Statistical atomic models with minimal-basis-set-type electron densities

Eduardo Hernández and José L. Gázquez

Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México 20, D.F.

The accuracy of an energy-density functional that contains kinetic-energy terms up to fourth order in the gradient expansion and exchange-energy terms up to second order, is tested by constructing a trial charge density in the same way as is done in a minimal-basis-set-Hartree-Fock-type calculation. It is found that while the total energies for He, Ne, Ar, and Kr, obtained by optimization of the parameters through the statistical functional differ slightly from those determined by the Hartree-Fock method. The electron densities are poorly described, especially in Ar and Kr. The results for the molecules CH_4, NH_4^+, BH_4^-, SiH_4, and GeH_4 within the one-center approximation are also reported and compared with similar Hartree-Fock calculations to test the accuracy of the model to predict equilibrium distances. The same type of density is used in connection with an energy-density functional whose kinetic-energy part is given by a partitioned-density model recently proposed by Bader, which leads to similar results.

I. INTRODUCTION

The theorems of Hohenberg and Kohn[1] provide the fundamental basis for the search of the exact energy-density functional. Unfortunately, except for the trivial case of one-electron system, the correct kinetic-energy-density, $T[\rho]$, and exchange-correlation energy-density, $K[\rho]$, functionals are not as yet known. However, recently it has been shown[2,3] that when a Hartree-Fock or even better charge density is used, the kinetic ener-gy may be computed quite accurately from the truncated expansion

$$T[\rho] = T_0[\rho] + T_2[\rho] + T_4[\rho], \tag{1}$$

where

$$T_0[\rho] = \tfrac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3} d\tau, \tag{2}$$

$$T_2[\rho] = \tfrac{1}{72} \int \frac{(\nabla\rho)^2}{\rho} d\tau, \tag{3}$$

and

$$T_4[\rho] = \frac{1}{540(3\pi^2)^{2/3}} \int \rho^{1/3} \left[\left[\frac{\nabla^2\rho}{\rho} \right]^2 - \frac{9}{8} \left[\frac{\nabla^2\rho}{\rho} \right] \left[\frac{\nabla\rho}{\rho} \right]^2 + \frac{1}{3} \left[\frac{\nabla\rho}{\rho} \right]^4 \right] d\tau. \tag{4}$$

The term T_0 is the kinetic energy of a free-electron gas, T_2 is $\tfrac{1}{9}$ of the original Weizsacker[4] correction for inhomogeneity as recently strongly argued[1,5,6] and T_4 is the fourth-order correction as given by Hodges.[7]

On the other hand, it has been shown[8] that, within the Kohn-Sham formalism,[9] the exchange energy density (the correlation energy being neglected) can be approximated reasonably well by

$$K[\rho] = K_0[\rho] + K_2[\rho], \tag{5}$$

where (for the spin-restricted case)

$$K_0[\rho] = -\tfrac{9}{4}\alpha \left[\frac{3}{8\pi} \right]^{1/3} \int \rho^{4/3} d\tau, \tag{6}$$

with

$$\alpha = \frac{n_\uparrow \alpha_\uparrow + n_\downarrow \alpha_\downarrow}{n_\uparrow + n_\downarrow},$$

$$\alpha_\uparrow = 0.68926 \frac{\left[1 + \dfrac{2.69571}{n_\uparrow} \right]}{\left[1 + \dfrac{4.04357}{n_\uparrow} \right]^{2/3}},$$

and

$$K_2[\rho] = -\tfrac{3}{2}\beta \left[\frac{3}{\pi} \right]^{1/3} \int \frac{|\nabla\rho|^2}{\rho^{4/3}} d\tau, \qquad (7)$$

with

$$\beta = \frac{n_\uparrow \beta_\uparrow + n_\downarrow \beta_\downarrow}{n_\uparrow + n_\downarrow},$$

$$\beta_\uparrow = 0.002\,065 \frac{1 - \dfrac{1}{n_\uparrow}}{\left[1 + \dfrac{4.043\,57}{n_\uparrow} \right]^{4/3}},$$

$n_\uparrow$ is the total number of spin-up electrons.

