Modified Statistical Treatment of Kinetic Energy in the Thomas−Fermi Model[†]

Jeng-Da Chai[*,‡] **and John D. Weeks**[‡,§]

Institute for Physical Science and Technology, and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

We try to improve the Thomas−Fermi model for the total energy and electron density of atoms and molecules by directly modifying the Euler equation for the electron density, which we argue is less affected by nonlocal corrections. Here we consider the simplest such modification by adding a linear gradient term to the Euler equation. For atoms, the coefficient of the gradient term can be chosen so that the correct exponential decay constant far from the nucleus is obtained. This model then gives a much improved description of the electron density at smaller distances, yielding in particular a finite density at the nucleus that is in good qualitative agreement with exact results. The cusp condition differs from the exact value by a factor of 2. Values for the total energy of atomic systems, obtained by coupling parameter integration of the densities given by the Euler equation, are about as accurate as those given by the very best Thomas−Fermi−Weizsäcker models, and the density is much more accurate. Possible connections to orbital-free methods for the kinetic-energy functional in density functional theory are discussed.

I. Introduction

Density functional theory (DFT) has proved to be a powerful way to determine equilibrium and dynamic properties of atoms, molecules, and extended systems.[1−5] The modern conceptual framework was established by Hohenberg and Kohn (HK),[6] who proved that the exact ground-state energy of a system of N electrons is a functional $E[\rho]$ of the ground-state electron density $\rho(r)$ only, where

$$E[\rho] = \int \rho(r)V_{ext}(r)\, dr + F[\rho] \qquad (1)$$

and $F[\rho]$ is an unknown but universal functional of the density and is independent of the external potential $V_{ext}(r)$.

Kohn and Sham (KS)[7,8] showed that $F[\rho]$ can be usefully partitioned into two dominant (kinetic and potential energy) terms and a residual correction

$$F[\rho] = T_s[\rho] + \frac{1}{2}\int \frac{\rho(r')\rho(r)}{|r - r'|}\, dr'\, dr + E_{xc}[\rho] \qquad (2)$$

The first term on the right of eq 2 is the KS *kinetic-energy density functional* $T_s[\rho]$. This gives the kinetic energy of the ground state of a reference or model system of N noninteracting electrons in a self-consistent field chosen so that the ground-state density equals $\rho(r)$. The second term is the classical (Hartree) *electron−electron potential energy* (atomic units are used in this paper), and the last term is the *exchange-correlation density functional* $E_{xc}[\rho]$, which formally accounts for *all* remaining smaller corrections.

If these functionals were known, then one could obtain density $\rho(r)$ from the variational principle (Euler equation) associated with eq 1

$$\mu = V_{T_s}(r;[\rho]) + V_{eff}(r;[\rho]), \qquad (3)$$

and then determine the total energy of the inhomogeneous system from the energy functional $E[\rho]$. All other physical quantities related to the ground-state density could also be determined. Here

$$V_{T_s}(r;[\rho]) \equiv \delta T_s[\rho]/\delta\rho(r) \qquad (4)$$

is the KS *kinetic potential*,[9] formally defined as a functional derivative of $T_s[\rho]$, μ is the chemical potential (the Lagrange multiplier associated with the normalization condition $\int \rho(r)\, dr = N$), and $V_{eff}(r;[\rho])$ is an effective one-body potential for the KS partitioning, defined by

$$V_{eff}(r;[\rho]) \equiv V_{ext}(r) + \int \frac{\rho(r')}{|r - r'|}\, dr' + \frac{\delta E_{xc}[\rho]}{\delta\rho(r)} \qquad (5)$$

Through the efforts of many workers, we now have rather accurate expressions for the *exchange-correlation potential* $V_{xc}(r;[\rho]) \equiv \delta E_{xc}[\rho]/\delta\rho(r)$ in eq 5, and the main problem in solving the Euler eq 3 is in finding an accurate approximation for the kinetic potential as a functional of the density.[1,10] The most straightforward way to proceed would be to develop approximations for $T_s[\rho]$ itself and obtain $V_{T_s}(r;[\rho])$ by functional differentiation, but this has proved to be a very challenging problem. As discussed below, simple local density approximations for $T_s[\rho]$ based on the Thomas−Fermi (TF) theory are not very accurate and make several qualitatively incorrect predictions.

To bypass such problems, KS suggested a different way to compute the numerical value of T_s exactly, not directly from the density itself but by introducing a set of N orbitals satisfying the N-coupled KS equations that describe the model system.[7,8] By use of these orbitals, one can determine both T_s and the total density $\rho(r)$.

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[*] To whom correspondence may be addressed. E-mail: jdchai@wam.umd.edu.
[‡] Institute for Physical Science and Technology, University of Maryland.
[§] Department of Chemistry and Biochemistry, University of Maryland.

