \frac{p''(r)p'(r)}{p(r)^2} + 3 \frac{p'(r)^4}{p(r)^4} + \frac{3}{r} \frac{p'(r)^3}{p(r)^3} - \frac{13}{4r^2} \frac{p'(r)^2}{p(r)^2} \\ & - 2 \frac{p'(r)}{p(r)} \delta(r) + 90p(r)^2 \left(-\frac{1}{12} \frac{p''(r)}{p(r)} - \frac{1}{24} \frac{p'(r)^2}{p(r)^2} - \frac{1}{6r} \frac{p'(r)}{p(r)} \right. \\ & \left. + U(r) + \mu + \frac{p(r)^2}{2} - \frac{\alpha}{\pi} p(r) \right) \quad (12) \end{aligned}$$

$$U''(r) = -2 \frac{U'(r)}{r} + 4\pi\alpha\rho_{\text{ext}}(r) - \frac{4\alpha}{3\pi} p^3(r) \quad (13)$$

where

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

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

$$\mu'(r) = 0. \quad (14)$$

In analogy to Stich *et al* (1982) we furthermore introduce the differential version of equation (9) (with radial symmetry),

$$\begin{aligned} N(r) & \equiv 4\pi \int_0^r x^2 dx \rho(x) = \frac{4}{3\pi} \int_0^r x^2 dx p^3(x) \\ N'(r) & = \frac{4}{3\pi} r^2 p^3(r) \quad (15) \end{aligned}$$

with the boundary conditions

$$N(0) = 0$$

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

The system of coupled equations (12-15) has to be solved under appropriate boundary conditions which are consistent with the differential equations.

3. Technical remarks

The asymptotic solutions of the differential equations (12) and (13) can be shown to be

$$p(r) \xrightarrow{r \rightarrow \infty} (13/90\mu)^{1/2}(1/r^2) + O(r^{-3}) \quad (16)$$

$$U(r) \xrightarrow{r \rightarrow \infty} -\frac{(Z - N_e)\alpha}{r} - \frac{\alpha}{9\pi} \left(\frac{13}{90\mu}\right)^{3/2} \frac{1}{r^4} + O(r^{-5}). \quad (17)$$

Besides the fact that the chemical potential enters in a crucial way, we see that the density behaves asymptotically as r^{-6} , as in the simple Thomas-Fermi model for neutral atoms.

The boundary conditions at the upper boundary a_R of the finite interval usual in the numerical solution have to be consistent with the asymptotic solutions the differential equations demand. This is most easily achieved by using the relationships between the various functions that enter into the differential equations which are equivalent to the asymptotic forms for $p(r)$ and $U(r)$ (compare Engel and Dreizler 1988),

$$\begin{aligned} N(a_R) &= N_e - (4/9\pi)a_R^3 p(a_R)^3 \\ U(a_R) &= -[(Z - N_e)\alpha/a_R] - (\alpha/9\pi)a_R^2 p(a_R)^3 \\ p''(a_R) &= -(6/a_R^2)[p(a_R) + a_R p'(a_R)] \\ p'''(a_R) &= (12/a_R^3)[4p(a_R) + 3a_R p'(a_R)]. \end{aligned} \quad (18)$$

As an upper boundary we choose a value a_R , for which the correct electron number N_e deviates from $N(a_R)$ by less than 10^{-9} in absolute value. Due to the asymptotic form of $p(r)$ this upper boundary depends on the nuclear charge and the electron number via the chemical potential. It decreases smoothly with increasing Z and with decreasing N_e .

For the discussion of the limit $r \rightarrow 0$ one can use the fact that a solution containing a $\delta(r)$ -type term is mathematically incompatible with the differential equation. With a power series ansatz for the solution in the vicinity of the origin one readily establishes that

$$p'(0) = 0. \quad (19)$$

As a consequence, the distribution term in equation (12) vanishes and Kato's theorem (Kato 1957, Steiner 1963) is not satisfied by the variational solution. The additional boundary conditions are

$$\begin{aligned} N(0) &= 0 \\ \lim_{r \rightarrow 0} (rU(r)) &= -Z\alpha \\ p'''(0) &= \frac{45}{2}Z\alpha p(0)^3. \end{aligned} \quad (20)$$

The system of coupled non-linear differential equations (12-15) in one dimension was solved (after transformation to the variables $W(r) = rU(r)$, $y = \sqrt{r}$) with the program package COLSYS (Ascher *et al* 1979, Ascher 1980).