Thus, the total energy can be computed from the energy-density functional

$$E[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + K[\rho], \qquad (8)$$

where $V_{ne}[\rho]$ is the nuclear-electron attraction energy

$$V_{ne}[\rho] = -Z \int \frac{\rho}{r} d\tau, \qquad (9)$$

and $J[\rho]$ is the classical Coulomb repulsion energy between ρ and itself,

$$J[\rho] = \tfrac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2. \qquad (10)$$

This functional is identical to the one just proposed by Shih, Murphy, and Wang[22] except that they use a constant value for α of $\tfrac{2}{3}$ and a constant value for β of 3.723×10^{-3} [this value corresponds to the definition given in Eq. (7) and it is obtained from the value of 5.5×10^{-3} given in their definition Eq. (5) of Ref. 22]. They found very good agreement with Hartree-Fock values when the Hartree-Fock density was used.

Although Eq. (8) combined with Eqs. (1) and (5) seems to be adequate for computation of the energy from an accurate electron density, it leads variationally to an inadequate equation for the density if only the normalization constraint is imposed[10,11] (some of the terms will diverge as r approaches infinity). However, if the atomic density is constrained to have an exponential decay,[12,13] the energies and charge densities thus obtained are improved over those obtained by the Thomas-Fermi method and its modifications.[14,15] In particular, Wang and Parr[15] have shown that the shell structure of atoms can be obtained through simple energy-density functionals assuming that the charge density is piecewise exponentially decaying.

The object of the present work is to impose the shell structure from the beginning by building up a charge density which is identical in its functional form to that of a minimal basis set (MBS) Hartree-Fock calculation.[16] The parameters are determined by requiring the total energy, calculated through Eq. (8), to be a minimum with respect to them. This way, we can also test the accuracy of this functional to determine the charge density by a direct comparison of the parameter values with those obtained from a Hartree-Fock MBS calculation.

We have also carried out the same type of calculations with an energy-density functional in which the kinetic energy is approximated by

$$T_B[\rho] = \tfrac{3}{10}(3\pi^2)^{2/3} \int \rho_2^{5/3} d\tau$$

$$+ \tfrac{1}{8} \int \frac{(\nabla\rho_1)^2}{\rho_1} d\tau + \tfrac{1}{8} \int \frac{(\nabla\rho_2)^2}{\rho_2} d\tau, \qquad (11)$$

where

$$\rho = \rho_1 + \rho_2 = \rho(0)^{-2Zr} + \rho_2, \qquad (12)$$

as proposed by Tal and Bader[11], because the Weizsacker term by itself reproduces very well the kinetic-energy density close to the nucleus.

II. THE ATOMIC DENSITY

In a MBS calculation each occupied orbital is approximated by a single Slater-type function,

$$\phi_{nlm}(r,\theta,\phi) = Nr^{n-1} e^{-\zeta_{nl}r} Y_l^m(\theta,\phi), \qquad (13)$$

where N is a normalization factor and ζ_{nl} is a parameter, whose value is fixed by minimizing the expectation value of the energy expression corresponding to a single-determinant wave function, constrained to the orthonormality of the set $\{\psi_i\}$. This procedure was originally proposed by Zener[17] and by Slater[18] who did not carry out the variational procedure but rather gave a set of rules to determine the values of ζ_{nl} for any atom. Later, Clementi and Raimondi[16] optimized the orbital exponents in SCF calculations for atoms with 2 to 86 electrons to ensure the energy minimum.

The charge density resulting from such MBS is given by (for a closed shell)

$$\rho(r) = \sum_{i=1}^{\text{occ}} n_i \psi_i^*(r)\psi_i(r), \qquad (14)$$

after integration over θ and ϕ. Here, n_i is the number of electrons in the ith orbital.

In our calculations, the charge density is given by Eq. (14) and the orthonormality constraint is fulfilled by carrying out a Schmidt orthogonalization between those orbitals with the same value of the azimuthal quantum number l. The effective charges are then determined through Eq. (8). One advantage of this procedure over the piecewise exponential model of Wang and Parr is that we can include T_4 in our calculations, and therefore test its importance when a variational calculation is done. In the piecewise exponential model, T_4 cannot be included due to the discontinuities of the first and second derivatives of the charge density.