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This accurate treatment of the kinetic energy played a central role in the development of DFT as a quantitative method.[1] The KS method has yielded very accurate ground-state densities and energies for many systems using currently available $E_{xc}[\rho]$. In many cases, even a simple local density approximation for $E_{xc}[\rho]$ proves adequate, and we will use this in the results reported here. However, the numerical cost of self-consistently determining N orbitals rapidly increases for large N. An accurate treatment of the kinetic energy as well as the potential-energy contributions in terms of the electron density only, as originally envisioned in the work of HK, would certainly be desirable.

To that end, there has been renewed interest in developing "orbital-free" (OF) approximations for the kinetic-energy density functional $T_s[\rho]$, with some notable successes in describing extended systems.[10−15] The main advance has been to introduce *nonlocal* density functionals that reproduce known exact results for the linear response of the density of the model system to small perturbations. Similar ideas led to the development of nonlocal weighted density functional theories for classical nonuniform fluids, again with some notable successes.[16] However, in both cases, it has proved difficult to gain a physical understanding of how best to incorporate essential nonlocal effects directly into the kinetic-energy (or classically, the free-energy) functional through various weighting kernels and to understand what errors in the density will likely arise from given approximations to these functionals.

We pursue here an intermediate strategy between the ultimately desirable goal of determining $T_s[\rho]$ as a functional of the density and the KS method, which avoids direct use of the density and uses orbitals to calculate numerically both T_s and the density. We focus instead on approximating the kinetic potential $V_{T_s}(r;[\rho])$ as a functional of the density. The connection to the density response is more direct and physically suggestive, and we believe that nonlocal effects in $V_{T_s}(r;[\rho])$ could be less problematic than in the full $T_s[\rho]$.

II. Nonlocal Effects in $T_s[\rho]$ and $V_{T_s}(r;[\rho])$

$T_s[\rho]$ can be formally related to $V_{T_s}(r;[\rho])$ by a (functional) integration over the density changes in all space, as the density is changed from a uniform to the final nonuniform value.[17,18] Because of this spatial integration, $T_s[\rho]$ is a more nonlocal functional of the density than is $V_{T_s}(r;[\rho])$. Other detailed theoretical arguments suggesting that V_{T_s} is more local have recently appeared.[19] A second consequence of this integration is that the numerical value of $T_s[\rho]$ depends mainly on smoothed or spatially averaged properties of $\rho(r)$. Thus the inverse problem of accurately determining $\rho(r)$ from eq 3 at all values of r using a $V_{T_s}(r;[\rho])$ derived from an approximate $T_s[\rho]$ in eq 4 can be poorly conditioned; very large errors in the density at particular values of r can arise from an approximate $T_s[\rho]$, whose numerical value differs by only a relatively small amount from the correct value. For example, as discussed below, a self-consistent solution of eq 3 using a $V_{T_s}(r;[\rho])$ arising from the local TF approximation to $T_s[\rho]$ and a $V_{eff}(r)$ appropriate for an Ar atom predicts an *infinite* density at the nucleus, although the numerical value for T_s is only about 30% above the correct value.

But there is another way to make progress. If we can find a reasonably accurate way to calculate $\rho(r)$ directly from eq 3 for a variety of $V_{ext}(r)$, then we can integrate the induced density changes as the field is "turned on" to obtain the total energy E and T_s. See eq 16. Now the smoothing property of the integration helps make the results for E less sensitive to whatever errors remain in $\rho(r)$, and we would expect good results.[17]

However, in general the integration must be carried out numerically over a range of density changes, and simple analytical approximations to $V_{T_s}(r;[\rho])$ do not automatically translate into equivalently simple analytical expressions for $T_s[\rho]$. If accurate direct approximations for $T_s[\rho]$ could be found, the corresponding determination of E and T_s would require only the (final) equilibrium density $\rho(r)$ and would certainly be simpler. It remains to be seen whether the benefits of focusing first on $V_{T_s}(r;[\rho])$ will outweigh this cost. In the interim, our approach still preserves many of the potential advantages of OF methods over the more complicated KS procedure of determining T_s numerically using orbitals, and we believe that insights gained from its use may lead to better direct approximations for $T_s[\rho]$.

Similar ideas has been successfully applied to classical nonuniform fluids[17,18,20,21] where the density response and free-energy change arising from a wide variety of external fields $V_{ext}(r)$ have been accurately determined from the classical analogue of eq 3. The terms in that equation can be given physically suggestive interpretations, and the results are comparable to those arising from the best versions of classical weighted density functional theories. In the simplest version of this theory, appropriate for very slowly varying effective fields, one arrives at a (local) differential equation involving only the density and a *linear* second derivative term, as in the classical van der Waals theory of the liquid−vapor interface.[18] Nonlocal effects arising from more rapidly varying fields can be taken into account directly in the density response by using an optimized version of linear response theory.[18,17,20,21]

In this paper, we consider only local approximations to $V_{T_s}(r;[\rho])$ that at each r involve the local density $\rho(r)$ and its lowest-order gradients, motivated by analogous approximations made for $T_s[\rho]$ in the TF theory and the von Weizsäcker modifications and by the equivalent theory for classical fluids. In future work, we plan to examine nonlocal corrections suggested by an optimized version of linear response theory and thus make contact with current work on OF methods and earlier related work by Pratt and co-workers.[22]