The numerical precision of the solutions μ , $N(r)$, $p(r)$ and $W(r)$ was better than 10^{-8} for large nuclear charge Z and better than 10^{-11} for very small Z ($Z \leq 4$). The (numerical) accuracy of the resulting energy values is best demonstrated by the precision with which the virial theorem is satisfied. Figure 1 indicates an upper limit for this numerical error of 3×10^{-8} .

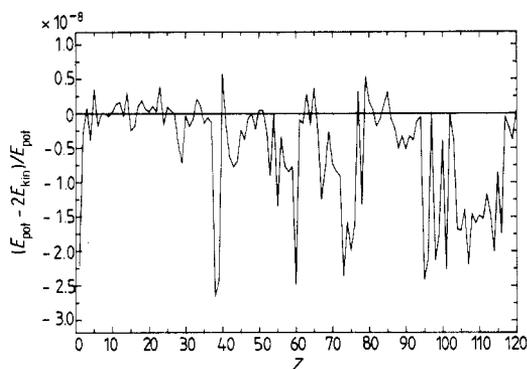


Figure 1. Precision of the virial theorem in the extended TFDW model.

4. Results and discussion

We present results for neutral atoms and positive ions with nuclear charge $Z \leq 120$ in comparison with non-relativistic Hartree-Fock data (Desclaux 1973). In table 1 we list some representative results for the various kinetic energy contributions (hydrogen and noble gases) in comparison with the HF kinetic energy. For a view over the complete periodic table we refer to figure 2 where the percentage deviation of the kinetic energy from HF results is plotted for the TFDW¹W (i.e. solution of the second-order variational equation) and the extended TFDW model. In view of the fact that the virial theorem is accurately satisfied for the density functional as well as the HF calculations, the same statement applies for the accuracy of the total energy.

The values for the kinetic energies obtained from the solution of the variational equations do not confirm (as one might have expected) the estimates of Murphy and Wang (1980) in magnitude, nor in their dependence on Z . We illustrate this point directly in figure 3, where the ratios of the kinetic energy components obtained in the fourth-order calculation are shown as a function of Z . For large values of Z the second-order contribution is about 4% of the zeroth-order one. However, the fourth-order contribution constitutes 27% of the second-order one (amounting to more than 1% of the total energy). The relative importance of the fourth-order contribution is even more emphasised in situations with $N_e = 1$. The binding energy of the single

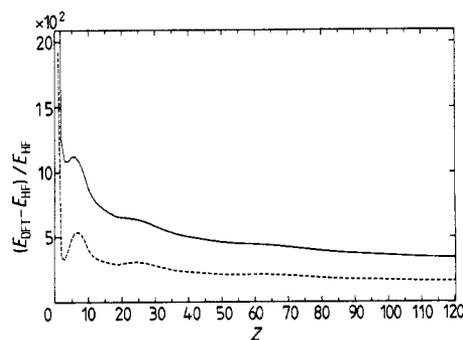


Figure 2. Percentage deviation of TFDW and extended TFDW energies. —, second order; - - -, fourth order.

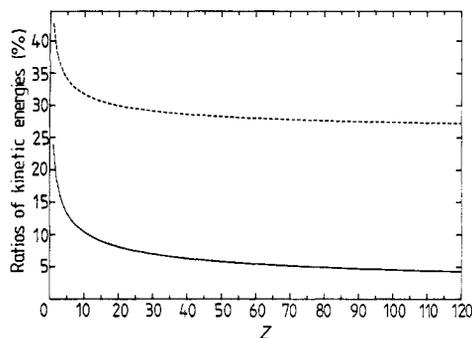


Figure 3. Ratios of the contributions to the kinetic energy: —, $T^{[2]}[\rho^{[4]}] / T^{[0]}[\rho^{[4]}]$ and - - -, $T^{[4]}[\rho^{[4]}] / T^{[2]}[\rho^{[4]}]$.

bound electron in Ar^{17+} is found to be 250.36 au in a second-order calculation whereas the fourth-order calculation leads to 227.02 au. Here $T^{[2]}$ represents 22% of $T^{[0]}$ and $T^{[4]}$ about 40% of $T^{[2]}$. For neutral systems the ratio $T^{[2]}$ to $T^{[0]}$ satisfies the $Z^{-1/3}$ law ($T^{[2]}/T^{[0]} \approx 0.210 \times Z^{-1/3}$) expected from $1/Z$ expansion and the ratio $T^{[4]}/T^{[2]}$ is best characterised by $0.46 \times Z^{-1/9}$. However, it is obvious that the addition of the fourth-order kinetic energy terms does not improve the TFDW kinetic energy by the same order of magnitude as the addition of the second order improves TF theory.