TABLE I. Total energy and parameters for the ground state of He (atomic units).

Model[a]	ζ_{1s}	$-E$
Hartree-Fock		2.861
HF-MBS[b]	1.6875	2.847
$TFX\frac{1}{9}W$	1.6747	2.886
$TFX\frac{1}{9}WH$	1.6252	2.800
$TFXWB$	1.9998	2.893

[a]See text for a definition of the various models.
[b]These values taken from Ref. 16.

III. CALCULATIONS

We label the various calculations as follows:

$TFX\frac{1}{9}W$: $E[\rho] = T_0[\rho] + T_2[\rho] + V_{ne}[\rho]$

$$+ J[\rho] + K_0[\rho] + K_2[\rho], \qquad (15)$$

$TFX\frac{1}{9}WH$: $E[\rho] = T_0[\rho] + T_2[\rho] + T_4[\rho]$

$$+ V_{ne}[\rho] + K_0[\rho] + K_2[\rho], \qquad (16)$$

$TFXWB$: $E[\rho] = T_B[\rho] + V_{ne}[\rho] + J[\rho]$

$$+ K_0[\rho] + K_2[\rho], \qquad (17)$$

HF-MBS: Single-determinantal wave function with a minimal basis set.

All models make use of Eq. (14) for the density, and the energy expression is minimized with respect to the effective charges (which are the independent parameters) in the density subject to the orthonormality constraint. The virial theorem is always satisfied for the final energy for the $TFX\frac{1}{9}W$ and the $TFX\frac{1}{9}WH$ models as one can prove by Fock's method.[19] In the $TFXWB$ model the virial theorem is not satisfied because of the term neglected.[11]

A. Helium and neon

Results for the He atom ($1s^2$) are presented in Table I. The total energies and the parameter values agree quite well with the HF-MBS values. The $TFX\frac{1}{9}WH$ lies above the HF-MBS energy

while the $TFX\frac{1}{9}W$ lies below, however, the electron density is slightly better described in the $TFX\frac{1}{9}W$ than in the $TFX\frac{1}{9}WH$ model.

Results for the Ne atom ($1s^2 2s^2 sp^6$) are presented in Table II and in Fig. 1. It is found with the $TFX\frac{1}{9}WH$ model that the effective charge of the $2s$ orbital is too small when compared to the HF-MBS value, while the effective charge of the $2p$ orbital is too large when compared to the HF-MBS value. This leads to a poor description of the radial distribution function in the region of the L shell, particularly in the position and magnitude of the minimum and the maximum. However, in particular for Ne, the HF-MBS method predicts the same value for the $2s$ and the $2p$ effective charges.[16] This suggested to us that we impose the constraint $\zeta_{2s} = \zeta_{2p}$ in the calculation. The resulting parameters and consequently, the radial distribution function, agree much better with HF-MBS. Since this type of restriction, namely, $\zeta_{ns} = \zeta_{np}$ lies in the spirit of Slater's rules, and since the values obtained by Clementi and Raimondi for ζ_{ns} and ζ_{np} are, in general, very close to each other, it was imposed in all the other computations. This increases the energy, but it improves the electronic density description.

One can see from Fig. 2 that the calculation with the $TFX\frac{1}{9}W$ model with this type of charge density agrees better with the HF density than the two-zone exponential ρ of Wang and Parr. The difference between the $TFX\frac{1}{9}W$ and the $TFX\frac{1}{9}WH$ electronic densities is negligible in this case (Fig. 1), while the energy is slightly larger for $TFX\frac{1}{9}WH$ than for $TFX\frac{1}{9}W$. The $TFXWB$ ρ is in very good agreement with HF-MBS.

TABLE II. Total energy and parameters for the ground state of Ne (atomic units).[a]

Model	ζ_{1s}	ζ_{2s}	ζ_{2p}	$-E$
Hartree-Fock				128.547
HF-MBS	9.6421	2.8792	2.8792	127.812
$TFX\frac{1}{9}W$	9.4684	2.9634	2.9634	127.353
$TFX\frac{1}{9}WH$	9.2449	2.9668	2.9668	125.352
$TFX\frac{1}{9}WH^{b}$	9.6313	0.9540	3.5977	128.577
$TFXWB$	9.6662	2.8559	2.8559	125.312

[a]See footnotes of Table I.
[b]Allowing ζ_{2s} to be different than ζ_{2p}.