III. TF and von Weizsäcker Approximations for $T_s[\rho]$

The first direct approximation for the kinetic-energy functional was found in the TF model,[23,24] where

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(r)\, dr \qquad (6)$$

Here

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

The TF kinetic-energy functional, $T_{TF}[\rho]$, is derived by local use of a uniform free-electron gas model and is known to be exact in the limit of an infinite number of electrons.[25]

However, for an atomic system, the number of electrons N is finite and the effective potential is very rapidly varying near the nucleus. As a result, there are many deficiencies in the TF model for such applications. The total energies predicted for atomic systems give at best an order of magnitude estimate and cannot be relied on for quantitative calculations. More serious errors can be seen in the density response at particular values of r as determined from the Euler eq 3. As mentioned above, the TF model predicts an infinite electron density at the nucleus. In addition, the density does not decay exponentially in the classically forbidden region (the tail region), and it does not

show any shell structure. Furthermore, the TF model predicts no atomic bonding to form molecules or solids.[26,27]

Though the TF model has many shortcomings, it is a natural local approximation and gives a simple analytical expression for the kinetic-energy density functional and the kinetic potential. Moreover, it is known that greatly improved results can be obtained for atomic and molecular ground-state energies[28−31] if better-quality densities are used in $T_{TF}[\rho]$ instead of the self-consistent variational densities arising from a solution of eq 3. For example, if the Hartree−Fock (HF) density[32] for Ar is used in $T_{TF}[\rho]$, the kinetic energy is only 7% below the correct result. This suggests that improvements to the TF model should focus directly on the Euler eq 3 and the density response it predicts.

In this paper, we show that the Euler eq 3 can give surprisingly accurate results for atomic densities and energies if the kinetic potential derived from the original TF model is augmented by a simple gradient term that helps satisfy important boundary conditions both near and far away from the nucleus. The specific form of this correction was inspired by the von Weizsäcker modification of the TF kinetic-energy density functional, which we now describe.

By considering modified plane waves of the form $(1 + \boldsymbol{a} \cdot \boldsymbol{r}) e^{i\boldsymbol{k} \cdot \boldsymbol{r}}$, with $\boldsymbol{a}$ a constant vector and $\boldsymbol{k}$ the local wave vector, von Weizsäcker[33] derived a correction

$$T_W[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})} \, d\boldsymbol{r} \qquad (7)$$

to the TF kinetic-energy functional. A generalized total kinetic-energy functional incorporating a correction of this kind can be written as

$$T_{TF\lambda W}[\rho] = T_{TF}[\rho] + \lambda T_W[\rho] \qquad (8)$$

where λ is a parameter. $\lambda = 1$ corresponds to the original von Weizsäcker correction, and its self-consistent use in eq 3 for atoms not only yields a finite electron density at the nucleus with the exact cusp condition[34] satisfied but also gives the correct exponential decay of the density far from the nucleus[35,36] for the exact μ. We refer to this as the TFW model. Disappointingly, however, the kinetic energy given by this approach is not much better than that of the original TF model. For example, the results for Ar are 29% below the correct value.

Other values of λ have also been examined. All TFλW models predict a finite electron density at the nucleus, and exponential decay far from nucleus but only $\lambda = 1$ satisfies the exact cusp condition and gives the correct exponential decay constant. $\lambda = 1/9$ has been shown to give the correct second-order gradient expansion correction to the TF functional and to reproduce the exact linear response of a homogeneous electron gas under a long wavelength perturbation,[37] but energy predictions for atoms again are inaccurate. Tomishima and Yonei[38] found empirically that rather accurate atomic ground-state energies for a wide range of Z can be obtained by using $\lambda = 1/5$. However, the inaccurate description of the electron density near and far from nucleus and the absence of shell structure are still present, and part of this good agreement probably comes from a cancellation of errors.

These models use simple gradient corrections suggested by the von Weizsäcker theory to try to improve the TF kinetic-energy functional directly. However, nonlocal effects certainly must be important in $T_s[\rho]$, as is recognized in recent OF methods, and these must be taken into account before this approach is likely to be quantitatively useful.

IV. Modified Euler Equations for the Density Response

As argued above, it may be more profitable to examine simple gradient corrections directly in the more local Euler equation. The Euler equation arising from use of the TFλW expression for $T_s[\rho]$ is

$$\mu = \frac{5}{3} C_F \rho^{2/3}(\boldsymbol{r}) + \frac{\lambda}{8} \frac{|\nabla \rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})^2} - \frac{\lambda}{4} \frac{\nabla^2 \rho(\boldsymbol{r})}{\rho(\boldsymbol{r})} + V_{eff}(\boldsymbol{r}) \qquad (9)$$

There is a local term in the density from the TF model and *two* terms involving density gradients. Both terms must be present with specified coefficients if we insist on using simple local expressions of the von Weizsäcker form directly in $T_s[\rho]$ with no compensating terms from nonlocal corrections. However the first nonlinear gradient term does not have a simple physical interpretation and does not appear in the analogous classical van der Waals equation for the liquid−vapor interface.[18] A linear gradient correction like the second term would be expected on quite general grounds. Moreover, we find that the second term alone is responsible for producing a finite density at an atomic nucleus with $V_{ext}(\boldsymbol{r}) = V_{ext}(r) = -Z/r$, effectively building in the uncertainty principle, and of course this term alone contributes to the linear response of the density to weak fields. Finally this term yields exponential decay far from the nucleus.