In table 2 we indicate results for which the gradient correction to the exchange energy in lowest order of α , equation (8), has been included in the variational equation. Though this term is relevant for the behaviour of the density for $r \rightarrow \infty$ as well as in the vicinity of the origin it does not alter the boundary conditions (equations (18–20)). As before, the density $\rho(r)$ falls off like r^{-6} for large r and its derivative vanishes at the origin. For helium the value of $E_x^{[2]}$ is about half as large as the value of $T^{[4]}$, but it becomes less important for $Z \geq 10$, where the contribution of $E_x^{[2]}$ is less than 0.37% of the total energy (e.g. 0.02% for radon).

Finally, in figures 4–6 we compare the densities obtained in second- and fourth-order calculations, for the example of neutral krypton.

The difference between the radial densities $r^2\rho(r)$ for the two approximations is small (figure 4). In order to reveal the different asymptotic structures for $r \rightarrow \infty$ one has to enlarge the figure considerably (figure 5). The main difference in the binding energy is due to the much smaller density of the fourth-order computation at the origin

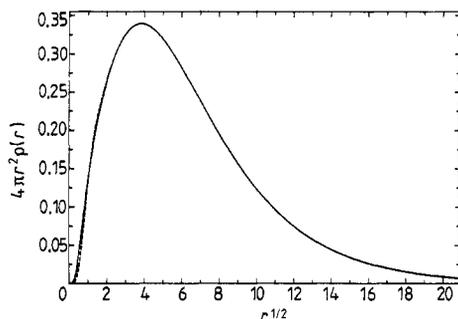


Figure 4. Radial density of krypton ($\hbar = c = m = 1$). —, second order; - - -, fourth order.

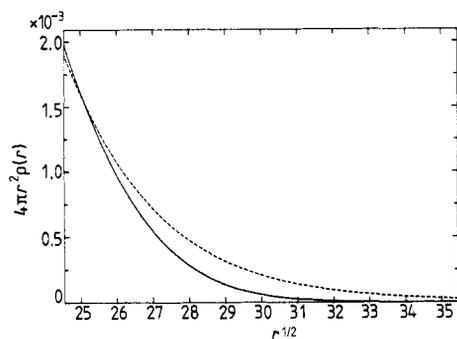


Figure 5. Radial density of krypton in the asymptotic region ($\hbar = c = m = 1$). —, second order; - - -, fourth order.

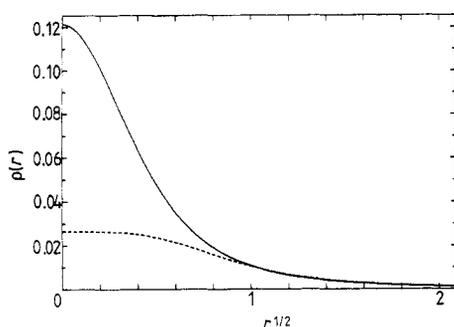


Figure 6. Density of krypton in the vicinity of the origin ($\hbar = c = m = 1$). —, second order; - - -, fourth order.

(figure 6). The density obtained in a second-order calculation drastically overestimates the HF value ($\rho_{\text{HF}}(0) = 0.0125$) for the density at the origin (Clementi and Roetti 1974),

$$\rho_{\lambda=1/9}(0) = 0.1213$$

$$\rho_{\lambda=1/5}(0) = 0.0492.$$

Figure 6 indicates that the result of the fourth-order calculation ($\rho(0) = 0.0265$) is much closer to the HF value, although the difference is still a factor of 2. The fourth-order gradient terms lead to a similar accuracy for the density at the origin as did, for example, the method of Plumer and Stott (1985). Thus we find essentially a slight decrease in quality of the behaviour of the density for $r \rightarrow \infty$ and an improvement at $r = 0$ compared with the second-order gradient expansion.