B. Argon and krypton

Although the results obtained for He and Ne are good, the results for Ar and Kr (Tables III and IV) show a rather large disagreement with the HF-MBS values, especially the description of the radial charge distribution in the region of the outermost shell. In Kr not only the description is poor, but the shell structure is partially lost and the total energies are much deeper than the HF-MBS energy, except for the $TFX\frac{1}{9}WH$ model whose energy lies above the HF-MBS energy.
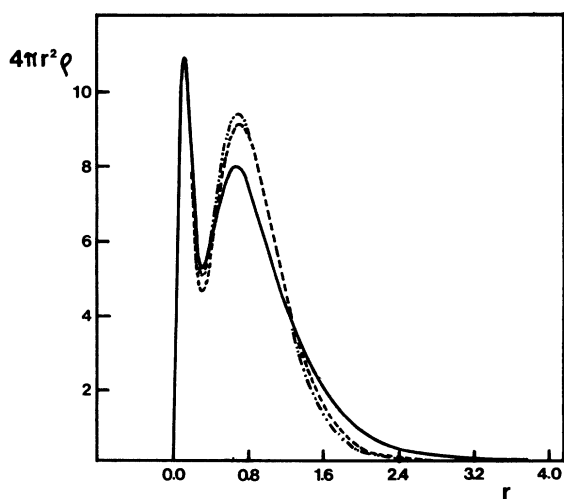
C. AH$_4$ molecules

As a first test of these functionals to predict molecular constants such as the equilibrium distance, we have done calculations on several AH$_4$ molecules within the one-center approximation.[20,21] Thus, one has to include additional terms in the functional. The electronic charge-proton attraction is approximated by

$$V_{pe}[\rho] = -4 \int \frac{\rho(\underline{r})}{|\underline{r} - \underline{R}|} d\tau, \qquad (18)$$

FIG. 1. Radial distribution function for the ground state of Ne. (———) Hartree-Fock; HF-MBS and $TFXWB$ are identical (— — — —); $TFX\frac{1}{9}W$ and $TFX\frac{1}{9}WH$ are identical (— · — · — · —).
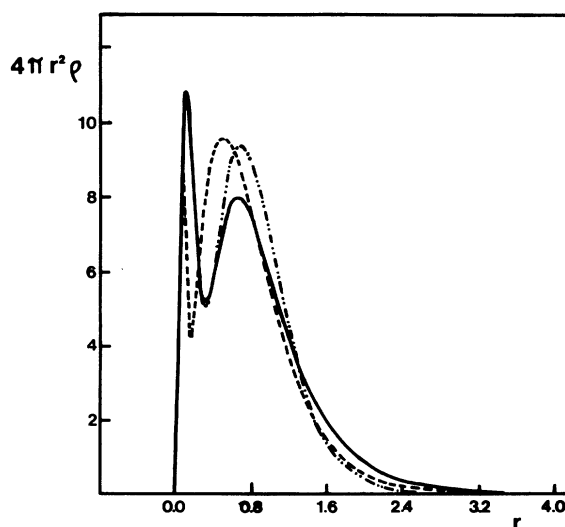
FIG. 2. Radial distribution function for the ground state of Ne. (———) Hartree-Fock; (— — — —) zone-exponential model, see Ref. 15; (— · — · — · —) $TFX\frac{1}{9}W$.