Thus we propose as the simplest correction to the TF kinetic potential a modified Euler equation where only the linear gradient term appears, with a coefficient chosen to best describe the density response. To avoid confusion in notation, λ is changed to α in our new Euler equation

$$\mu = \frac{5}{3} C_F \rho^{2/3}(\boldsymbol{r}) - \frac{\alpha}{4} \frac{\nabla^2 \rho(\boldsymbol{r})}{\rho(\boldsymbol{r})} + V_{eff}(\boldsymbol{r}) \qquad (10)$$

Note that we use a $V_{eff}(\boldsymbol{r})$ that includes the effects of exchange and correlation in all the calculations reported herein. Thus eq 10 does not reduce to the classical TF model when $\alpha = 0$.

We first examine the predictions of this model for atoms. It is easy to show that the density at the nucleus is finite for any choice of α and satisfies

$$\frac{\rho'(0)}{\rho(0)} = - \frac{2Z}{\alpha} \qquad (11)$$

The exact cusp condition[34] for the logarithmic derivative of the density at the origin can be satisfied if $\alpha = 1$, as in the TFW model. However, this choice does not guarantee correct values for $\rho(0)$ and $\rho'(0)$ separately, and indeed the TFW model gives very poor results for these terms. For example, for Ar, $\rho(0)$ is 72% below the HF value. Moreover, the nonlinear gradient term in the TFW model does not seem to improve the density at intermediate values of r when compared to the results of our model.

Equation 10 also produces exponential decay of the density at large r, where

$$\rho(r) \approx \exp[-(-4\mu/\alpha)^{1/2} r] \qquad (12)$$

When $\alpha = 1/2$, the correct exponential decay constant for the exact μ is predicted.

By use of this one-parameter model, we cannot satisfy both the exact cusp condition and asymptotic decay condition with the same α, and it is clear that no oscillatory shell structure will be generated by the simple gradient term. (As is the case for the classical van der Waals theory of interfaces, nonlocal corrections are required to get oscillatory structure.)[18] But we
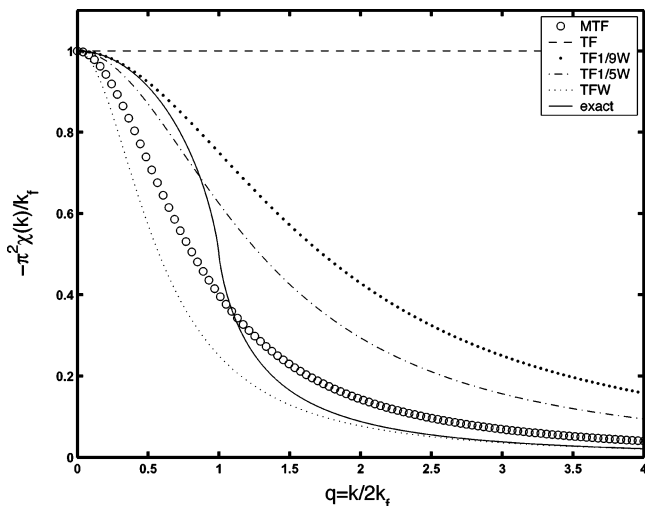
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Figure 1. Linear response functions of a uniform system of independent fermions as given by the various models.

TABLE 1: Electron Density at the Nucleus $\rho(0)$ Using the Various TF-Type Models, the KS Method, the HF Method, and the MTF Model

	MTF	HF[a]	TF$^{1}/_{5}$W	TFW	KS
H	0.5820	0.3183	2.390	0.1029	0.2728
He	5.208	3.596	19.29	0.9515	3.525
Ne	788.2	619.9	2595	169.6	614.5
Ar	4811	3840	15482	1093	3819
Kr	40064	32236	126491	9579	32146
Xe	137631	112219	431005	33710	111005

[a] The HF data is taken from Clementi et al.[32]

TABLE 2: $\langle r^{-1} \rangle$ Using the TF$^{1}/_{5}$W Model, the KS Method, and the MTF Model

	MTF	TF$^{1}/_{5}$W	KS
H	1.000	1.249	0.9208
He	2.907	3.261	3.312
Ne	30.56	30.75	31.00
Ar	69.93	69.63	69.62
Kr	183.5	181.7	182.7
Xe	321.2	317.8	317.8

can hope that a proper choice of α could give a smoothed electron density that reproduces important overall features and gives improved atomic energies when compared to the TF model. Since any α produces a finite density at the nucleus and thus corrects a major shortcoming of the TF model, we choose $\alpha = {}^{1}/_{2}$ to give the correct exponential decay of the density far from the nucleus. This is the region that should be most important in chemical bonding. In the following, we refer to eq 10 with $\alpha = {}^{1}/_{2}$ as the modified TF (MTF) model. We show below that the MTF model gives atomic energies comparable to those of the best TFλW model with $\lambda = {}^{1}/_{5}$ along with a much better description of the density distribution.