Our results indicate that the commonly used test of density functionals by insertion of HF or other 'good' densities is not entirely conclusive. The convergence of the gradient expansion of the (non-interacting) kinetic energy, evaluated consistently with the solutions of the corresponding variational equation is much slower than indicated by these tests (compare tables 1 and 2). Variational results obtained for the locally asymptotic scheme of Pearson and Gordon (1985) would be of interest in this connection.

The density obtained as solution of the extended TFDW variational equation is well behaved (even for the case of inclusion of the terms in sixth order) and shows systematic

Table 1. Kinetic energy of the extended TFDW model. Contributions $T^{(0)}$, $T^{(2)}$, $T^{(4)}$, $T^{(0)}$, $T^{(2)}$, $T^{(4)}$, ratios $T^{(2)}/T^{(0)}$ and $T^{(4)}/T^{(2)}$ and precision of the total kinetic energy compared with HF kinetic energy (in au).

Z	$T^{(0)}$	$T^{(0)} + T^{(2)}$	$T^{(0)} + T^{(2)} + T^{(4)}$	T^{HF}	$T^{(2)}/T^{(0)}$	$T^{(4)}/T^{(2)}$	$(T^{\text{TFDW}} - T^{\text{HF}})/T^{\text{HF}}$
1	0.444 745	0.550 813	0.596 087	0.500 000	0.239	0.427	0.1922
2	2.358 79	2.794 07	2.960 99	2.861 68	0.185	0.384	0.0347
10	117.640	129.863	133.743	128.547	0.104	0.317	0.0404
18	488.626	529.709	542.117	526.818	0.084	0.302	0.0290
36	2 599.71	2 770.03	2 819.12	2 752.06	0.066	0.288	0.0244
54	6 883.69	7 273.65	7 383.55	7 232.14	0.057	0.282	0.0209
86	20 972.7	21 978.8	22 256.3	21 866.8	0.048	0.276	0.0178

Table 2. Gradient correction to the exchange energy of neutral noble-gas atoms: zeroth, second and fourth order of the kinetic energy and zeroth and second order of the exchange energy and their percentage contribution to the total energy (in au).

Z	$T^{(0)}$ (% cont.)	$T^{(2)}$ (% cont.)	$T^{(4)}$ (% cont.)	$E_x^{(0)}$ (% cont.)	$E_x^{(2)}$ (% cont.)	$-E_{\text{tot}}$ (% error)
2	2.423 76 (79.6)	0.448 19 (14.7)	0.172 95 (5.68)	0.757 70 (24.9)	0.084 71 (2.78)	3.044 90 (6.40)
10	118.056 (87.9)	12.282 (9.2)	3.904 2 (2.91)	10.444 (7.8)	0.500 48 (0.37)	134.242 (4.43)
18	489.440 (90.1)	41.188 (7.6)	12.451 (2.29)	27.585 (5.1)	0.962 78 (0.18)	543.079 (3.09)
36	2 601.50 (92.2)	170.53 (6.0)	49.170 (1.74)	87.085 (3.1)	2.0789 (0.07)	2 821.20 (2.51)
54	6 886.52 (93.2)	390.26 (5.3)	110.03 (1.49)	170.84 (2.3)	3.2564 (0.04)	7 386.81 (2.14)
86	20 977.4 (94.2)	1006.6 (4.5)	277.69 (1.25)	370.53 (1.7)	5.4417 (0.02)	22 261.8 (1.81)

improvement, if one discounts the exponential asymptotic behaviour for the TFDW model. The asymptotic part of the density is found to be essentially unchanged (from a numerical point of view) and the behaviour at the origin is improved if one compares second- and fourth-order results. Unfortunately the improvement at the origin does not manifest itself as strongly in the energy values due to the statistical weight involved in the integration. The structure of the higher-order gradient terms allows the speculation that the correct asymptotic form of the density and the cusp structure at the origin (as well as shell oscillations) are at best built up very slowly if one adds higher and higher order gradient terms.

The application of the Hohenberg-Kohn variational principle is rather appealing, as the calculational effort is independent of particle number. However, substantial improvements to the accuracy indicated can only be expected with resummed or alternative forms.

The usefulness of the direct variational approach is so far still restricted to situations where an overview rather than accuracy is required. It can, however, also be employed as a first step towards more accurate results as in the two-step scheme first suggested by Latter (1955) for atomic systems.

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