TABLE III. Total energy and parameters for the ground state of Ar (atomic units).[a]

Model	ζ_{1s}	ζ_{2s}	ζ_{2p}	ζ_{3s}	ζ_{3p}	$-E$
Hartree-Fock						526.817
HF-MBS	17.5075	6.1152	7.0041	2.5856	2.2547	525.765
$TFX\frac{1}{9}W$	17.2049	6.6965	6.6965	2.8018	2.8018	527.562
$TFX\frac{1}{9}WH$	16.7808	6.7145	6.7145	2.8009	2.8009	521.296
$TFXWB$	16.8731	7.1419	7.1419	3.0391	3.0391	525.359

[a]See footnote of Table I.

which corresponds to having spread uniformly the four protons over the surface of a sphere of radius R. The nuclear-nuclear attraction for a tetrahedral geometry is exactly given by (AH_4),

$$V_{pp} = \frac{4}{R}\left[Z + \frac{3\sqrt{6}}{8}\right],\qquad(19)$$

where Z is the nuclear charge of the central atom A. These two terms have to be included in the three models considered. The results for CH_4, NH_4^+, BH_4^- SiH_4, and GeH_4 are presented in Table V and compared with similar calculations. It may be seen that the $TFXWB$ model is surprisingly accurate in predicting the equilibrium distance, except in the case of SiH_4, while the other models tend, in general, to underestimate it. The energies obtained are very similar for all models.

IV. CONCLUSIONS

Since we have used approximate functionals, there is no guarantee that the energy should lie above E_{HF}. However, the energy obtained from the constrained calculations reported, is in several cases already lower than E_{HF}. This indicates that the results that would be obtained carrying out the full variation and solving the corresponding differential equation, would be in larger disagreement with the HF values. Thus, at least for the functionals based on a gradient expansion, it is necessary to incorporate additional constraints from the beginning, besides the normalization.

However, there is no guarantee that such constrained calculations (like using HF-minimal basis set type densities or piecewise exponentially decreasing densities) would greatly improve the description. As a matter of fact, the poor results

TABLE IV. Total energy and parameters for the ground state of Kr (atomic units).[a]

Model	ζ_{1s}	ζ_{2s}	ζ_{2p}	ζ_{3s}	ζ_{3p}	ζ_{3d}	ζ_{4s}	ζ_{4p}	$-E$
Hartree-Fock									2752.056
HF-MBS	35.2316	13.1990	16.0235	7.0109	6.8114	6.8753	2.8289	2.4423	2744.520
$TFX\frac{1}{9}W$	30.8603	9.7397	9.7397	12.8800	12.8800	3.1148	13.4287	13.4287	2793.115
$TFX\frac{1}{9}WH$	33.8603	7.3183	7.3183	12.5204	12.5204	2.2577	12.9476	12.9476	2737.933
$TFXWB$	31.3685	20.2288	20.2288	3.5668	3.5668	9.4217	2.8807	2.8807	2857.838

[a]See footnote of Table I.

TABLE V. Total energy and equilibrium distance for various molecules within the one-center approximation (atomic units).

Model	CH_4		NH_4^+		BH_4^-		SiH_4[c]		GeH_4[c]	
	$-E$	Re	$-E$	Re	$-E$	Re	$-E$	Re	$-E$	Re
Experimental	40.53	2.07	56.84	1.96	27.20	2.37		2.78		2.89
Hartree-Fock[a]	40.23	2.07					291.24	2.80	2077.80	
Hartree-Fock[b]	40.07	2.08					290.79	2.76	2076.80	3.02
HF-MBS	39.05	2.19	56.30	1.91	26.62	2.24	290.31	2.97		
$TFX\frac{1}{9}W$	38.37	1.86	55.38	1.76	25.85	2.14	289.48	2.49	2093.53	3.63
$TFX\frac{1}{9}WH$	39.06	1.86	54.42	1.76	25.38	2.14	285.70	2.49	2071.68	3.50
$TFXWB$	38.55	2.09	54.62	1.91	25.53	2.38	286.55	2.19	2119.29	2.82

[a]Hartree-Fock limit, without the one-center approximation.
[b]Hartree-Fock limit, within the one-center approximation.
[c]Experimental and Hartree-Fock values taken from J. P. Desclaux and P. Pyykkö, Chem. Phys. Lett. 29, 534 (1974).

obtained for Ar and Kr indicate that the present approach does not provide a systematic and simultaneously useful (predictive) method. Nevertheless, the results reported give some information about the level of accuracy that can be achieved through these functionals. However, they should not be used to reach any preference between the different models.

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