V. Results for the MTF Model

A. Linear Response Function. We first examine the predictions of the various models for the linear response of the density of the model system to a weak perturbing potential. In Fourier space, this can be written as

$$\delta\rho(\boldsymbol{k}) = \chi(\boldsymbol{k})\delta V(\boldsymbol{k}) \tag{13}$$

Here $\chi(\boldsymbol{k})$ is the Fourier transform of the linear response function for a uniform system of noninteracting electrons, which can be derived exactly from first-order perturbation theory[39]

$$\chi(\boldsymbol{k}) = -\frac{k_{\mathrm{f}}}{\pi^{2}}\left(\frac{1}{2} + \frac{1-q^{2}}{4q}\ln\left|\frac{1+q}{1-q}\right|\right) \tag{14}$$

where k_{f} is the Fermi wave vector and $q = k/2k_{\mathrm{f}}$ is a dimensionless momentum.

The corresponding response function for the TF λW model, eq 8, is given by[40]

$$\chi(\boldsymbol{k})_{\mathrm{TF}\lambda\mathrm{W}} = -\frac{k_{\mathrm{f}}}{\pi^{2}}\left(\frac{1}{1+3\lambda q^{2}}\right) \tag{15}$$

as can be seen from eq 9 for an infinitesimal V_{eff}. It is easy to see that the nonlinear gradient term in eq 9 does not contribute to the linear response function. As a result, the linear response function for the MTF model, derived from eq 10 with $\alpha = {}^{1}/_{2}$, is the same as the TF$^{1}/_{2}$W model. As shown in Figure 1, the TF$^{1}/_{9}$W model is exact for long-wavelength perturbations but becomes worse in the high-k region, while the TFW model is exact for short-wavelength perturbations but fails in the low-k regions. The MTF model gives a qualitatively reasonable

average description of the exact linear response function, especially in the important region near the singularity at $q = 1$. Wang et al.[10] have suggested that reproducing the singularity and the overall form of the linear response function are important for obtaining the correct physics from OF methods, particularly for producing the shell structure of atoms. While no simple gradient-type model can describe the singularity exactly (or give shell structure), the MTF model captures the average behavior of the linear response function and shows better accuracy in the physically significant region near $q = 1$.

B. Atoms. We carried out benchmark calculations on the hydrogen atom and the rare gas atoms based on our MTF model. Our results are compared with the TF model and its von Weizsäcker-type gradient corrections. We examined $\lambda = {}^{1}/_{9}$, ${}^{1}/_{5}$, ${}^{1}/_{2}$, and 1 but report results only for $\lambda = {}^{1}/_{5}$ and 1 and for the KS and HF methods. The local density approximation (LDA)[41−44] for the exchange-correlation functional is used for all the models. The standard method for solving Euler equations derived from the TFλW model[45] was implemented to solve the Euler equation for the MTF model and the KS theory. Our TF$^{1}/_{5}$W and KS results are in very good agreement with previous calculations[46] using a slightly different LDA parametrization.[47] The code uses the finite difference method with the Gauss−Chebyshev (of the second kind) radial quadrature, proposed by Becke et al., consisting of 1000 points, and Becke's algorithms for solving Poisson's equation for the Hartree potential.[48]

As shown in Table 1, the electron density at the nucleus, $\rho(0)$, calculated by the MTF model, is close to the HF results. As discussed above, the TF model predicts an infinite value for the electron density, while the TF$^{1}/_{5}$W model overestimates the density by a factor of 4. The TFW model considerably underestimates the density, despite satisfying the exact cusp condition. It is known[49] that $\rho(0)$ is related to the density moments $\langle r^{-1} \rangle$ and $\langle r^{-2} \rangle$. Thus the MTF model would be expected to give good results for these expectation values, as is shown in Tables 2 and 3, respectively.

In Table 4 we compare the chemical potential μ for the MTF theory, calculated by a self-consistent solution of eq 10, with that given by the KS equation and find very good agreement. This means that the asymptotic behavior of the density predicted by the MTF model is close to the prediction of the KS theory, since the MTF model would give exact results for the exact μ. Since the accuracy of the density in the tail is an important indicator of chemical bonding,[1] we believe that this desired behavior could lead to chemical bonding in molecules.

TABLE 3: $\langle r^{-2} \rangle$ Using the TF$^1/_5$W Model, the KS Method, the HF Method, and the MTF Model

	MTF	TF$^1/_5$W	KS	HF[a]
H	2.394	4.720	1.749	-
He	11.50	20.06	11.71	11.99
Ne	394.7	599.7	411.9	414.9
Ar	1390	2056	1459	1465
Kr	6025	8705	6318	-
Xe	14101	20148	14799	14818

[a] The HF data is taken from Porras et al.[57]

TABLE 4: Atomic Chemical Potential μ Using the Various TF-Type Models, the KS Method, and the MTF Model

	MTF	TF	TF$^1/_5$W	TFW	KS
H	−0.2825	−0.08039	−0.09549	−0.09773	−0.2337
He	−0.3822	−0.06290	−0.1013	−0.1393	−0.5702
Ne	−0.4400	−0.04959	−0.1093	−0.2188	−0.4978
Ar	−0.4304	−0.05034	−0.1112	−0.2346	−0.3823
Kr	−0.4224	−0.05017	−0.1130	−0.2485	−0.3464
Xe	−0.4192	−0.05034	−0.1138	−0.2552	−0.3100

The Euler eq 10 for the MTF model is not derived by a functional derivative of an energy functional. As a result, we cannot immediately obtain the energy once we have determined the density, as would be possible in OF methods that give direct approximations for $T_s[\rho]$. Instead, we can use a coupling parameter approach[22,50−53] to calculate the energy change as the external potential is turned on

$$E = E_{\lambda=0} + \mu \int [\rho_{\lambda=1}(r) - \rho_{\lambda=0}(r)]\,dr +$$
$$\int_0^1 d\lambda \int \rho_\lambda(r)V_{\text{ext}}\,dr \quad (16)$$

Here the external potential V_{ext} is linearly scaled by a coupling parameter λ (not to be confused with the λ parameter in the TFλW methods), and the corresponding density is ρ_λ. E is the total energy of the system, and $E_{\lambda=0}$ is the total energy at the same μ in the absence of the external potential.

If exact values for ρ_λ were used, eq 16 would give exact results and a variety of different integration pathways (e.g., nonlinear scaling of V_{ext}) could be used. Since we make approximations, there will be errors in our predicted E values and different pathways could (incorrectly) give different results. However, our experience for the analogous classical problem suggests that these errors are small if the density is reasonably accurate,[17] as seems to be the case here.

We note that $\rho_{\lambda=0}$ and thus $E_{\lambda=0}$ vanish for the uniform electron gas because of the fixed negative value of the chemical potential. Therefore, E, the total energy, can be straightforwardly computed from eq 16 by numerical integration over a series of λ values. For the benchmark calculations reported here for the total energy, 1000 points are used between $\lambda = 0$ and $\lambda = 1$, though reasonable results can be obtained with about 10 points. The kinetic energy can then be found by subtracting the potential energy (calculated from the potential-energy density functionals) from the total energy. This way of obtaining kinetic energy is equivalent to integrating the kinetic potential directly as discussed above, but we believe it is numerically more accurate. As shown in Table 5, the total energy of the MTF model is comparable to that of the TF$^1/_5$W model, the best TFλW model for the total atomic energy.

In Figures 2−5, we compare the radial density distribution $r^2\rho(r)$ of the MTF model to that predicted by other theories. Although the MTF model shows no shell structure when compared to the essentially exact KS theory, it gives a nice averaging of the electron density, with slightly more emphasis on the principle peak than in the TFλW models, along with
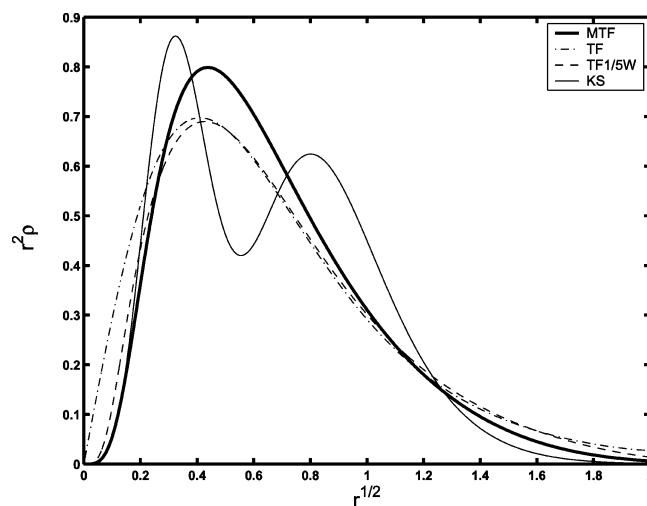
Figure 2. Radial density $r^2\rho$ of the neon atom with the various TF-type models, the KS method, and the MTF model.
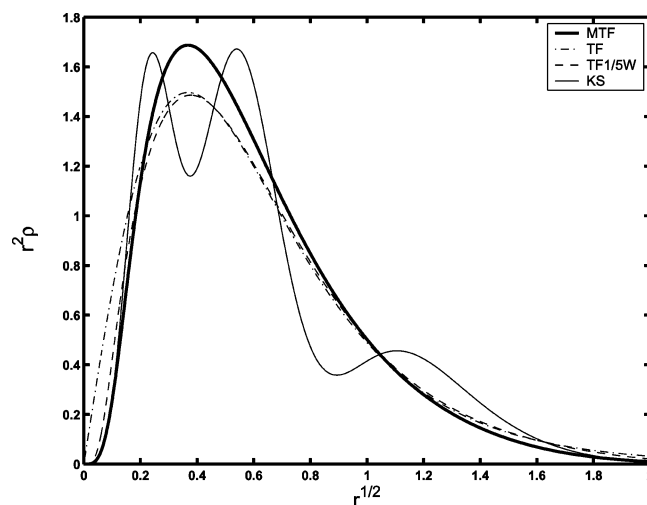
Figure 3. Radial density $r^2\rho$ of the argon atom with the various TF-type models, the KS method, and the MTF model.

TABLE 5: Atomic Energy E Using the Various TF-Type Models, the KS Method, and the MTF model

	MTF	TF	TF$^1/_5$W	TFW	KS
H	−0.6092	−1.076	−0.6085	−0.2927	−0.4459
He	−2.902	−4.756	−2.917	−1.559	−2.834
Ne	−129.5	−176.6	−129.5	−86.40	−128.2
Ar	−529.0	−681.1	−526.2	−375.5	−525.9
Kr	−2774	−3378	−2747	−2099	−2750
Xe	−7293	−8643	−7214	−5701	−7229

significantly better results both near and far from the nucleus. The fact that a smooth density can give such accurate energies illustrates the point that the integration in eq 16 renders it less sensitive to small errors in the density.

C. Diatomic Molecules. Gordon and Kim (GK) suggested a simple model for calculating the intermolecular potential of closed-shell molecules.[54] By the assumption that the molecular density of a diatomic molecule can be expressed as the sum of the two separate atomic densities, reasonable bonding potentials for closed-shell molecules can be obtained. Instead of using the inaccurate TF atomic densities, GK used the atomic HF densities and inserted these into the original TF kinetic-energy functional, together with the classical electron−electron and nuclear−electron potentials and a local density approximation for the exchange-correlation functionals.
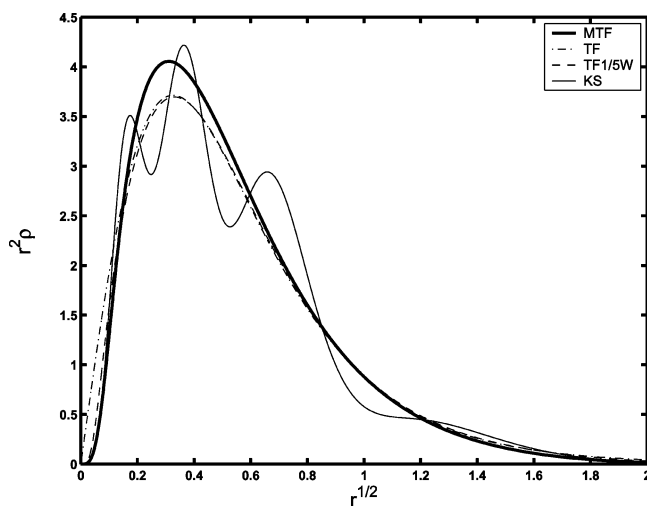
Kinetic Energy in the Thomas−Fermi Model

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Figure 4. Radial density $r^2\rho$ of the krypton atom with the various TF-type models, the KS method, and the MTF model.
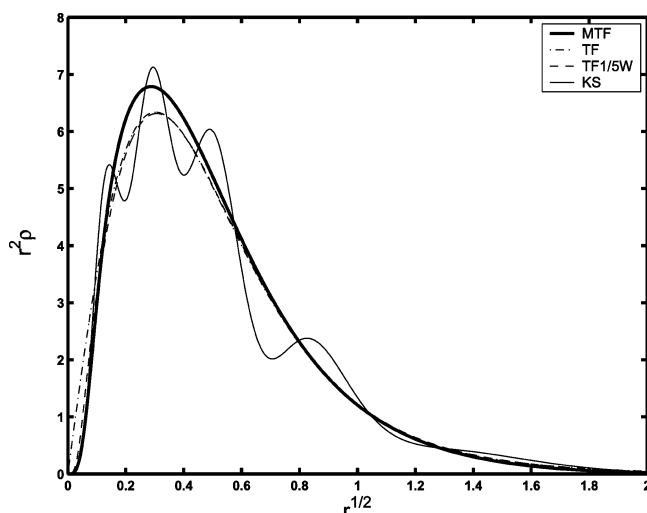

Figure 5. Radial density $r^2\rho$ of the xenon atom with the various TF-type models, the KS method, and the MTF model.

We followed GK's simple approach, using atomic densities for the Ar atom given by the various models discussed here. Becke's atomic partition, the Gauss−Chebyshev (of the second kind) radial quadrature, and the Clenshaw-Curtis angular quadrature with 1000 radial points and 500 angular points are used in the numerical calculations.[55,56]

We found that the KS bonding potential is very similar to the HF result, as is expected due to the high quality of its atomic density. As we can see in Figure 6, the strength of the bonding of the TFλW models increases as λ increases. However, the bonding energy is consistently overestimated, even for the smallest value of λ. The MTF model predicts a reasonable bonding curve, with both its strength and bond length close to the HF and KS methods. Note that even the TF density can give a qualitatively accurate bonding curve using the GK method, though a self-consistent solution of the molecular density using the TF model is known to give no bonding.[26]

VI. Possible Generalizations

We used heuristic arguments to suggest the form of the MTF eq 10. One might hope that a more systematic search using generalized forms of this kind could yield even better results. Since the MTF model has only one parameter, α, we considered
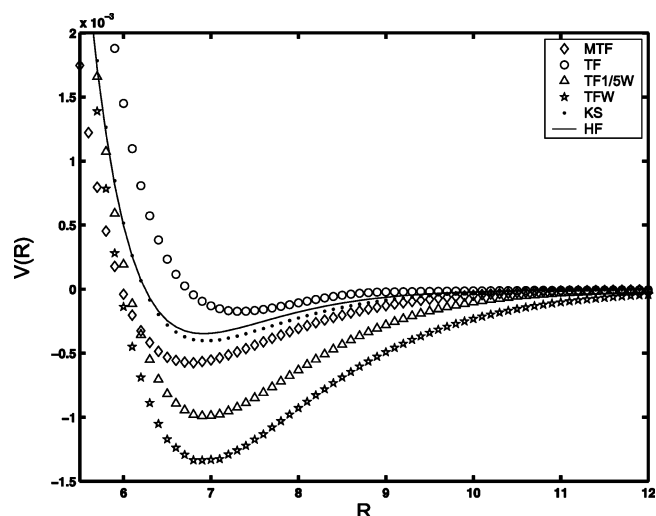

Figure 6. Ar−Ar interaction potential via the GK approach.

one such generalization of the gradient term in (10) that allows for the introduction of a second parameter, β, and that interpolates between the MTF and the TFλW models

$$-\frac{\alpha}{4}\frac{\nabla^2\rho^\beta}{\rho^\beta} = -\frac{\alpha}{4}\left\{\beta(\beta-1)\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2} + \beta\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}\right\} \quad (17)$$

For $\alpha = 1/2$ and $\beta = 1$, this reduces to the MTF form, while the TFλW models correspond to $\{\alpha,\beta\} = \{2\lambda,1/2\}$, as can be seen from eq 9.

By use of this generalized form in eq 10 for atomic systems, the density at the nucleus is finite and satisfies a modified cusp condition

$$\frac{\rho'(0)}{\rho(0)} = -\frac{2Z}{\alpha\beta} \quad (18)$$

When $\alpha\beta = 1$, the exact cusp condition is satisfied. This form also produces an exponentially decaying density in the tail, satisfying

$$\rho(r) \approx \exp\left[-\left(\frac{-8\mu}{2\alpha\beta^2}\right)^{1/2}r\right] \quad (19)$$

When $2\alpha\beta^2 = 1$, the correct asymptotic decay constant is found for the exact μ.

However only when $\{\alpha,\beta\} = \{2,1/2\}$ (i.e., the original von Weizsäcker model with $\lambda = 1$) can both conditions be satisfied simultaneously. Since all values give a finite density at the origin, we also considered the one-parameter family of models with $2\alpha\beta^2 = 1$ that give the correct exponential decay constant. However, the best overall results for the atomic energy and density were still found using the MTF model with $\{\alpha,\beta\} = \{1/2,1\}$. Evidently the nonlinear gradient term in eq 17 that is generated when $\beta \neq 1$ does not improve the simple MTF model and other forms should be examined.

VII. Final Remarks

In summary, we have argued that it may be profitable to focus first on the Euler equation determining the electron density when correcting the TF model and more generally in developing OF approximations in DFT. Nonlocal effects may be less severe, as is suggested by the generally good results found from use of the simple gradient correction discussed here. In future work,

we hope to take account of nonlocal corrections to the density response by using an optimized version of linear response theory.[18,22]

As presently implemented in eq 16, a coupling parameter integration is required to determine the total energy directly from the density response. This is numerically more costly than would be the case if accurate, variationally stable, direct OF approximations for $T_s[\rho]$ can be found that yield good results for $\rho(r)$ for all r when the associated $V_{T_s}(r;[\rho])$ is used in the Euler equation.

A less ambitious goal that may prove almost as useful is to develop approximate energy functionals that, while not variationally accurate enough to use directly in the Euler equation, still give good numerical results for the kinetic and total energies of particular classes of systems if reasonably accurate densities are supplied as input. The use of such functionals in theories such as ours would eliminate the need for the coupling parameter integration and simplify the calculation of the total energy. As the simplest such example, if the MTF density is directly inserted into the TF kinetic-energy functional, the deviation of the kinetic energy from the MTF value is less than 10% (except for the lightest atoms H (20%) and He (17%)). We found empirically that the TF^1/$_7$W functional gives results to within about 1% for the heavier atoms, though there is no real justification for such a choice and a more systematic procedure is called for. We are currently investigating whether these ideas can be further developed and usefully applied to molecules and extended systems.

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